INTERACTION OF PERSONALITY VARIABLES WITH INDUCTIVE AND DEDUCTIVE TEACHING STRATEGIES.

A thesis submitted by

COLIN FRANCIS LUCAS

a candidate for the

degree of

MASTER OF SCIENCE.

University Of Aston.

MAY 1971.

SUMMARY.

Male and female Students were separately classified as high or low in intelligence and high or low in anxiety. Students from each of these four categories were then randomly assigned to work through either an inductive or a deductive self instructional programme on Enzyme Kinetics. A 2 x 2 x 2 analysis of variance design was then used to analyse the results for males using gain score, errors on the programmes and time as the dependent variables. Female results were then treated similarly.

Significant main effects and interaction effects were found for females but not for males. Although this may be due to sex differences replication with larger numbers of males is needed to confirm these findings.

The major result for females was that the amount of successful learning by different types of female depends on the difficulty of the learning situation. High anxious females achieve higher gain scores after learning by deduction than they do after learning by induction. This may be attributable to the increase in task irrelevant responses emitted by high anxious females in difficult learning situations, where the probability of making errors is higher than in easy learning situations. On the other hand low anxious females are relatively higher in need achievement than high anxious females and they achieve higher gain scores after learning by induction than they do after learning by deduction. Possibly this is due to high success probability not being attractive to females with high need achievement.

Whereas high intelligent females learn equally well by induction and by deduction, low intelligent females make fewer errors and attain higher gain scores after learning by deduction.

High intelligent females take longer to work through both versions of the programmes than low intelligent females. Also females take longer to work through the inductive version of the programme than they do through the deductive version.

ACKNOWLEDGMENTS.

The author wishes to express his sincere thanks to Dr. J. Rushton for his help and encouragement during the past three years.

CONTENTS

APPENDIX.

LIST OF T ABLES

LIST OF FIGURES.

CHAPTER 1.

STATEMENT OF PROBLEM.

"Discovery learning" in its many forms has been investigated by many researchers. The results are often contradictory and confusing, although the general consensus of opinion is that "discovery" methods when compared with some other variously specified learning process lead to increased retention and transfer of principles. One problem arises out of the fact that there is no consensus of agreement as to what is an operational definition of the term discovery. In particular the amounts and kinds of direction given to the learner vary greatly from study to study. At the outset of this research therefore precise definition of "discovery" is needed in terms of behaviour of the learners. This is accomplished by preparing two self instructional programmes (one inductive the other deductive) on a modified Kersh and Wittrock (1962) paradigm. According to them the model for "discovery"learning" is equivalent to learning by induction, that is instances of each principle are given to the learner from which he must abstract and then verbalise the principle. At the opposite pole of the learning continuum is deductive learning in which a statement of the principle is given followed by allowing learner practice in completing examples of that principle. No abstraction process is involved.

Experiments comparing the effectiveness of inductive with deductive methods of teaching abound, but there is a dearth of information on the interaction of these strategies of teaching and personality.

Indeed Ansubel (1963) cites 68 references concerned with discovery learning and only that of Maltzman (1950) contains reference to any personality variables. Wittrock (1966) in an article entitled "The learning by Discovery Hypothesis" states that :-

> "Interaction among student types, subject matter, and methods of instruction will not be found unless designs are used which evidence them. With complex human behaviour we should expect these interactions to occur and measure them when they do occur." (P.68)

The argument for a multidimentional analysis of the outcomes of learning is taken up by Cronbach (1966). In an article called "The logic of Discovery" he states:-

> "There will be a need for more complex experiments planned along quite different lines from those in the past literature. We have to explore the five fold interaction, subject matter, with types of instruction, with timing of instruction, with type of pupil, with outcome." (P.91 - 92)

Granted that there is a need for investigation into the possible interactions between individual differences and teaching strategy, a theoretical framework which can serve as a guide line within which the experiment is to be conducted is needed. Atkinson and Feather's (1966) Theory of Achievement Motivation was chosen for this purpose for the following reasons:-

(1). Firstly, it opens up a completely new dimension because what little work has already been done in this field, has been carried out in relation to the concepts of Hullian drive theory, with only moderate success.

(11) Secondly, Achievement Motivation Theory has much to say about the performance of high and low motivated subjects working at simple and complex learning tasks, i.e., tasks where the probability of successful responding is high and low respectively. In an inductive

learning sequence errors have a higher probability of occurrence than in a deductive learning sequence. Thus one would hope to use Achievement Motivation Theory to relate efficiency of performance by high and low motivated subjects to the degree of task difficulty which in this case corresponds to type of teaching strategy.

(111) Thirdly, to test Cronbach (1966) speculations about "Constructionists" (high need achievement low anxiety subjects) profiting from a shift from deductive teaching to learning discovery, and "defensives" (low achievement motivated, high anxious subjects) who profit most if teacher maximises the opportunity for dependence.

To conclude, the interaction of personality and method of instruction is likely to be a fruitful field of investigation pedagocially and theoretically.. Exploratory work is needed employing fairly complex experimentation to permit a multi-dimensional analysis.

CHAPTER 11.

REVIEW OF THE LITERATURE.

The survey of the literature proper which now follows has for convenience been divided into two sections. The first one on Theory of Achievement Motivation and the second on the relevant research comparing inductive and deductive strategies of teaching.

Theory of Achievement Motivation.

Those engaged in education have long believed that motivation is of prime importance in human performance and learning. Only in recent years, however, have investigators made systematic efforts to relate motivation and performance variables experimentally in the classroom learning situation.

Murray (1937) identified one motivational variable, which he called need achievement as the motive to strive to do things well and as quickly as possible. Owing to its complex nature and lack of suitable measuring instruments, Psychologists made little attempt to define the motive more precisely until (McClelland (1953) developed a method for measuring this motive, using the pictures from Murray's (1937) Thematic Appeception Test (T.A.T.) From their work they concluded that the achievement motive if aroused would lead to a competition with a self imposed standard of excellence, i.e., a striving to increase or keep as high as possible one's capability in all activities in which a standard of excellence is thought to apply.

The McClelland group found the relatively unstructured task of a projective technique, where an individual has to "project" his characteristic mode of response into the task, the most effective method for measuring need achievement.

The essential procedure followed is that the tester shows the subject an ambiguous picture and then asks the subject to tell a story about it. Finally the tester scores the story on the basis of the number of schievement themes it contains. One of the drawbacks of this procedure is the time and skill needed to score each response. Lack of proper training as McClelland (1958) points out can result in appreciably lower reliability estimates.

In an attempt to develop a more objectively scored method of measuring achievement imagery Hedlund (1953) devised a multiple choice form of the T.A.T. which is identified as the Lowa Picture Interpretation Test (I.P.I.T.). Each T.A.T. picture has four alternative responses which subjects are told to rank in order on the basis of how well they describe what is happening. Although I.P.I.T. has received only modest attention, it has proved extremely useful in the prediction of certain learning and performance behaviour.

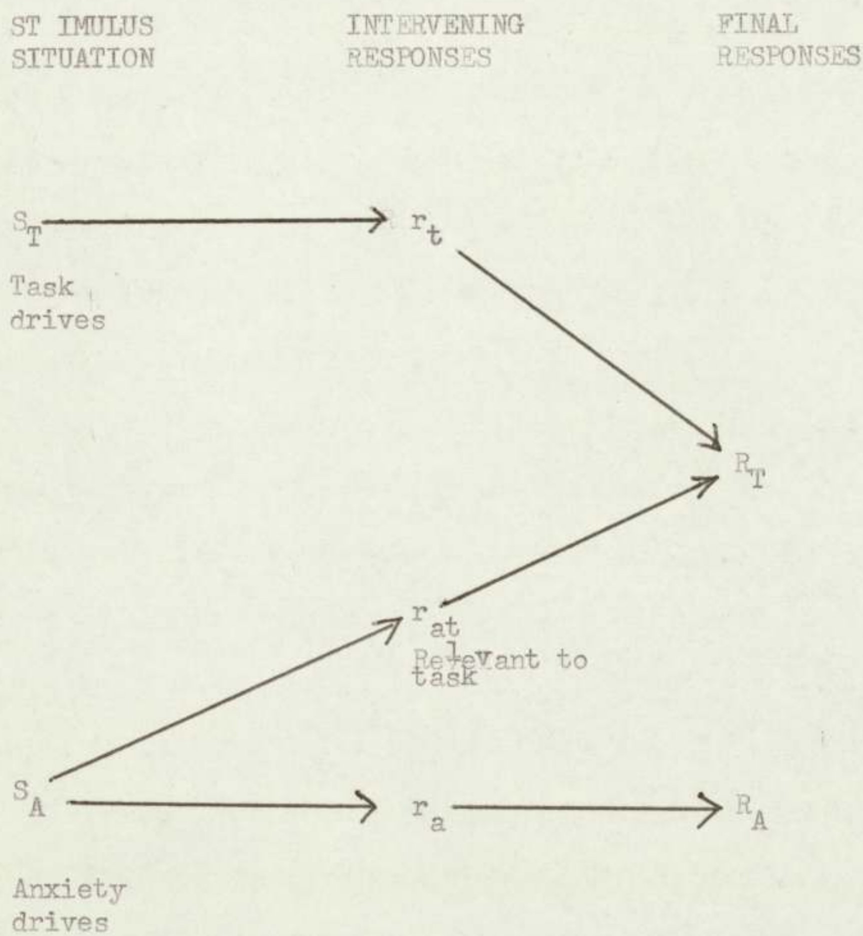
Hurley (1953), Johnson (1955) and Williams (1954) found that subjects who scored high on the achievement imagery scale of the I.P.I.T. were superior in performance to subjects with low achievement imagery on a variety of tasks. These included a serial learning task, a simple arithmetic task, and a maze learning task, all of which were conducted without special motivating instructions, when motivating instructions are included this difference in performance between high and low subjects on the achievement imagery scale tends to disappear.. Later Hurley (1957) showed that college subjects under low motivating instructions (i.e., "relaxed"as opposed to "try hard" instructions) on a task involving nonsense syllables revealed a positive correlation which was significant between the 0.06 and 0.07 levels of significance.

In general, results have shown that subjects with high need achievement perform better than subjects with low need achievement when the importance of good performance is not stressed. The difference between performance levels tends to disappear when instructions do stress doing well on the task.

The original research of McClelland (1953) yielded evidence suggesting that there might be two measurable aspects of achievement motivation, one directed towards success and the other towards failure. However, according to Moulton (1958) efforts to use the categories of the need achievement system as a subsystem for fear of failure have not been encouraging. Ideally an independent measure of fear of failure is required rather than reliance on low need achievement. For this reason Atkinson and Litwin (1960) have subsequently suggested that the need achievement section of the Thematic Apperception Test, measures the motive to approach success, while the Mandler Sarason Test Anxiety Questionaire (T.A.Q.) (1952) measures the motive to avoid failure.

Mandler and Sarason (1952) developed the T.A.Q. to indicate the extent to which a subject experiences anxiety before during and after three typical kinds of testing situation. According to the Mandler Sarason Theory, test anxiety when aroused is a function of two sets of stimuli (1) Specific situational ones (e.g. instructions, tasks, etc.) and (2) learned anxiety drive ones generalised to a new performance. This latter generalised anxiety drive may elicit two types of response (a) those which aid the completion of the task, i.e. task relevant responses, By this they mean responses which are considered to be specific to the task, are not available in the response repertory of an individual, but are evoked, reinforced, and learned in the course of task performance (b) those which interfere with completion of the task i.e., task irrelevant responses, e.g. hand tremor, inattention, lapse of memory, etc. Figure 1. is a diagrammatic presentation of the drives and responses evoked in the testing situation according to Mandler and Sarason.

FIGURE 1. DIAGRAMMATIC REPRESENTATION OF DRIVES AND RESPONSES EVOKED IN THE TEST ING SITUATION



The proportion of task irrelevant responses which occur should increase in relation to task difficulty if Mandler-Sarason theory is true. Thus a person who has high test anxiety would exhibit more task irrelevant responses in a complex learning situation and more task relevant responses on simple tasks, where the probability of success is highest. In the latter case, this results in greater output and learning on the part of high test anxious individuals.

In the Theory of Achievement Motivation put forward by Atkinson and Feather (1966) these two motives; the motive to approach success, which is given in symbol M_s, and the motive to avoid failure which is given the symbol M_{AF} are both converted into standard scores. M_{AF} is then substracted from M_s to give a total resultant tendency score called for short T_R. For the approach motive (M_S) one speaks of probability of success which usually written P_S and the incentive value of success, i.e., the relative attactiveness of specific goal which written I_S. While for avoidance motivation one speaks of the probability of failure (P_F) and the incentive value of failure (I_F). Tendency is assumed to be multiplicative function of motive, expectancy, and incentive. Thus the product of the motive to approach success, the probability of success and the incentive value of success yields the tendency to approach success called T_S. Or symbolically -

$$T_S = M_S \times P_S \times I_S$$

The product of the motive to avoid failure the probability of failure, and incentive value of failure leads to negative tendency to avoid failure. Or symbolically -

$$T - F = M_{AF} \times P_F \times I_F$$

T_S and T_{-F} denote achievement oriented tendencies and are thus assumed to be present only in response to achievement oriented situations. Achievement oriented activities are empirically defined as tasks requiring skill, and for which the individual believes he has some control over his performance and its subsequent outcome, (for instance a programmed learning task).

Atkinson and Feather (1966) states that when both the tendency to approach success and the tendency to avoid failure are simultaneously aroused by specific situational cues, the resultant achievement oriented tendency to act (T_R) is the algebraic sum of approach tendency and the avoidance tendency. In symbolic terms

$$T_R = (M_S \times P_S \times I_S) - (M_{AF} \times P_F \times I_F).$$

It can be seen from this model that if the tendency to approach success is greater than tendency to avoid failure, i.e., $T_S > T_{-F}$, the resultant achievement oriented tendency will be positive and approach oriented. On the other hand if the tendency to avoid failure is greater than the tendency to approach success, then the resultant achievement oriented tendency will be negative and avoidance oriented.

Elaborating the assumption put forward by Festinger (1942) and Lewin et al. (1944). Atkinson makes the assumption that incentive value of success increases in proportion to the difficulty of obtaining the goal. In other words incentive value of success is made a function of the expectancy of success, equalling $1 - P_S$. The more difficult the task then the lower the probability of success and the higher the incentive value or positive feeling that accrues to the individual, if in fact he succeeds in the goal. If the task is perceived as being easy, that is the probability of success is quite high one would not feel any unusual sense of accomplishment, for having attained the goal. Here the incentive value of success would be low.

Since motive is considered to be a relatively stable characteristic of the individual and the incentive value of success, I_S, is a function of the probability of success, P_S, it could be shown that when a individual is confronted by a particular stimulus situation, the sole determinant of the resultant tendency, T_R, is the probability of success, P_s . As the probability of success P_s , is conceived as a probability term, it varies from 0 - 1. thus the probability. Thus the probability of success, P_S , plus the probability of failure, P_F, must sum to unity, or stated another way the probability of failure = 1 minus the probability of success, i.e., P_f , = 1 - P_S. With appropriate substitutions the model can be reduced to -

$$T_R = (M_S - M_{AF}) (P_S [1 - P_S])$$

In this form it becomes obvious that the relative values of motive to avoid failure, M_{AF}, and the motive to approach success M_S , dictate both the sign of the resultant tendency, T_R, and its relative magnitude where the motive to approach success, M_S , is greater than motive to aboid failure, M_{AF} , the tendency to approach success, T_S, is the predominent tendency, and the resultant tendency, T_R, is positive. Thus the achievement task will be undertaken. If the motive to avoid failure is greater than the motive to approach success, then the tendency to avoid failure, T_{-F} , is the predominent tendency and the resultant tendency, T_R , is negative, so that the achievement task will be avoided or resisted. In other words given a particular probability of success level it is the two relatively stable motives that operate to determine the magnitude and sign of the resultant achievement oriented tendency.

The probability of success P_S, will function to determine whether the achievement oriented motives brought into a particular situation are engaged by the stimulus situation. If the probability of success P_S is either zero or one, the second term P_S $(1 - P_S)$ will be zero. In the first case when the probability of success, P_S, is zero, the individual is certain of his inability to perform the task, while in the second case when the probability of success equals one there is no ego involvement, because an individual is certain of his ability to do something. In both cases there is no motive involvement when the probability of success takes on a value between zero and one, by definition there must be incentive value, and thus the achievement motives are engaged.

According to this model the greatest tendency to approach or avoid should occur when the probability of success, P_S, equals 0.5, and thus by assumption the incentive of success, $I_S = 0.5$, since the product of P_S and I_S is maximised when the probability of success P_S equals 0.5. Thus in a situation in which an individual was working at an achievement task, which he originally thought to be easy, i.e., the probability of success was greater than 0.5, began to experience failure then he would revise his estimate of the probability of success, P_S, downwards. If this individual was a person whose motive to approach success is greater than his motive to avoid failure, then his positive resultant tendency, T_R, should increase as the probability of success drops towards 0.5. Thus individuals whose motive to approach success is greater than their motive to avoid failure, should persist longer at the task than individuals whose motive to avoid failure, exceeds their motive to approached success, because the probability of success has dropped into the intermediate range. On the other hand, individuals in whom the motive to avoid failure exceeds the motive to approach success should have their tendency to avoid failure increasing to a maximum. in this range.

The relationship between achievement motivation and intelligence has not been adequately researched. To the present author the achievement motivation model which has just been outlined is deficient in failing to incorporate individual differences in intelligence. For it would seem clear that the probability of success at a task would vary directly with intelligence. Perhaps the inclusion of intelligence measures into experimental designs using the achievement motive model would increase the accuracy of its predictions.

The achievement motivation model has recently been criticised by Heckhausem (1968) on the grounds that there is an infinitely large number of relationships between incentive and probability of success. He presents empirical evidence to show that incentive equals 0.7 minus the probability of success i.e., ($I = 0.7 - P_S$ and not $I = 1-P_S$). Birney, Burdick and Teevan (1969) are also critical of the Atkinson and Feather achievement motivation model. They say that the strategy of theorising by Atkinson and Feather (1966) has led to a degree of theoretical sophistication, which tends to outrun the power of their measures.

Thus there is some disagreement about the finer points of the achievement motivation model and the exact range of difficulty where the motives are engaged. Nevertheless some broad generalisations are possible from achievement motivation theory. For instance Heckhausen (1968) predicts from the model that :-

> "High success probability is not attractive to hope to hope of success subjects, (in whom the motive to approach success is greater then the motive to avoid failure), but does serve to arouse fear failure subjects, (in whom the motive to avoid failure is greater than the motive to approach success)" P.144.
>
> "Hope of success subjects prefer goals whose probability of success is lower than 50%" P.143.

It would be interesting to see if these predictions from the theory of achievement motivation are of any value in enabling us to forecast, with any degree of accuracy how subjects with predominently approach or avoidance motivation would perform in various types of learning situation.

Glaser (1966) states -

> "Discovery (inductive) learning implies a low probability of making a successful response. Such being the case errors have a high probability of occurrence. P.15."

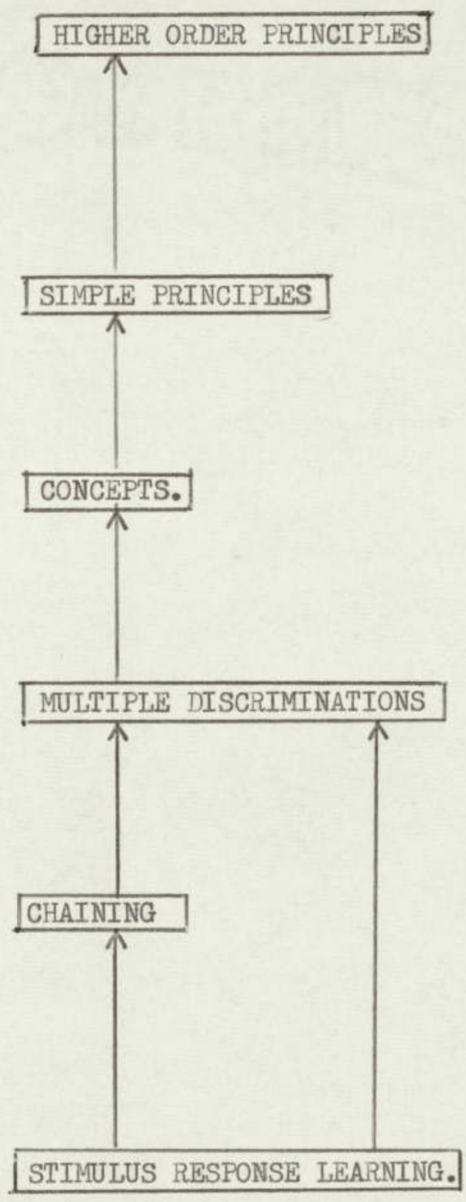
Thus one would expect to find that subjects in whom the motive to approach success was greater than the motive to avoid failure would perform better in an inductive discovery learning situation than subjects in whom the motive to avoid failure was greater than the motive to approach success. On the other hand, in a deductive reception learning situation, the converse should be true.

Learning by "Discovery".

Many of the new science curricula (e.g. Biological Sciences Curriculum Study: Chemical Bond Approach: Chemical Education Material Study: Physical Science Study: Nuffield Ordinary and Advanced Level Chemistry; Biological and Physics etc.,) all stress the importance of principle learning, and the importance of using these acquired principles to solve novel problems and transfer situations. In line with these new trends we shall confine our attention in this review to examining the research literature on the effectiveness of principle learning by induction and deduction. As an index of this effectiveness we shall be particularly interested in performance on transfer problems.

Principle learning and problem solving need operational definition because they are not clearly defined in the literature. Gagné (1965) conceptualises principle learning as being at the pinacle of a learning herarchy as shown in figure 2. Gagné says that simple principles are combinations of concepts describing either a new relationship between concepts which are independently defined, e.g., Round things roll.

FIGURE 2. SCHEMATIC REPRESENTATION OF A GAGNÉ HIERARCHY SEQUENCE FOR CUMULATIVE LEARNING.



or to give a new concept by combining old concepts.

e.g. Work = force x distance

in which work is only defined operationally in terms of force and distance.

In the absence of any disuasive evidence i.e., that the conditions under which they are learned are different. Gagné tentatively places both of the above types of principle into the same psychological category.

Most principles are not learned in isolation but are learned as a set of principles pertaining to a larger topic. What the student learns is organised knowledge i.e., organised in the psychological sense that the learning of some principles is a necessary prerequisite to the learning of higher order principles. The psychological organisation of knowledge may be represented by a hierarchy of principles. It has been stated earlier that two or more concepts may be a necessary prerequisite to learning a simple principle so two or more principles may be necessary for learning a superordinate principle.

Gagné (1966) - defines problem solving as -

> "Inferred change in human capability that results in acquisition of a generalisable rule, which is novel to the individual, which cannot be established by direct recall, and which can manifest itself in applicability to the solution of a class of problems." (P.132.)

Two aspects of this definition need further elaboration. Firstly, the new rule is created by correctly combining lower order subordinate rules or principles, which the student has searched for and selected from amongst his repertoire of principles. For instance Gagné (1965) says that if the student has the following three principles in his repertoire:-

(1) Power = $\frac{\text{Work}}{\text{Time}}$

(11) Work = Force x distance

(111) Velocity = $\frac{\text{Distance}}{\text{Time}}$

then if he is called upon to find the relationship between power and force, he can solve this problem by scanning the lower order principles and coming up with the new principles.-

Power = force x velocity

Another point about Gagné's definition is that the equates problem solving with the discovery of the new principle. For example, Gagné (1966) says -

> "If I ask an individual to supply the next two numbers in the number series 1 2 5 14 - - he has a problem. If I tell him the principle, multiply by 3 and subtract 1 there is no problem." (P.147)

There would be learning in this latter situation, but as the student is told the new principle it is not an example of problem solving.

Both principle learning and problem solving involve the acquisition of a new generalisable rule. Hence the form of the test item will be the same. The test item will require the student to make a prediction about the particular state of concept B. once he knows the parameters of concept to which concept is related by a particular operation. The test situation should also confront the student with several instances and non instances of the principle, and should require him to state that the operation described by the principle is not applicable in the case of non instances and is applicable in the case of positive instances. In investigating the effects of the two teaching methods on final problem solving ability, one is comparing their relative effectiveness in enabling the student to solve and remember problems presented in the example frames of the programme after having acquired governing principle by induction or deduction.

Having defined the differences between principle learning and problem solving operationally, it is now necessary to make an unequivocal statement as to what is meant by inductive guided discovery learning and deductive reception learning. In order to do this effectively, as modified Kersh and Wittrock (1961) model is employed using the symbolism of Evans, Homme and Glaser (1962) as shown in table 1.

TABLE 1. A MODIFIED VERSION OF KERSH AND WITTROCK'S MODEL FOR INDUCTIVE AND DEDUCTIVE LEARNING.

Inductive guided discovery learning	Deductive reception learning.
$\tilde{eg}_1$	Ru $\tilde{eg}_1$
eg_1	eg_1
$\tilde{eg}_2$	$\tilde{eg}_2$
eg_2	eg_2
$\tilde{eg}_3$	$\tilde{eg}_3$
eg_3	eg_3
$\tilde{Ru}_{(n-1)}$	$\tilde{Ru}_{(n-1)}$
$Ru_{(N-1)}$	$Ru_{(n-1)}$
$\tilde{eg}_n$	$\tilde{eg}_n$
eg_n	eg_n

KEY. $\tilde{eg}$ --- is a test item requiring application of a new rule either on its own or in combination with previously acquired rules in solving a problem.

eg --- is the answer to a test frame.

$\tilde{Ru}$ --- is the penultimate frame of teaching sequence in which the student verbalises the rule which it is hoped he has discovered by now.

Ru --- is the correct statement of this principle by the programme.

It will be noticed that in both teaching strategies that the student is asked to verbalise the rule or principle (Ru) at the end of the teaching sequence. Whether the principle should be verbalised once it has been inductively discovered is a point of contention. amongst proponents of discovery. Hendrix (1947, 1961) not only extols the virtue of discovery learning but it goes one step further by distinquishing between the internal act of discovery and the formal verbalisation of the discovery. She asserts that immediate verbalisation of the discovery is not only unnecessary for the generation and transfer of ideas but may actually be harmful when used for these purposes. It is necessary because according to her language is only a label on the emerging subverbal insight. It serves communicative purposes only. The substance of the idea resides in the subverbal insight. Verbalisation is potentionally harmful because of the possible inhibitory effects of imprecise verbalisation on the emerging concept or principle. Some concepts and principles are formed by an individual continually change - being expanded and modified by the individuals experience - a premature verbalisation may either inhibit growth or reinforce non critical attributes.

Ausubel (1963) feels that Hendrix has overstated her case. He grants the value of the subverbal state to young children and to older individuals unsophisticated in a particular subject matter area. According to him, for these subjects, verbalisation is liable to be ambiguous and imprecise leading to a decrease in transferability. For all other subjects, however, Ausubel (1963) is of the opinion that verbalisation is superior to subverbal insight. It does more than encode subverbal insight into words.

> "It involves complex processes of categoration differentiation, abstraction and generalisation, the rejection of alternative possibilities, and the exclusion of less precise or over inclusive meaning". (P.148).

Research findings seem to support Ausubel's position. For instance Heidbreder and Zimmerman (1955) have shown that verbal generalisation is particularly important for concept attainment in cognitively sophisticated learners. Also Gagne and Smith (1962) have demonstrated the facilitating effect of verbalisation on the discovery of general principles and their use in problem solving.

What light has research shed on the effectiveness of "discovery" learning over "reception" learning for enhancing retention and transfer ? In order to answer this question without losing clarity and perspective amidst a plethora of research, it will be necessary to impose the following restrictions:-

(a). Studies on "discovery" versus "reception" learning but involving comparisons other than the inductive-deductive dimension will be ignored. Thus for example Hilgard Irving and Whipple (1953) who taught card tricks by induction and deduction, confounded their results by making the deductive treatment rote, and the inductive treatment meaningful. Another example of a study in which the variation of factors other than induction and deduction confuse the issue is that of Gagne and Brown (1962). These experimenters compared the effectiveness of teaching number series by, deduction, discovery and guided discovery. Unfortunately, there were also differences in (1) what was practised i.e., whether the rule was written or not, and (11) how it was practised, i.e., the prompting and fading conditions were varied. This latter condition, together with small and large steps was also varied in Shadbolt's (1969) experimental programmes in which genetics was taught to college students.

(b) Only researches using subjects of high ability in the 15+ age range will be considered since according to Ausubel (1963) chronological age and ability are liable to interact with method of teaching.

(c) Finally we shall concern ourselves only with research involving principle learning and problem solving. This of course eliminates concept formation research which may be thought to be relevant, for instance those experiments reviewed by Bruner Goodnow and Austin (1956). Carrol (1964) cites several reasons for the lack of applicability of concept formation research to learning in the classroom. Firstly, concepts taught in a psychological experiemnt are generally artificial combinations of familiar attributes like the concept "three blue squares", rather than constituent parts of a meaningful subject matter area. As such they do not depend upon a network of related or prerequisite concepts as do those which are taught in a school setting. Another difference is that concepts taught in the psychological laboratory are of a conjunctive nature (two or more attributes must occur together) whereas school concepts are not that simple. They are apt to be of a relational character, that is, establishing them may involve detecting relations among attributes rather than just noting their combined presence or absence.

When these restrictions are taken into account, the following research studies comparing induction with deduction survive:-

(1) Craig (1956) in which college students had to find one of five words that did not belong to the other four according to some principle.

(11) Haselrud and Myers (1958) compared the results of learning by induction or deduction of 20 principles governing the coding of words in sentences. This study was carried out with college subjects.

(111) Corman (1957) who used Katona's match stick problems, where students were required to form new geometrical designs from old ones by the manipulation of a certain number of matches.

(1V) Wittrock (1963) taught students to decipher transpositions codes by different permutations of rule, example and answer.

(V) Guthrie (1967) has also completed a study involving scrambled words, but whereas Wittrock showed that a rule only group was superior to rule + worked out example group, in Guthrie's experiment the rule + example has a better performance on a post test.

These researches reviewed here seem to show that rule example procedure (i.e. deduction) produce faster, more error free acquisition, and more retention than example rule procedures (i.e.induction). The order in which the rules are presented seems to have no effect on the transfer of training.

Gagne & Rowher (1969) after reviewing much work on "learning by Discovery" conclude -

> " tasks set for the learner --- appear to cover the range from merely peculiar to the downright esoteric."

In order to overcome this objection of the irrelevance to the classroom of much of the learning material in experiments comparing induction with deduction, it is necessary to select material which has the maximum ecological validity. That is to say, it must contain learning material which is representative of that undertaken in the lecture and tutorial room.

CHAPTER 111.

EXPERIMENTAL METHOD.

Subjects.

College of Education Biology students serve as subjects in this study. Their lecturers said that they had not been exposed to the topic of Enzyme Kinetics in their previous work, but they had all taken sixth form courses in science subjects and could therefore be considered as having similar amounts of background knowledge. The great majority of these students taking Biology were females; in fact only 32 males were obtained in a total sample of 176 subjects.

Timetable for the Experiment.

Week 1. Carry out Iowa Picture interpretation Test, Test Anxiety Questionaire and AH/S Intelligence Test.

Week 2. Work through Pre-test and first Section of the Programme.

Week 3. Work through section two of the programme.

Week 4. Work through Section three of the programme.

Week 4. Work through Post Test.

The Programmes.

The subject matter to be used in the experiment was Enzyme Kinetics. The study imposes many requirements upon the topic to be chosen. It should be representative of meaningful subject matter taught to students if the results are going to be applicable to any general degree to the college setting. As such it should involve an inter-related interdependent sequence of principles. It must lend itself to being broken down into constituent principles whose defining attributes may either be discovered or given directly to the student. These principles should be easy verbalised, once they are inductively discovered. Enzyme Kinetics was chosen as a subject fulfilling these requirements. Furthermore, if permitted the development of these principles from an analysis of experimental results. In the programmes only a minimum of technical terms and stated principles are included.

Two linear programmes were written in order to control practice effects. Each programme required the subject to make this same number of statements of principles and to complete the same number of examples. The two programmes were designed to overcome the criticism of typical method studies, that two methods cannot be compared because of so many uncontrolled variables. By equating the programmes on the basis of required responses and amount of practice, only the parameter of teaching method, i.e., how the material is sequenced becomes relevant. Thus one is able to eliminate much that leads to difficulties in interpretation.

The inductive programme was written before the deductive programme. Following accepted programming procedure a statement of objectives in operational terms was first made. (The principles comprising the terminal behaviour are shown in table 2). Then using a Gagne hierarchy the principles comprising the terminal behaviour were placed in a suitable teaching sequence (as shown in figure 3). Next teaching frames on average about eight per principle were then written. Thus the step size can be large, which together with the large frame size will present a challenge to the more mature student and prevent the pall effect from setting in. After writing the initial draft of the inductive programme, it was validated using 10 third year College Of Education Students who were studying biology at principal subject level. These students were told that if their answers to the frames were wrong they were not to erase them but that they were to indicate using Bjerstedt (1966) symbolism whether they did not understand the subject matter or did not understand what to do with it, or both. After further revision of certain frames, in the light of the results obtained on this first trial, the programme was further tested, this time individually with five students. At this time it was felt that the programme was now sufficiently close to the final form that a deductive reception programme could now be written. This was a simple task consisting of merely placing statements of the appropriate principles at the beginning of each teaching sequence of the inductive programme.

In the final trial these two programmes together with the rough drafts of the pre and post tests were administered to twenty College of Education Biology Students. The two programmes were then randomly allocated to the twenty subjects. After the subjects had worked through the pretest, programmes, and post test a two tailed t test was performed to find if there was any significant difference between gain scores of the eubjects working through the two versions. No such differences were found hence it was concluded that the two programmes were equivalent teaching instruments.

Figure 3. A HIERARCHY OF PRINCIPLES COMPRISING THE TOPIC ENZYME KINETICS

(The Roman Numerals refer to principles listed in table 2)

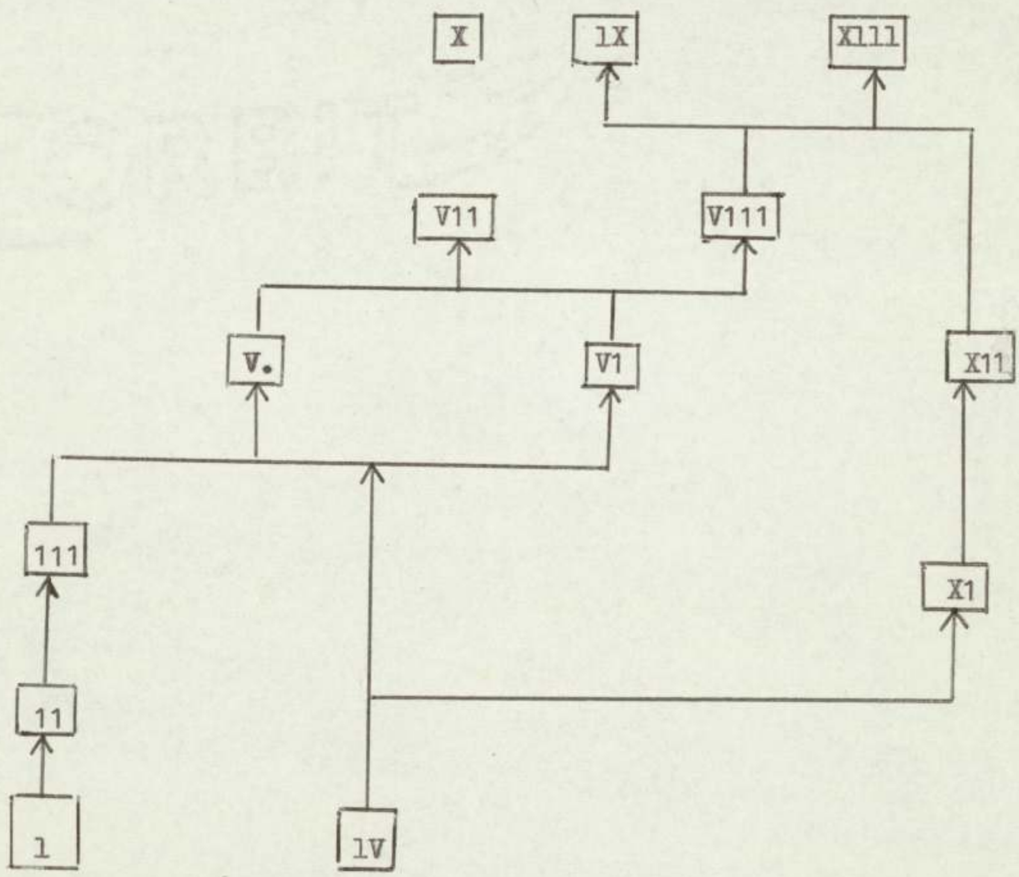


TABLE 2. LIST OF PRINCIPLES COMPRISING TERMINAL BEHAVIOUR.

PRINCIPLE NUMBER.	STATEMENT OF PRINCIPLE.
1.	A rise in concentration of reactants in a chemical reaction means a higher reaction rate.
11.	Rate of chemical reaction = constant x concentration of reactants to raise some power n which is empirically determined.
111.	In a chain reaction, the reaction proceeds at the rate of the slowest step.
1V.	In an equilibrium mixture the product of the concentration of the products each raised to the power equal to the number of moles of that substance in the chemical equation divided by the concentration of reactants raised to a power equal to the number of moles these substances in the chemical equation is equal to a constant.
V.	The enzyme and substrate are at equilibrium with the enzyme substrate complex because the equilibrium is formed at a much faster rate than the breakdown of enzyme substrate complex into products.

V1. It cannot be assumed for all enzyme reactions that the enzyme, substrate and enzyme substrate complex exist in equilibrium, because very often the rate of breakdown of the enzyme substrate complex back into reactants approximates the rate at which it gives the products. A more valid assumption is that the enzyme substrate complex exists in a steady state i.e., its concentration is steady (fixed over the period of time taken to measure the initial velocity).

V11. K_m (or K_s) is numerically equal to the substrate concentration that gives half maximum velocity.

V111. The intercept on y ax is = $\frac{1}{VMAX}$ and the intercept on the x AXIS = $\frac{-1}{Km}$ when the reciprocal of both velocity and substrate concentration are plotted on a graph.

1X. For an enzyme reaction $\log V_{MAX} = K - \frac{E}{\text{Temperature } o_A}$.

X. In the case of heat inactivation of enzymes, the reaction is endothermic (i.e. ΔH is +ve) but there is a large accompanying increase in Entropy (i.e., ΔS is +ve) This means that at relatively low temperatures ΔG is negative hence the reaction is spontaneous.

X1. When the concentration of a conjugate acid equals the concentration of a conjugate base, $pH = -\log K$.

X11. At a point half way between the pH values only one form of a polyprotic weak acid exists in solution.

X111. An enzyme has an optimum pH because only one form of the enzyme substrate complex breaks down into products and this is mainly present at the optimum pH.

MEASURES.

A total of six measured were obtained for each subject who participated in this experiment . These measures comprise :-

1. A measure of achievement motivation (Iowa picture Interpretation Test).
2. A measure of test anxiety (Test Anxiety Questionnaire)
3. A measure of intelligence (A H/5)
4. A measure of gain score.
5. A measure of errors made on the programme.
6. A measure of time to complete.programme.

TRIAL EXPERIMENT.

As stated earlier in order to gain higher scorer reliability with the Need Achievement Test, Hedlund (1953) has developed a multiple choice version known as the lowa Picture Interpretation Test (I.P.I.T). According to McClelland (1958) it is questionable, however, whether higher reliability has been achieved at the expense of loss of validity.

Feather (1966) reports 6 studies all using subjects in which the correlations between the projective measure of need achievement (n.ach) and the Test Anxiety Questionaire (T.A.Q.) of Mandler and Sarason (1952) vary between r = + 0.11 and r = -0.15.That is to say when the number of subjects are taken into account they are all low and non-significant. The rationale underlying this trial is that if I.P.I.T. is measuring the same motive as the projective measure of n.ach. then one would expect to find a similar relationship with T.A.Q.

In the initial stages of the present investigation 144 females and 32 male college of education students were tested under neutral conditions using the Johnson (1957) ranking form of the I.P.I.T. In this test students were required to make forced rankings of the alternative responses given to each of the 24 T.A.T. pictures. Each picture was flashed on the screen for 1-minute. Scores for each student were then obtained by summing the ranks assigned to each picture. The scores were inverted so as to run in the same direction as the concept of motivation used.

Following the administration of the I.P.I.T. students completed the T.A.Q. Overall Test Anxiety Scores were obtained by summing their scores from the individual items of the T.A.Q. As in previous investigations e.g., Feather (1963), these item scores were obtained by dividing the rating scale of each item into five equal parts and scoring responses from one to five in the direction of increasing anxiety.

Using the r to t. transformation, following by a two tailed test significance the correlation between I.P.I.T. and T.A.Q for both males and females were found to be significant at the 5% level. For males the correlation was 0.420; df = 30 p 0.05 and for females the correlation was 0.193. df = 142 p 0.05.

~~These results suggest rather suprisingly that for both males and females I.P.I.T. and T.A.Q. have enough variance in common to be considered alternative manifestations of the same motive~~. Since these measures are positively correlated little purpose seemed to be served in converting both to 2 scores so that a final resultant

tendency could be measured. Under these circumstances it was decided to eliminate from the study the dubious I.P.I.T. but to retain the well validated T.A.Q. measure. Moreover the absence of any correlation between n ach scores and T.A.Q. scores is well documented in a series of articles in Feather and Atkinson's (1966) "Theory of Achievement Motivation". This means that the average need achievement scores is the same among high and low T.A.Q. groups. Hence relative to the strength of Test Anxiety (which has been measured), need achievement is a more potent influence on the behaviour of persons scoring low than high on test anxiety.
By using this line of reasoning it is possible using T.A.Q. only to investigate the hypotheses formulated in Chapter 1.

MEASURE OF INTELLIGENCE.

Immediately after completing the I.P.I.T. and the T.A.Q. the subjects worked through an intelligence test. Subjects in this experiment were expected to be in the uppermost quartile as regards intelligence in relation to the population as a whole. Thus an intelligence test is needed which discriminates strongly between subjects in this quartile. Such a test is the AH/5 of Heim (1947). This is a group test comprising verbal and non verbal parts and is used for testing high grade intelligence. Two other points in its favour are firstly its convenient testing time of just over 1-hour, and secondly its high test -retest reliability of 0.80 over a period of 1-year.

PRE AND POST TESTS FOR MEASURING GAIN SCORES.

Items for any test have to be selected from an infinite universe of items, thus in order to make selection of the items valid, the rationale underlying the test has to be stated at the outset. Thepurpose of these tests is to see if there is any difference in principle learning and problem solving performance by difference kinds of subject after learning enzyme kinetics by different strategies.

Part one of this test consists of a variant of the matching form of the objective test known as the Master List, in which the student has to select from a constant group of alternatives, the one that best applies to each member of the group of items. The main advantage of this type of test is the compact form in which the relationships between many principles can be measured. When the split halves method was performed on part one of the test, using 20 subjects in the trial experiment, a reliability co-efficient of 0.76 was found.

The second part of the test consists of multiple choice items. To solve the problems in this part of the test, Subjects have to make novel combinations with the principles they had learned. These combinations necessary to solve problems were made by random selection as shown in Table 3.

TABLE 3. COMBINATION OF PRINCIPLES NEEDED TO ANSWER A PARTICULAR QUESTION IN T HE PRE AND POST TESTS

	23.	24.	25.	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.	37.	38.	39.	40.
1.																		
11.	x	x	x			x		x										
111.		x		x	x				x		x	x			x	x		
1V.	x		x							x				x				x
V.					x	x	x										x	
V1.								x	x	x		x	x					
V11.				x			x				x							
V111.													x					
1X.																	x	
X.																		x
X1 .														x				
X11.																x		
X111.															x			

Key Roman numerals indicate the number of the principle

Arabic numerals indicate the question numbers.

X indicates which principles are necessary to answer a particular question.

It was possible only to justify test content on these logical grounds, no tests of predictive or concurrent validity were possible.

If the test is to be valid, high reliability is discriminability are necessary but they are not so easily achieved since they are both related to the variance of the tests which in turn depend upon efficiency of the self-instructional programmes. In other words, as Gronlund (1967) points out the same test can have different reliability and discriminabilities when used with different versions of the same teaching instrument. Furthermore, it is not permissable to contrive high reliability and discriminability by the usual methods. of field testing and subsequent item selection, because this will effect content validity. In pilot studies part two of the test was found to give a low mean score and a low standard deviation. Examination of the choice of incorrect alternatives revealed that in part 2. of the test the subjects found difficulty in applying several of the newly learned concepts all at once. Discrimination between subjects was found to be increased by giving credit to subjects who chose distractors corresponding to the correct application of all but one of the principles (A complete marking scheme is given with the test in the Appendix.)

If problem solving behaviour is being measure does this demand a constructed response rather than a multiple choice format? Ideally, yes, because with multiple choice items a subject will be selecting from a number of items which will be less than all the possibilities for a particular item. In practice, however, constructed reponses would be extremely difficult to mark. Objectively, therefore, a decision was made to construct a multiple choice test.

What is to be done about guessing, which will increase error variance. Stopping guessing altogether reduces discriminability because subjects with only partial knowledge for which they should receive credit will not gain any benefits from guessing after using their partial knowledge to eliminate some of distractors. Taylor (1966) compared the number of items omitted or unattempted in a test given to 3 different groups of 15 year olds, each group answering a moderately difficult maths test under different sets of test instructions :-

1. Instructions intended to inhibit guessing. ("Do not record answer until you have studied the question carefully, and do not record answer unless you are certain it is correct").

2. Instructions intended to have a neutral effect. ("Your aim should be to do as well as you can").

3. Instructions intended to encourage guessing. ("It is important that you get as many right as possible. In order to do this you may need to guess what the answer is. Do not be afraid to guess and have a go at every question").

Assuming that the number of items unfinished or omitted is an indication of guessing. It is found that the number of unfinished or omitted items decreased as follows with the items 1 2 3. It was, therefore, decided to adopt a compromise position and use set of instructions given under number 2.

Will these instructions interact in any way with the personality variables we are investigating ? There is some experimental evidence that they may do. For instance, Sherriffs and Boomers (1954) found that the tendency to guess at items of a multiple choise test was related to the maladjustment scale of the M.M.P.l. which is related to anxiety. We are, however, in no position to chose instructions which would give maximum validity, since this would imply knowledge of a true relationship between problem solving achievement and personality variables which is what we are setting out to discover. Therefore we can only continue by defining problem solving with a particular set of instructions, which then have self defining validity.

Turning finally to the timing of the test, it was found that the 50 minutes allotted to the test in trials was more than adequate for all subjects to attempt every item. If a lower time limit was placed on the test it would have effect of making the later items in the test appear more difficult than they really are.

The same test in this investigation serves as both pre and post test, thus the difficulty of preparing two equivalent forms of the same test is obviated. Gain scores are obtained by taking the score on pre test away from score on post test.

ERRORS AND TIME MEASURES.

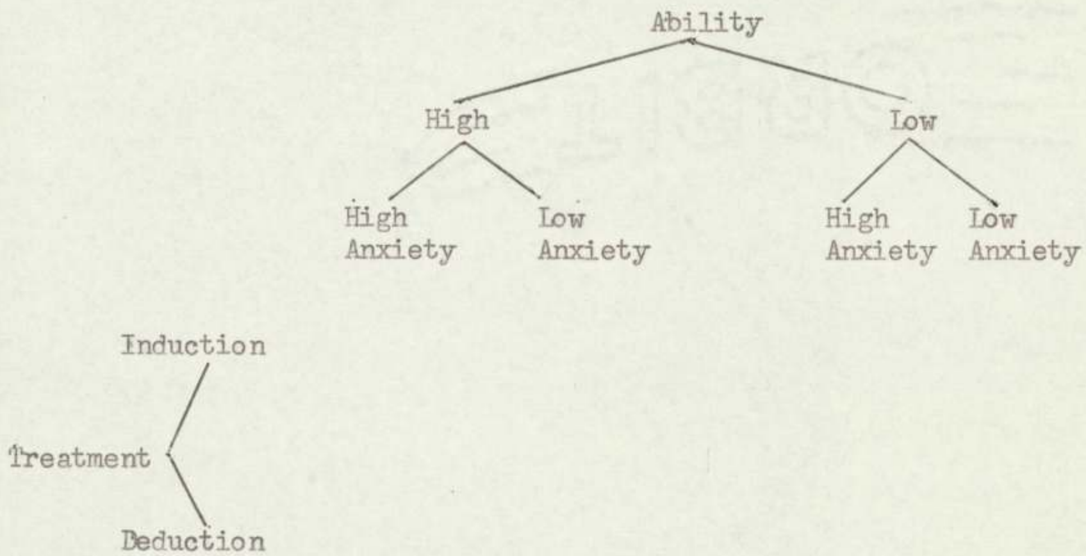
Both of these measures were obtained from subjects response sheets. It is possible that subjects may falsify their response sheets, however, on examination of the literature on the evaluation of programmes cheating never seems to be discussed or recorded. The experiment in the present study tried to reduce cheating by asking for co-operation of subjects at beginning of the programme. Perhaps the only way to really avoid cheating would be to use machines instead of book programmes but the cost was prohibitive in this study.

In this investigation time alone is used as one of dependent variables rather than an efficiency index where the gain score is divided by the time to give a measure of learning per unit time. This has been criticised by Holland (1965) on the grounds that it violates the following principles of measurement, i.e., to perform this division one treats test scores as though they formed a ratio scale, when in fact they are an ordinal scale because they do not provide valid statements regarding magnitude of differences and have no absolute zero.

DESIGN.

Females were first disnotomised according to ability on AH/5. Then both high and low ability subjects were separately classified according to whether they had high test anxiety, as shown in Figure 4.

FIGURE 4. ALLOCATION OF VARIOUS SUBJECTS TO THE DIFFERENT TREATMENTS.



High and low referring to above and below median respectively. High test anxious and high ability female subjects were then randomly allocated to the two treatments, i.e. inductive and deductive. This is followed similarly by the random allocation of the remainder of the female groups to these two treatments. This is shown diagramatically in Table 4.

The dependent variables are gain score, time to finish task and number of errors made when performing the task, using a 2 x 2 x 2 analysis of variances model the hypothesis below were tested separately at the 0.05 and 0.01 level of significance using the three different dependent variables:-

TABLE 4. FIRST SET OF HYPOTHESES FOR FEMALES USING GAIN SCORE. AS THE DEPENDENT VARIABLES.

Hypothesis.	Statement in n form.
1.	The mean of the high ability group is not significantly different from the mean of the low ability group.
11.	The mean of the high anxiety group is not significantly different from the mean of the low anxiety group.
111.	The mean of the inductive learners group is not significantly different from the mean of the deductive learners group.
1V.	There is no significant interaction between ability and anxiety.
V.	There is no significant interaction between treatment and anxiety

Hypothesis.	Statement in null form
Vl.	There is no significant interaction between treatment and ability.
Vll.	There is no significant interaction between ability anxiety and treatment.

TABLE 5. SECOND SET OF HYPOTHESES FOR FEMALES USING ERRORS ON PROGRAMMES AS THE DEPENDENT VARIABLE.

Hypothesis.	Statement in null form.
V111.	The mean of the high ability group is not significantly different from the mean of the low ability group.
1X.	The mean of the high anxiety group is not significantly different from the mean of the low anxiety group.
X.	The mean of the inductive learners group is not significantly different from the mean of the deductive learners group.
X1.	There is no significant interaction between ability and anxiety.
X11.	There is no significant interaction between treatment and anxiety.
X111.	There is no significant interaction between treatment and ability
X1V.	There is no significant interaction between treatment, ability and anxiety.

TABLE 6. THIRD SET OF HYPOTHESES FOR FEMALES USING TIME TO COMPLETE PROGRAMME AS THE DEPENDENT VARIABLE.

Hypothesis.	Statement in null form.
XV.	The mean of the high ability group is not significantly different from the mean of the low ability group.
XV1.	The mean of the high anxiety group is not significantly different from the mean of the low anxiety group.
XV11.	The mean of the inductive learners group is not significantly different from the mean of the deductive learners group.
XV111.	There is no significant interaction between ability and anxiety.
1XX.	There is no significant interaction between treatment and anxiety.
XX.	There is no significant interaction between ability and treatment.
XX1.	There is no significant interaction tetween ability, anxiety and treatment.

The whole experiment is then repeated using male subjects instead of females. Due to the disparity between numbers of males and females, also to the difficulty of interpreting complex interactions, the factor sex is not included in the analysis of variance thus avoiding a 2 x 2 x 2 x 2 model.

As Edwards (1965) says :-

> "One is better able to make sense out of analysis of variance if an attempt is made not to include too many factors."

TABLE 7. FIRST SET OF HYPOTHESES FOR MALES USING GAIN SCORE AS THE DEPENDENT VARIABLE.

Hypothesis.	Statement in null form.
XX11.	The mean of the high ability group is not significantly different from the mean of the low ability group.
XX111.	The mean of the high anxiety group is not significantly different from the mean of the low anxiety group.
XX1V.	The mean of the inductive learners group is not significantly different from the mean of the deductive learners group.
XXV.	There is no significant interaction between ability and anxiety.
XXV1.	There is no significant interaction between treatment and anxiety.
XXV11.	There is no significant interaction between treatment and ability.
XXV111.	There is no significant interaction between ability, anxiety, and treatment.

TABLE 8. SECOND SET OF HYPOTHESES FOR MALES USING ERRORS ON PROGRAMMES AS THE DEPENDENT VARIABLE.

Hypothesis	STATEMENT IN NULL FORM
XX1X.	The mean of the high ability group is not significantly different from the mean of the low ability group.
XXX.	The mean of the high anxiety group is not significantly different from the mean of the low anxiety group.
XXX1.	The mean of the inductive learners group is not significantly different from the mean of the deductive learners group.
XXX11.	There is no significant interaction between ability and anxiety.
XXX111.	There is no significant interaction between treatment and anxiety.
XXX1V.	There is no significant interaction interaction between treatment and ability.
XXXV.	There is no significant interaction between treatment anxiety and ability.

TABLE 9. THIRD SET OF HYPOTHESES FOR MALES USING TIME TO COMPLETE PROGRAMME AS THE DEPENDENT VARIABLE.

Hypotheses	STATEMENT IN NULL FORM.
XXXV1.	The mean of the high ability group is not significantly different from the mean of the low ability group.

XXXV11. The mean of the high anxiety group is not significantly different from the mean of the low anxiety group.

XXXV111. The mean of the inductive learners group is not significantly different from the mean of the deductive learners group.

XXX1X.- There is no significant interaction between ability and anxiety.

XL. There is no significant interaction between treatment and anxiety.

XL1. There is no significant interaction between treatment and ability.

XL11. There is no significant interaction between treatment, ability and anxiety.

CHAPTER 1V.

RESULTS.

Prior to carrying out the experiment with the programmes, it was necessary to classify each male and each female separately as high (H) or low (L) on the variables of intelligence and Test Anxiety. On AH/5 test of intelligence 33 was the median score for females, 6 subjects had this score and to maintain equal numbers in the high and low AH/5 cells two of these 6 subjects were randomly assigned to the high cell and the remainder were put in the low cell. 127 was the median score on the Test Anxiety Questionnaire made by the females. 6 Females had this score, so in order to maintain equal numbers in the high and low T.A.Q. cells 2 of these 6 subjects were assigned randomly to the high cell and the remaining 4 subjects to the low cell. For males the medians for AH/5 and T.A.Q. were 117.5 and 32.5 respectively. In both cases these medians very conveniently divided the male subjects into two equal high and low cell levels. A summary of the raw score means, standard deviation and other statistics for each level are presented in table 8.

TABLE 10 DESCRIPTIVE ANALYSIS OF SCORES ON THE EXPERIMENTAL VARIABLES.

	Intelligence		Test Anxiety	
	High	Low	High	Low
Male numbers. (N)	16	16	16	16
Mean (X)	38.75	28.5	131	101.5
Standard deviation	6.5	3.1	12.3	15.0
Median	37	29	126	104
Range	59.33	32.19	159-118	117-70
Female numbers. (N)	72	72	72	72
Mean (X)	38.56	27	142	109
Standard Deviation.	3.9	3.8	11.22	14.4
Median.	38	27.5	141	112.4
Range	54-33	33-13	172-127	127-60

From an inspection of these data it may be seen that the high and low classification for each variable based on a medium split is meaningful for both males and females.

For males on the AH/5 Subjects classified as "high" averaged 10.25 points above those classified as "low" while on the T.A.Q. those labelled as "high" averaged 29.5 points above those identified as "low". In both cases the standard deviations are low enough to assure significant differences between "High" and "Low" categories.

For females on the AH/5 Subjects classified as "high" averaged 11.56 points above those classified as "low". On the Test Anxiety Questionaire those labelled as "high" averaged 33 points above those labelled as "low". In both cases the standard deviations are low enough to assure significant differences between "high" and "low" categories.

The close agreement between mean and median scores for each separate level indicates that the distributions are not markedly skewed and that the assumption of normality of population, which is an assumption of the analysis of variance model is not violated.

Having thuse ensured that each experiemntal measures differentiates between "high" from "low" Subjects with respect to a particular variable, all the subjects in each of the four possible combinations - "high", "Low", Test Anxiety and intelligence were randomly assigned to the appropriate treatments.

The following combinations ensued: -

Intelligence.	Test Anxiety	Treatment.
High	High	Deductive
High	High	Inductive
High	Low	Deductive
High	Low	Inductive
Low	High	Deductive
Low	High	Inductive
Low	Low	Deductive
Low	Low	Inductive

At the end of the experiemnt it was found that 6-males had failed to complete programmes. In order to equalise numbers in the cells for the analysis of variance two more males were randomly dropped. Although the experiment started with 144 females, 19 failed to finish the experiment. So to equalise the numbers in the cells a further five were dropped randomly. This left 15 Females in each of the cells of the analysis of variance.

The decision to equalise numbers in the cells was made for the following reactions:-
1) to simplify computation, 2) so that results could be worked out on the University of Aston Computer where a suitable programme was available, 3) To make superfluous the preliminary testing for homogeneity of variance prior to carrying out analysis of variance (Hays (1965).

In the following sections of this chapter details of significant main effects and interactions, together with post-hoc analysis where appropriate will be given.

GAIN SCORES.

TABLE 11 COMPLETE ANALYSIS OF VARIANCE FOR MALES ON PRE - POST TEST GAIN SCORES.

Source.	Sum of Squares	Df	Mean Square	F	P
Treatment	150.000	1	150.000	3.06	
Intelligence	24.000	1	24.00		
Anxiety	2.667	1	2.67		
Tr x Int.	10.667	1	10.67		
Tr x Anx.	80.667	1	80.67	1.63	
Int x Anx.	0.667	1	0.67		
Trx Int x Anx.	66.667	1	66.67	1.35	
Within	784.000	16	49.00		
Total.	1119.333	23	48.67		

F0.05 df 1:16 = 4.49

F0.01 df 1:16 = 8.53

NB. In this table and subsequent tables F values which are obviously less than one will not be given.

From these resulta of gain scores for a small group of males, neither main effects nor interaction effects managed to produce any significant values. The only result approaching significance at conventional level was treatment which was significant at 0.1 level.

TABLE 12. COMPLETE ANALYSIS OF VARIANCE FOR FEMALES ON PRE-POST TEST GAIN SCORES.

Source.	Sum of Squares.	df.	Mean Square	F	P
Treatment	49.4083	1	49.4083		
Intelligence	195.075	1	195.075	2.81	
Anxiety	126.075	1	126.075	1.80	
Tr x Int.	460.208	1	460.208	6.57	0.05
Tr x Anx.	385.208	1	385.208	5.50	0.05
Int x Anx.	1.875	1	1.875		
Tr x Int x Anx.	85.0083	1	85.008	1.22	
Within	7894.13	112	70.483		
Total	9196.99	119	77.285		

F 0.05 df 1 : 100 = 3.94

F 0.01 df 1 : 100 = 6.90

Appearing in the above table are the results of the second analysis involving gain scores of females as a measure of performance. None of the main effects appear to be significant but the interactions of treatment with intelligence and treatment with anxiety are both significant at the 0.05 level, the former almost approaching significance at the 0.01 level. Further graphical representation and numerical analysis follows so as to make interpretation easier.

TABLE 13. MEAN SCORES OF SIGNIFICANT FIRST ORDER INTERACTIONS TREATMENT X INTELLIGENCE ON GAIN SCORES FOR FEMALES.

Levels of Intelligence	Induction	Deduction.
High	26.8	24.3
Low	20.6	25.7

Figure 5 MEANS FOR LEVELS OF INTELLIGENCE FOR EACH TEACHING STRATEGY ON GAIN SCORE FOR FEMALES.

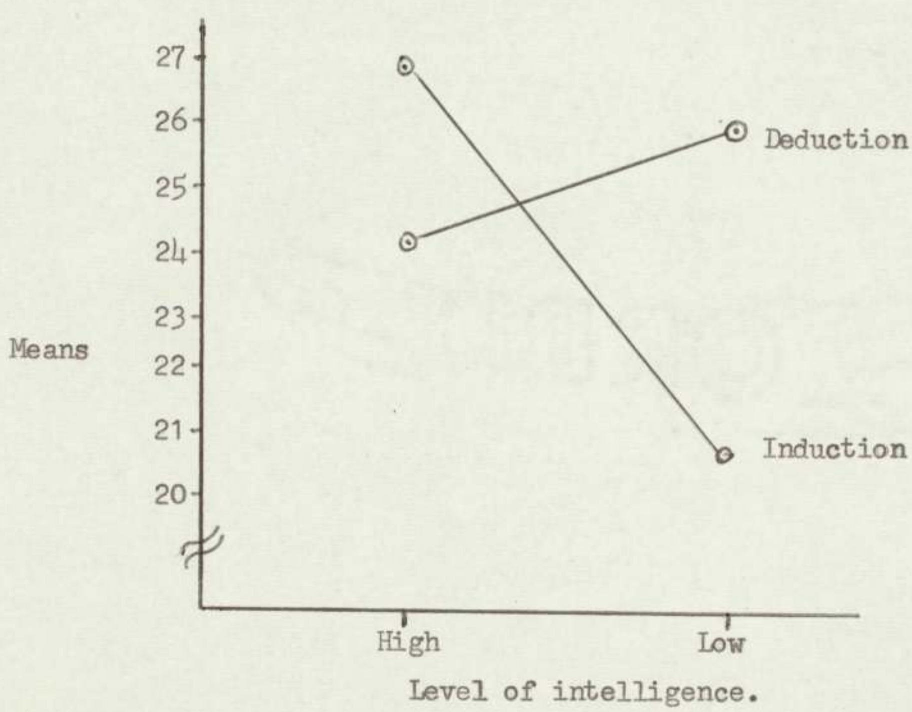


TABLE 14. SIGNIFICANCE OF DIFFERENCE BETWEEN MEAN SCORES OF SIGNIFICANT FIRST ORDER INTERACTION TREATMENT X INTELLIGENCE ON GAIN SCORES FOR FEMALES.

	df	t	P
High intelligence on Induction, High intelligence on deduction.	112	1.13	
Low intelligence on Induction. Low intelligence on deduction	112	2.34	0.05
High intelligence on Induction. Low Intelligence on Induction.	112	2.5	0.05
Low intelligence on Deduction High intelligence on Deduction.	112	0.64	

t 0.05 df 100 = 1.98

t 0.01 df 100 = 2.63

Using the method given in Lewis (1968) i.e., taking the within groups mean square as an estimate for population variance for each of the groups, the standard error of the difference between the two means is found. From this value t is computed. As can be seen from the above table, Low intelligence Subjects obtain significantly high scores on the deductive than on the inductive version of the programme. Also high intelligent Subjects obtain significantly higher gain scores than low intelligent Subjects on the inductive programme.

TABLE 15. MEAN SCORES OF SIGNIFICANT FIRST ORDER INTERACTIONS TREATMENT X ANXIETY ON GAIN SCORES FOR FEMALES.

Levels of ANXIETY	INDUCTION	DEDUCTION.
High	23.1	27.9
Low	26.6	22.2

FIGURE 6. MEANS FOR LEVELS OF ANXIETY FOR EACH TEACHING STRATEGY FOR FEMALES.

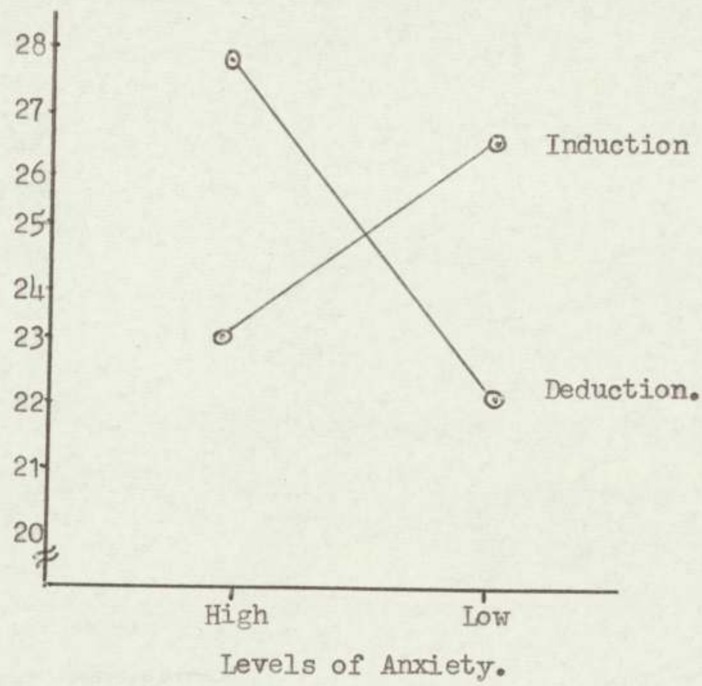


TABLE 16. SIGNIFICANCE OF THE DIFFERENCE BETWEEN MEAN SCORES OF THE SIGNIFICANT FIRST ORDER INTERACTION ANXIETY X TREATMENT ON GAIN SCORES FOR FEMALES.

		df.	t	P
High Anxiety on Induction	High Anxiety on Deduction.	112	2.2	0.05
Low Anxiety on Induction	Low Anxiety on Deduction.	112	2.03	0.05
Low Anxiety on Deduction	High Anxiety on Deduction.	112	2.6	0.05
High Anxiety on Induction	Low Anxiety on Induction.	112	1.6	

t 0.05 df 100 = 1.98

t 0.01 df 100 = 2.63

High Anxious Subjects obtain significantly higher gain scores from the deductive programme than they do from the inductive version, whereas for low anxious Subjects the reverse is true. High anxious Subjects also obtain higher gain scores after working through deductive programmes.than low anxious Subjects.

ERRORS ON PROGRAMMES.

TABLE 17. COMPLETE ANALYSIS OF VARIANCE FOR MALES USING RESPONSE ERRORS MADE ON THE PROGRAMMES AS DEPENDENT VARIABLE.

Source.	Sum of Squares	df.	Mean Square	F.	P.
Treatment	253.500	1	253.500	2.24	
Intelligence	28.167	1	28.167		
Anxiety	$16.263\ (10^{-18})$	1	0.0		
Treatment X Int.	48.167	1	48.167		
Treatment x Anx.	32.667	1	32.667		
Int. x Anx.	294.000	1	294.000	2.59	
Tr x Int. x Anx.	112.667	1	112.667		
Within	181.67	16	113.416		
Total	2583.83	23	112.340		

$F_{0.05}$ df 1:16 = 4.49

$F_{0.01}$ df 1:16 = 8.53

Analysis of variance indicates that there are no significant differences even approaching a conventional level of significance for either main effects or interation effects when the number of incorrect responses made by males on the programmes are used as the dependent variable.

TABLE 18. COMPLETE ANALYSIS OF VARIANCE FOR FEMALES ON RESPONSE ERRORS MADE ON PROGRAMMES.

Source.	Sum of Square	df.	Mean Square	F.	P.
Treatment	770.13	1	770.13	7.7	0.01
Intelligence	294.53	1	294.53	2.9	
Anxiety	83.33	1	83.33		
Tr. x Intell.	790.53	1	790.53	7.9	0.01
Tr. x Anx.	76.80	1	76.80		
Anx. x Intell.	333.33	1	333.33	3.3	
Tr. x Anx. x Intell.	4.80	1	4.80		
Within	11281.20	112	100.72		
Total.	13634.70	119	114.57		

F 0.05 df 1:100 = 3.94

F 0.01 df 1:100 = 6.90

The probability of obtaining by chance an F as high as the one above for the main effect between treatments is less than 1%. Examination of the means of errors for the two treatments, indicated that the mean number of errors made by females on the inductive programme was 40.7 which was significantly higher than the mean number of errors made by females on the deductive programmes i.e., 35.5.

There now follows a closer scrutiny of the treatments x intelligence interaction which was also significant for errors for females at the 0.01 level.

TABLE 19. MEAN SCORES OF SIGNIFICANT FIRST ORDER INTERACTIONS TREATMENT X INTELLIGENCE FOR ERRORS MADE BY FEMALES.

Levels of Intelligence	Induction.	Deduction.
High	36.5	36.6
Low	44.8	34.6

FIGURE 7. MEANS FOR LEVELS OF INTELLIGENCE FOR ERRORS ON EACH TEACHING STRATEGY FOR FEMALES.

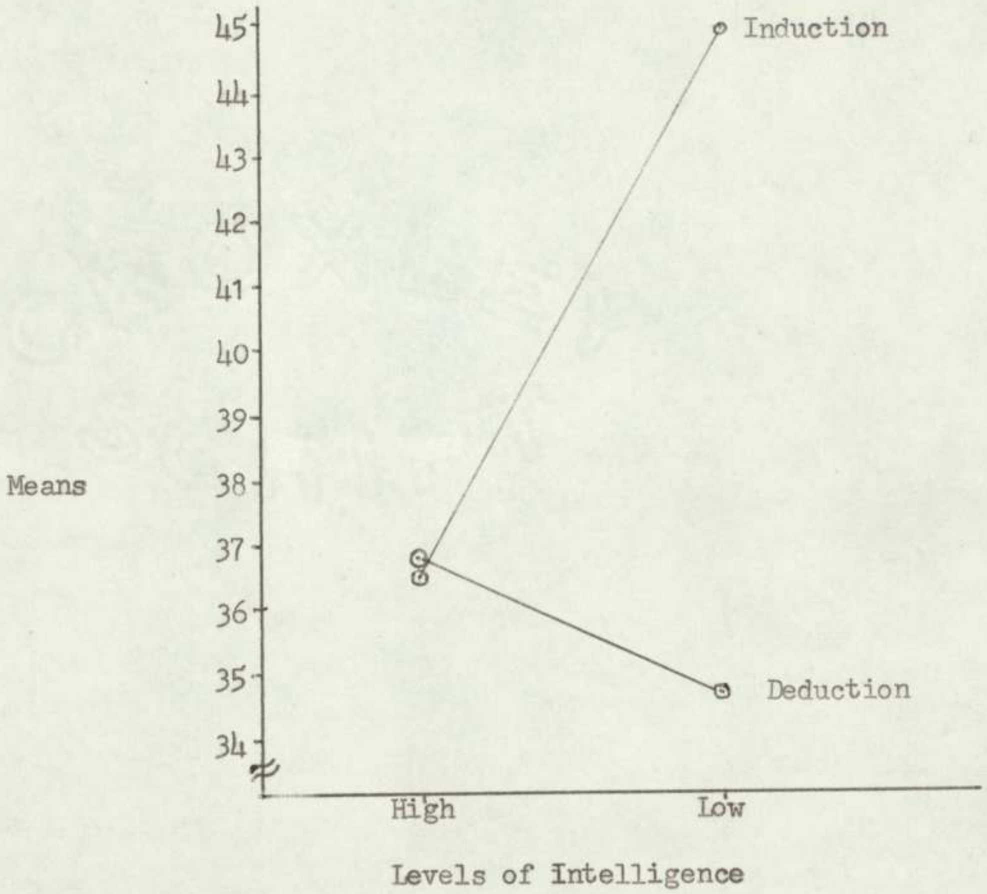


TABLE 20. SIGNIFICANCE OF THE DIFFERENCE BETWEEN MEANS OF ERRORS FOR THE FIRST ORDER INTERACTION TREATMENT X INTELLIGENCE FOR FEMALES.

		df	t	P
High intelligence on Induction	High intelligence on Deduction.	112	0.039	
Low Intelligence on Induction.	Low Intelligence on deduction	112	4.02	0.01
High Intelligence on Induction.	Low Intelligence on Induction.	112	3.2	0.01
Low Intelligence on Deduction.	High Intelligence on Deduction.	112	0.77	0

t 0.05 df 100 = 1.98

t 0.01 df 100 = 2.63

Two facts emerge from applying t tests to the above data-

1. With low Intelligence make significantly more errors on the Inductive than on the Deductive version, whereas High Intelligence Subjects make approximately the same number of mistakes on both versions.

2. High Intelligent Subjects make significantly less mistakes on the Inductive than do low Intelligence Subjects working with the same version of the programme. On the other hand when a similar comparison is made between High and Low Intelligent Subjects on the Deductive version, there is no such significant difference in the number of mistakes commited.

TIME TAKEN TO COMPLETE PROGRAMMES.

TABLE 21. COMPLETE ANALYSIS OF VARIANCE FOR TOTAL TIME TAKEN TO FINISH PROGRAMMES FOR MALES.

Source.	Sum of Squares.	df	Mean Square	F	P
Treatment	1717.04	1	1717.04	1.42	
Intelligence	234.37	1	234.37		
Anxiety	900.37	1	900.37		
Tr. x Intell.	759.37	1	759.37		
Tr. x Anx.	0.04	1	0.04		
Intell. x Anx.	234.37	1	234.37		
Tr. x Anx. x Intell.	70.04	1	70.04		
Within	19368.00	16	1210.500		
Total.	23283.60	23	1012.33		

F (0.05) df 1:16 = 4.49

F (0.01) df 1:16 = 8.53

For males no significant differences between either effects, i.e., treatment, level of intelligence, levels of anxiety or between interactions of these factors was found when taking total time to complete programme as the dependent variable.

TABLE 22. COMPLETE ANALYSIS OF VARIANCE FOR TOTAL TIMES TAKEN TO FINISH PROGRAMMES FOR FEMALES.

Source.	Sum. of Squares.	df.	Mean Square	F.	P.
Treatment	24339.0	1	24339.0	20	0.01
Intelligence	11662.0	1	11662.0	10.5	0.01
Anxiety	837.4	1	837.4		
Treatment x Intell.	75.2	1	75.2		
Tr. x Anxiety	696.6	1	696.6		
Intell. x Anx.	8551.4	1	8551.4	7.2	0.01
Tr. x Intell.x Anx.	444.6	1	446.6		
Within	134271.0	112	1198.8		
Total	180877.0	119	1519.9		

F (0.05) df 1:100 3.94

F (0.01) df 1:100 6.90

The average time taken by females for working through the inductive version is 172.2 minutes, which is significantly longer than the females working through the deductive version who took on average 143.7 minutes.

High intelligent females took significantly longer to work through the programmes than low ability females. The average time for each of these groups was 167.8 minutes and 148.1 minutes respectively.

TABLE 23. MEAN SCORES OF SIGNIFICANT FIRST ORDER INTERACTIONS INTELLIGENCE X ANXIETY FOR TIME FOR FEMALES TO COMPLETE PROGRAMME.

Level of Intelligence.	Levels of Anxiety. High	Low
High	173.6 mins.	162.0 mins.
Low.	137.0 mins.	159.2 mins.

Levels of Intelligence.

Figure 8. MEANS OF TIME SPENT ON PROGRAMME FOR LEVELS OF ANXIETY AT EACH LEVEL OF INTELLIGENCE.

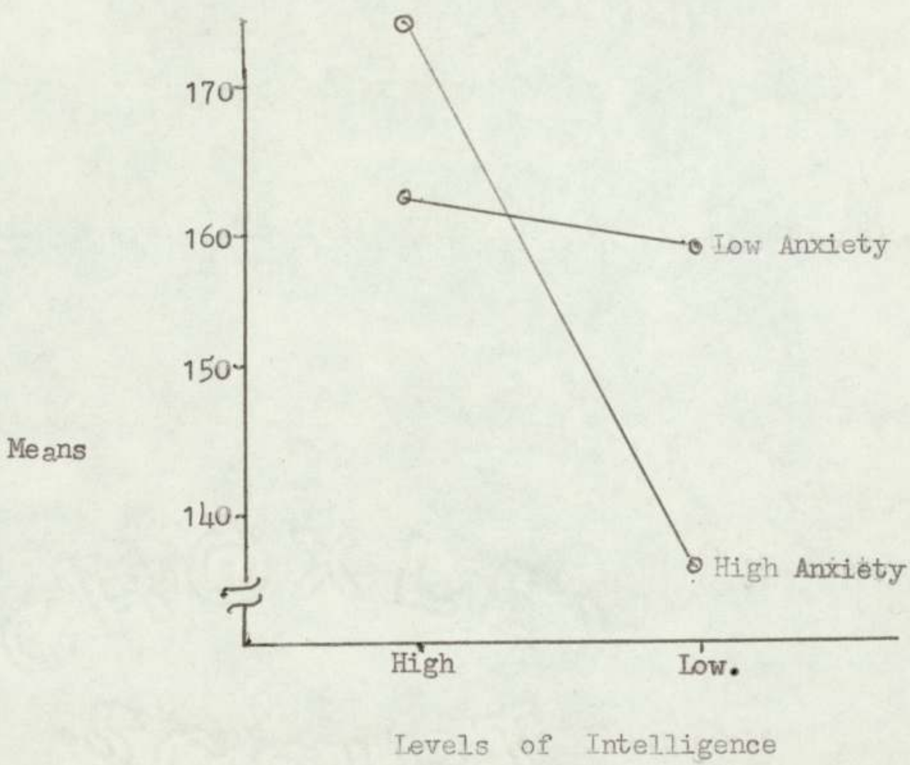


TABLE 24. SIGNIFICANCE OF THE DIFFERENCE BETWEEN MEAN TIMES OF FIRST ORDER INTERACTION ANXIETY X ABILITY FOR FEMALES.

	df	t	P
High Anx.on low Intell. High Anx.on High Intell.	112	4.12	0.01
High Anx.on low Intell. Low Anx.on Low Intell.	112	2.5	0.05
High Anx. on High Intell.Low Anx.on High Intell.	112	1.3	
Low Anx. on High Intell. Low Anx.on Low Intell.	112	0.3	

t 0.05 df 100 = 1.98

t 0.01 df 100 = 2.63

The above post hoc analysis reveals that High Anxious Subjects with High Intelligence take significantly longer to complete the programme than High Anxious Subjects with Low Intelligence. Also, High Anxious Subjects with Low Intelligence take less time than Low Anxious Subjects with Low Intelligence.

SUMMARY OF SIGNIFICANT RESULTS.

All the following results were obtained with females only. No significant results were obtained with males.

The hypothesis number (in Roman Numerals) refers to the particular null hypothesis listed at the end of Chapter 111.

Hypothesis.	Dependent Variable.	Significance Level.
V Tr. x Anx.	Gain Score	
$\mu_{H.Anx./Ded.} > \mu_{H.Anx./Ind.}$	"	0.05
$\mu_{L.Anx./Ind.} > \mu_{L.Anx./Ded.}$	"	0.05
$\mu_{H.Anx./Ded.} > \mu_{L.Anx./Ded.}$	"	0.05
V1. Tr x Int.		
$\mu_{H.Int / Ind.} > \mu_{L.Int./Ind.}$	"	0.05
$\mu_{L.Int./ Ded.} > \mu_{L.Int./Ind.}$	"	0.05
X Tr.	Errors.	
$\mu_{Ind} > \mu_{Ded.}$	"	0.01
X111 Tr x Int.		
$\mu_{L.Int./Ind.} > \mu_{H.Int/Ind.}$	"	0.01
$\mu_{L.Int./Ind.} > \mu_{L.Int/Ded.}$	"	0.01
XV Int.	Time.	
$\mu_{H.Int} > \mu_{L\ Int.}$	"	0.01
XV11 Tr.		
$\mu_{Ind.} > \mu_{Ded.}$	"	0.01
XV111 Anx. x Int.		
$\mu_{H.Anx./H.Int.} > \mu_{H.Anx./L.Int.}$	"	0.01
$\mu_{L.Anx./L.Int.} > \mu_{H.Anx./L.Int.}$	"	0.01

Key to abbreviations used in the above table.

μ	=	Mean	Tr	=	Treatment
H	=	High	Int.	=	Intelligence
Anx	=	Anxiety	Ded.	=	Deductive
$>$	=	is greater than	Ind.	=	Inductive.

CHAPTER V.

DISCUSSION OF RESULTS.

The first striking result of this experiment is the disparity between the results for males and females. All the results of any significance occurred with females; none of the results for males were significant. These differences between results could be due to the following reasons either :-

1. The experimental design.

or -

2. The intrusion of some unmeasured factor which although it is different for males and females in this experiment, is not different for males and females in general.

or -

3. Some real differences in the mental and behavioural traits of the sexes.

or -

4. Some combination of the above reasons. In the following few paragraphs each of these possibilities will be scrutinised and a possible explanation will be offered.

It could be asserted that the experimental design is faulty. It is unlikely, however, that faulty design was responsible because all the exigencies of the analysis of variance design have been met. Even so it could be argued that because of the small number of males in the cells of the analysis of variance design some important relationships failed to be revealed. However, when computing the probabilities for a result to be significant, the number of observations in the samples are taken into account. Furthermore these are significant differences between the high and low categories of the various independent variables for males, and consequently one would expect only differences between dependent variables to appear.

Turning now to another explanation, it may be that the results do reflect human behavioural sex differences. That such differences do exist is not open to doubt. Indeed, Gqrai and Scheinfeld (1968) in a recent extensive review of sex differences conclude -

> "Research has shown that men and women utilise different skills and abilities even when they learn similar subjects, and the conditions under which males achieve their optimum level of performance differ from those under which women function optimally".

Granted that such differences exist, what factors in our teaching strategies differentiate the various groups of women as regards performance, but at the same time apparently do not effect men ? Some research comparing males and females in problem solving situations helps to answer this question. Milton (1957) found that males in a problem solving situation preferred to analyse the situation rather than ask for help, or resort to a trial and error approach. Males also seem to be assisted in their analytic problem solving approach, by their greater "set breaking" ability and their greater facility in the utilisation of relevant clues. Kostick (1954) also observed male superiority on these latter two points in a transfer of learning situation in the scientific field. Perhaps therefore, males do not find problem solving situations in the inductive version of the programme so difficult or threatening as females. Evidence for this explanation is also to be found in the work of Carey (1958). He showed that men not only consistently exhibited a more favourable attitude to problem solving than women, but seemed to regard the solution of problems as a challenge rather than a threat. Men were also found to have greater ability to persist in their efforts to solve a problem than women, even under conditions of stress and frustration which had a detrimental effect on the performance of women. If these results were true generally they would explain why the interactions between teaching strategy and anxiety were found for women and not for men in the present investigation. Another piece of evidence supporting this position, is that of Russell and Sarason (1965) who, as in this study, used test anxiety to evaluate the effect of stress on task performance. They found that females who exhibited high test anxiety performed difficult anagrams problems more poorly than any other group, while males remained unaffected by test anxiety.

Although these other experiments give a plausible explanation of the differences observed between the interaction of anxiety and teaching strategy for males and females, they do not explain why no significant differences between high and low intelligent males were obtained, or why no interaction between intelligence and teaching strategy was observed for males In view of the fact that no significant differences were found for males in any of the three separate analyses of variance employing different independent variables, it may be that some other factor is masking the effects of the independent variables. Such a factor could be background knowledge for as Ausubel (1963) says subject matter sophistication must be taken into account in experimentation comparing inductive and deductive modes of learning. A t. test between the means for the entry bahaviour scores for males and females, however, failed to reveal any significant differences. It is recognised, however, that this is not completely satisfactory. What is needed in any replication of this experiment is a valid and reliable test of background knowledge which could be used as a covariate to adjust experimental gain scores. Perhaps in these circumstances, using analysis of covariance significant differences for males would be observed.

The rationale for error minimisation in programmes has been succintly stated by Glaser (1966) as follows:-

(1) When errors occur there is lack of control over the learning process, and opportunity is provided for the intermittent reinforcement of incorrect responses; this results in interference effects highly resistant to extinction.

(2) Richer learning, that is richer in associations takes place when the associative history of the learner is employed to extend his learning. This is accomplished by mediators or thematic promptings which make positive use of existing knowledge and serve to guide learning.

(3) Frustration and emotional effects difficult to control, are associated with extinction and interference. In contrast to this connectionist position configurationists argue that error rate is not optimally zero when considered in terms of instructional efficiency - i.e., a subject can learn from his mistakes. Work by Elley (1966) seems to reconcile these divergent opinions. He showed that with a meaningful non-arbitrary learning task, error rates were unrelated to end task performance, but with rote learning tasks efficiency was reduced under high error rate.

It is generally recognised that inductive learning results in a greater liklihood of error, for a subject has to generalise from a limited range of examples, and generalisations can be made which fit the data but are still wrong. This point of view received support from the present study where subjects made significantly more errors when learning by induction than they did by deduction, but as with Elley's experiment this difference in error rate had no apparent effect on the gain scores, which were not significantly different for subjects working on the two programmes.

This latter statement, however, does not have general validity for there is a first order interaction between anxiety and treatment, and between intelligence and treatment, when the dependent variable is gain score. Firstly, the significant interaction treatment x anxiety will be examined to see if it can fit into the context of need achievement. Both versions of the programmed learning task provide constant feedback to the subjects giving them knowledge of their objective probability of success. The results seem to indicate that where the objective probability of success is low i.e., where high error rate is experienced on the inductive version of the programme, then the high test anxious subjects become more emotionally tense and upset than the low anxious subjects. The effect of this emotionality is an increase in the number of task irrelevant responses leading to the disruption of performance which is reflected in their lower gain scores. In contrast, high test anxious subjects who have been learning in the more highly structured deductive learning situation where the objective probability of success is higher do not suffer a performance decrement in gain scores.

The second important point which these results show is that in the easy learning situation (i.e., with the deductive programme) high test anxious subjects are found to achieve higher gain scores than low test anxious subjects. This result could be explained by the fact that since need achievement and test anxiety are uncorrelated, the final resultant tendency to approach success is relatively higher in the low test anxious subjects than in the high test anxious subjects. As Heckhausen (1968) points out high probability of success is not attractive to hope of success subjects (i.e., those with high resultant tendency), but does serve to arouse fear of failure subjects (i.e., those with low resultant tendency).

It may be thought that the above results could have been predicted by extending to problem solving situations the Theory of Emotionally Based Drive of Spence & Spence (1966). They postulate that the Excitatory Potential (E) or impetus to respond is a multiplicative function of generalised drive (D) and learned or habitual patterns of response (H). Thus according to this theory high test anxious subjects all have higher drive than low test anxious subjects, this results in high test anxious subjects achieving superior results to low test anxious subjects in an easy learning situation where the probability of a successful response is greater. On the other hand in a difficult learning situation, high test anxious subjects are at a disadvantage when compared with low test anxious subjects, because their possession of higher drive means that there is a greater liklihood of competing erroneous responses being emitted.

Drive x habit theory, although explaining the above two results as well as need achievement theory could not explain why low test anxious subjects achieve higher gain scores in the difficult situation, than in the easy situation. Need achievement theory, however, in whose framework the present investigation is conducted, can, in addition explain the third result in the following manner.

Persons low in Test Anxiety have relatively high need achievement which is not engaged in the easy situation because here a person is sure of his ability to carry out the task and consequently the incentive value of the task is very weak. On the other hand low test anxious subjects find the difficult situation much more challenging. The incentive value of success is high and need achievement is aroused.

Turning now to the interaction between treatment and intelligence, an inverse relationship is observed between gain scores and errors when the significant differences between the means for each of these dependent variables are inspected. For instance, low intelligence subjects learning from the inductive programme make significantly more errors than the low intelligent subjects learning from the deductive programme. This situation is inversely reflected in the gain scores, low intelligent subjects making significantly higher gain scores when learning from the deductive programme than when learning from inductive programme. Furthermore when learning by the inductive method high intelligent subjects make significantly less errors than the low intelligent subjects learning by the same method. Again this is inversely reflected in the gain scores, where the group making fewer mistakes on the programme obtained significantly higher gain scores.

These results would seem to uphold the Skinner-Holland position on the rationale for minimisation of errors in learning by self instructional programme as succinctly stated by Holland (1965). Their position is that if errors occur as a result of the subjects not engaging in requisite precursory behaviour before making responses.

Also the Subjects having made errors have a high probability of repeating the error resulting in the establishment of inappropriate behaviour. This position would seem to be further strengthened by the fact that high intelligent Subjects do not make significantly more errors on the inductive version than on the deductive version, and subsequently there are no significant differences in gain scores when these two groups are compared. High intelligent Subjects appear to learn equally well by either method. The AH/5 intelligence test measures basic abstract mediational verbal and symbolic skills which are a great asset in transfer situations generally, thus enabling them to make the correct responses in the problem solving situations which are confronting them in the inductive programme. Also according to Zeaman & House (1967) highly intelligent Subjects will have a greater probability of making an observing response of cues and relationships in the learning sequence when compared with the low intelligence Subjects. Thus in the present study if this were true generally, the high intelligent Subjects would pick up thematic promptings more readily than the low intelligent Subjects resulting in their superior performance in the inductive learning situation.

Finally turning to the results of time data it is reasonable to expect that more time would be needed to discover principles than to receive them directly. This is seen for instance in the Hilgard et Al (1953) Study with Katona's card trick problems. Here the subjects who developed the rule for themselves worked with the material two to four times as long as those given the rule.

These present experimental results are no exception to this common sense view and it is found that subjects working through the inductive version took considerably longer than those working through the deductive version.

Proponents of lineor programming when stating their case against branching programmes have always argued that high intelligence subjects do not have their rate of progress impaired by working through the lineor programmes, for they are able to work such programmes very much more swiftly than the low intelligence subjects. A completely unexpected finding in this study is a reversal of this point of view. High intelligent subjects taking significantly longer to work through the programme than the low intelligence subjects. A possible explanation of thid fact could be that high intelligent subjects are able to carry out lengthy mediating behaviour before emitting a response to a frame, whereas low intelligence subjects are unable to engage in this necessary precursory behaviour and then pass on rapidly to the next frame.

A result more difficult to interpret is the significant first order interaction between test anxiety and intelligence using time as the dependent variable. One possible reason could be that low intelligent subjects who have low test anxiety and are therefore relatively higher in achievement motivation spend longer trying to reach a solution to the frames than highly test anxious subjects who also have low intelligence.

On the other hand, high anxious subjects with high intelligence behaviour take longer than low anxious subjects with high intelligence, because the latter group have their relatively higher achievement motive aroused, thus working at the task more conscientiously but differing from the low intelligence low anxiety group in that they are capable of performing the task correctly first time.

CONCLUSION.

Obviously the amount of valid generalisation that can be made from this single investigation is limited. The major limiting factors are first the highly selected sample taught by an unconventional method of programmed learning. Secondly, the limited quantity of instructional material. Thirdly, the short instructional period. It appears from this study that one method is not suited to all kinds of student, although the significant interactions observed, which enable us to make this statement, were only significant mostly at the 0.05 level - a significance level where there is greater probability of making a type I error (i.e., when null hypothesis is in fact true but we reject it) than at 0.01 level of significance.

As Eysenck says "perfection cannot be expected in pioneering studies" and in order to increase precision of any replication of this experiment the following alterations are suggested: -

1. The use of a more accurate measure of resultant tendency than just the Test Anxiety Questionaire. Perhaps using the Galvanic Skin Response or other physiological measures to validate the instruments used for measuring resultant tendency.

2. Increasing the numbers of subjects especially males, thus reducing the liklihood of a type 11 error (i.e. when the null hypothesis is false but the results of the test of significance fail to reject it).

3.- The construction of a valid Test of Background knowledge which could be used for adjusting the means of the various cells in an analysis of co variance design. Perhaps then some effects which were masked in the present study would make their appearance.

APPENDIX A.

RAW SCORE DATA.

RAW SCORE DATA.

Key to Symbols used in this appendix.

S = Subject.

A = Pre Test Score.

B = Post Test Score.

C = Gain Score.

D = Time to complete programme.

E = Errors on Programme.

F = Lowa Picture Interpretation Test Score.

G = Test Anxiety Questionaire Score.

H = AH/5 Intelligence Test Score.

TABLE 25. FEMALES WITH HIGH ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S.	A	B.	C	D	E	F	G	H
1	3	16	13	108	39	42	150	34
2	2	16	14	131	25	47	140	45
3	0	7	7	151	27	37	128	35
4	0	25	25	175	36	46	135	42
5	0	17	17	172	42	32	127	42
6	0	27	27	231	30	43	138	35
7	2	35	33	200	47	41	141	35
8	0	39	39	180	54	36	138	44
9	5	18	13	191	45	48	157	39
10	3	35	32	140	39	37	135	39
11	0	42	42	220	29	42	134	40
12	0	21	21	139	54	43	141	34
13	1	37	36	124	35	36	144	37
14	1	43	42	135	32	30	142	41
15	0	36	36	147	38	39	131	36

TABLE 26. FEMALES WITH HIGH ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE PROGRAMME

S	A.	B.	C.	D	E	F	G	H
1	0	36	36	184	30	36	142	44
2	4	32	28	180-	24	32	129	40
3	0	26	26	151	59	40	128	39
4	0	21	21	136	46	32	151	42
5	0	27	27	116	33	30	149	25
6	0	26	26	171	45	41	130	35
7	2	30	28	231	53	40	131	41
8	1	21	20	264	42	43	127	38
9	0	14	14	220	45	47	129	34
10	4	34	30	255	42	55	157	34
11	0	37	37	227	40	44	151	37
12	0	33	33	151	41	42	153	44
13	1	20	19	180	46	23	131	42
14	2	35	33	140	34	39	130	42
15	1	31	30	159	22	30	152	36
16	0	-	-	-	-	32	136	37

TABLE 27. FEMALES WITH HIGH ANXIETY AND LOW INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	3	38	35	117	29	37	152	23
2	0	37	37	173	32	45	134	24
3	0	16	16	101	28	30	142	23
4	0	35	35	124	27	30	146	22
5	0	30	30	116	25	38	130	27
6	0	31	31	123	39	54	164	32
7	0	24	24	104	43	45	139	25
8	0	28	28	132	31	49	129	31
9	1	17	16	120	60	51	160	26
10	0	27	27	136	16	34	156	31
11	5	28	23	160	23	36	149	33
12	0	36	36	120	52	30	152	27
13	0	28	28	104	21	40	151	32
14	0	38	38	115	33	36	140	30
15	0	35	35	116	39	32	151	25
16	0	-	-	-	-	46	135	33
17	0	-	-	-	-	38	152	19
18	0	-	-	-	-	46	136	26
19	0	-	-	-	-	28	132	24
20	0	-	-	-	-	32	145	28

TABLE 28. FEMALES WITH HIGH ANXIETY AND LOW INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	12	12	104	39	33	128	26
2	0	18	18	191	62	33	144	23
3	3	14	11	150	34	50	172	31
4	0	12	12	123	39	37	135	27
5	0	13	13	171	62	36	155	29
6	2	25	23	120	43	46	127	28
7	1	14	13	186	39	29	151	26
8	0	33	33	123	39	65	143	28
9	0	33	33	193	60	40	136	26
10	0	9	9	180	30	49	162	23
11	0	27	27	140	35	39	156	24
12	3	34	31	181	39	34	139	24
13	0	19	19	148	62	42	134	30
14	1	24	23	100	48	28	127	20
15	0	9	9	140	38	28	170	29
16	0	-	-	-	-	26	132	28
17	0	-	-	-	-	28	137	33
18	2	-	-	-	-	27	104	24
19	5	=	-	-	-	31	156	31
20	0	-	-	-	-	30	146	25
21	0	-	-	-	-	50	145	26

TABLE 29. FEMALES WITH LOW ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	17	17	144	29	42	119	39
2	0	26	26	160	31	32	94	54
3	5	44	39	148	37	30	107	36
4	3	9	6	116	35	31	127	40
5	4	35	31	108	20	31	104	41
6	0	19	19	116	26	39	122	37
8	0	24	24	172	31	41	93	38
9	0	17	17	116	19	25	97	46
10	0	24	24	140	36	31	83	35
11	7	30	23	179	42	36	99	39
12	1	32	31	159	40	26	85	34
13	0	25	25	147	61	36	98	38
14	2	23	21	140	40	33	88	36
15	0	23	23	159	40	34	123	36
16	0	-	-	-	-	30	104	41
17	0	-	-	-	-	43	111	43
18	0	-	-	-	-	33	111	36
19	1	-	-	-	-	39	102	40
20	2	-	-	-	-	23	120	34

TABLE 30 FEMALES WITH LOW ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE PROGRAMME

S	A	B	C	D	E	F	G	H
1	4	20	16	170	32	34	113	39
2	0	20	20	200	38	27	127	38
3	4	25	21	186	29	36	126	37
4	0	18	18	171	31	34	123	37
5	0	37	37	231	37	34	120	40
6	0	22	22	121	35	23	83	37
7	0	32	32	191	20	45	105	35
8	1	33	32	207	26	38	103	43
9	0	22	22	192	40	32	116	36
10	3	27	24	184	40	46	88	34
11	7	40	33	156	31	30	83	42
12	0	32	32	212	40	38	113	45
13	0	25	25	128	19	35	71	33
14	0	37	37	172	36	25	115	35
15	0	27	27	200	42	38	122	41
16	1	-	-	-	-	28	107	40
17	2	-	-	-	-	31	112	33
18	0	-	-	-	-	34	123	44
19	0	-	-	-	-	24	119	34
20	1	-	-	-	-	46	122	35

TABLE 31 FEMALES WITH LOW INTELLIGENCE AND LOW ANXIETY WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	33	33	92	17	42	83	30
2	0	32	32	137	27	45	126	32
3	2	15	13	192	26	35	121	26
4	3	25	22	99	33	37	126	31
5	1	14	13	187	30	44	121	26
6	1	21	20	115	46	44	116	29
7	0	39	39	144	52	37	95	29
8	0	22	22	228	41	36	97	32
9	0	26	26	113	46	41	110	18
10	0	6	6	104	21	41	116	26
11	1	36	35	95	46	38	115	13
12	0	17	17	220	35	32	92	26
13	0	24	24	144	55	40	120	30
14	2	16	14	149	21	27	104	24
15	0	17	17	160	45	38	120	31
16	0	-	=	-	-	39	119	30

TABLE 32 FEMALES WITH LOW INTELLIGENCE AND LOW ANXIETY WHO WORKED THROUGH THE INDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	4	12	8	165	44	24	123	29
2	0	30	30	220	49	33	115	32
3	1	24	23	204	44	34	120	31
4	0	15	15	130	45	45	121	32
5	0	33	33	132	40	31	126	32
6	0	26	26	171	48	29	105	25
7	0	27	27	127	46	39	110	23
8	0	20	20	188	57	34	109	29
9	0	29	29	195	47	40	109	26
10	3	22	19	133	54	44	114	26
11	0	30	30	127	45	30	104	28
12	0	26	26	150	39	29	116	29
13	0	17	17	206	54	39	109	31
14	1	22	21	239	29	35	124	27
15	2	12	10	210	35	42	123	33
16	0	-	-	-	-	54	60	31

TABLE 33 MALES WITH HIGH ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	26	26	146	33	39	120	37
2	0	-	-	-	-	35	124	34
3	3	20	17	144	29	42	118	36
4	0	10	10	127	43	38	126	33

TABLE 34 MALES WITH HIGH ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	20	20	104	50	27	126	40
2	0	11	11	191	62	28	118	38
3	2	26	24	149	42	39	142	37

TABLE 35. MALES WITH HIGH ANXIETY AND LOW INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	23	23	155	50	43	134	26
2	0	-	-	-	-	31	120	30
3	2	18	16	142	59	46	159	29
4	0	-	-	-	-	31	141	30
5	3	18	15	134	45	44	143	31

TABLE 36. MALES WITH HIGH ANXIETY AND LOW INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	6	18	12	187	58	44	143	31
2	0	15	15	123	48	27	123	27
3	0	17	17	195	53	40	140	32
4	2	-	-	-	-	39	119	27

TABLE 37 MALES WITH LOW ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	19	19	86	48	34	101	35
2	0	17	17	208	44	33	80	39
3	0	37	37	115	54	22	106	36
4	4	-	-	-	-	31	86	59

TABLE 38. MALES WITH LOW ANXIETY AND HIGH INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE VERSION.

S	A	B	C	D	E	F	G	H
1	0	-	-	-	-	31	102	33
2	0	10	10	173	62	42	115	39
3	0	9	9	120	42	27	110	48
4	2	16	14	123	50	34	93	35
5	0	-	-	-	-	28	117	41

TABLE 39. MALES WITH LOW ANXIETY AND LOW INTELLIGENCE WHO WORKED THROUGH THE DEDUCTIVE PROGRAMME.

S	A	B	C	D	E	F	G	H
1	0	29	29	123	40	36	70	31
2	0	10	10	93	28	35	112	19
3	0	-	-	-	-	35	117	28
4	0	13	13	144	59	25	117	27

TABLE 40 MALES WITH LOW ANXIETY AND LOW INTELLIGENCE WHO WORKED THROUGH THE INDUCTIVE PROGRAMME

S	A	B	C	D	E	F	G	H
1	0	8	8	180	32	38	102	29
2	3	17	14	140	52	30	82	31
3	1	19	18	140	60	40	114	29

APPEMDIX B.

Iowa Picture Interpretation Test

Response sheets.

Thematic Apperception Test

Pictures 1 - 24

Each of the pictures you will see is indicated in the booklet by a number. Underneath each number there are four descriptions for that particular picture. You are to rank the four descriptions according to your idea of what the picture expresses.

Each of the descriptions can be ranked from 1 to 4 on the basis of how well you think it fits the picture, that is tells what is happening. Read all four descriptions and decide which one you would most likely give. This one would rank as number one.
Then decide upon the one that seems next most likely. Rank it two, and so on. The description that you would least likely give should be ranked four.

Here is an example:

A. She is listening to her favourite radio programme.
B. She is annoyed because she has to work while her friends go out.
C. She feels that she cannot go to the party because no one ever asks her to dance.
D. She is looking forward to her opening night as the star of a great show.

If B is the most like your interpretation you would rank it one. Look at the separate answer sheet. Under the space marked example you would write a 1 after the letter B. You would then write down the ranks of the descriptions A. B. and D.

Each picture will be shown for one minute, you must rank each description. Even if you have difficulty deciding what rank should be make the best decision you can. Remember there are no right and wrong answers. Do not spend too much time trying to decide, indicate your first impressions.

Now take the answer sheet. Fill in your name and other information at the top. Now turn the page. Judge the statements for card one and rank them on the separate answer sheet.

DO NOT MARK THIS BOOKLET.

1. A. He is dreaming of the day when he will become a great musician.
   B. He is afraid that he will never be able to play the violin well.
   C. His Violin is on the table and he is waiting for his music lesson.
   D. He is angry at his mother because she makes him practice while he would rather be outside playing.

2. A. She feels only scorn for these people and their way of life.
   B. She is looking for a nice quiet place where she can read and get a little relaxation.
   C. She is rather sad because she doesn't fit in at school or on the farm.
   D. Her only ambition is to complete her education.

3. A. He very much wants to stay with her but is afraid of other people's contempt.
   B. He is determined to fight for what he thinks is right and will win through in the end.
   C. He is disgusted with her and is trying to get away as quickly as he can.
   D. He is a patient being helped into bed.

4. A. They are waiting for the taxi to take him to the station.
   B. He has told her that he resents her prying into his affairs.
   C. He is telling her that he must leave home because opportunities are greater in the big city.
   D. He is telling her that he has lost his job and has little hope of finding another.

5. A. The boy is determined to live up to the ideals and standards of the older man whom he greatly admires.
   B. The older man is telling about his childhood experiences.
   C. The father is telling his son if he does not stop his wild ways he will disown him.
   D. The boy is distressed because he feels he has let his father down.

6. A. The little girl has been left in the care of a governess and feels that she is less loved by her parents than other children.
   B. The little girl is resentful because her mother insists upon drilling her over her homework.
   C. Thelittle girl is listening to a story of Florence Nightingale and is thinking of the time when she might achieve so much.
   D.The little girl listens while her mother reads her stories.

7. A. He is remembering part of the movie he has just seen.
   B. He is dreaming of becoming a skilled and favour surgeon.
   C. He realises that the operation is doomed to failure and turns away.
   D. He hates his cruel stepfather and hopes he will not survive the operation.

8. A. He is thinking of ways of getting back at his father who wont let him leave the cabin.
   B. He is wondering why he is so unpopular and no one comes over to play with him.
   C. He is enjoying the warmth of the sunshine.
   D. He wishes he could grow up to be like Abraham Lincoln, who was also born in a log cabin.

9. A. Things have not worked out for him and he is wondering whether life is worth living.
   B. He is watching a plane passing overhead.
   C. He is wondering how he can revenge himself on those who have wronged him.
   D. He is thinking of great accomplishments.

10. A. He is demonstrating the way to climb a rope.
   B. He is watching his hated rival and hopes he will fall.
   C. He is a rope climbing contestent and is exerting every effort to win.
   D. Although he has tried his best he sees the race is lost.

11. A. She despises the man who is forcing his attention on her.
   B. He admires her for the success she has achieved in her carreer.
   C. She is sorry that she did not do more to make her marriage a happy one.
   D. They are considering whether to buy the attractive table.

12. A. He has resolved to do his best to keep up to her expectations.
   B. He has failed her in spite of her high hopes.
   C. They are at a party dancing to a Viennese Waltz.
   D. Despite his pretense and show of effection he secretly despises her.

13. A. She is furious because the lift is out of order and she must walk.
   B. She is on her way to catch a train.
   C. Although she is looking for work in the big city she has no real hope of success.
   D. Viewing the magnificance of the structure she is inspired to work harder towards her career.

14. A. She cannot succeed and is going to commit suicide.
   B. She is waiting to go on stage in what will be her greatest theatrical triumph.
   C. She is trying hard to hide her laughter after playing a mean practical joke.
   D. She is wiping a cinder out of her eye.

15. A. She is just coming home from a walk.
   B. This maid is planning revenge on her arrogant employers.
   C. She is eager for everything to be in perfect order, because her husbands boss is coming to dinner.
   D. She worries that her home is so shabby that it will make a poor impression.

16. A. She is rushing to tell her sister that they have won the contest.
   B. Shehas told her sister she must hurry if she wants to meet her friends,
   C. She feels only scorn for her sister and her wild ways.
   D. She feels inferior to her sister who is everything she had hoped to be.

17. A. He feels that there is no use trying and will join this band of hobos.
    B. He despises these men for their irresponsible behaviour.
    C. Watching the labourers he dreams of the success that will put him far above such a life.
    D. The men are resting after lunch.

18. A. The girl is watching the men and waiting for her husband to finish work.
    B. Seing her old waterfront neighbourhood she realises how great her success has been.
    C. She wishes that she had more self confidence but fears that she will never amount to much.
    D. She is furious having been kept waiting so long.

19. A. He hates the people who led him into this kind of life
    B. He realises now that he will never excape from the life he has been leading.
    C. He is tired and is leaving the party to get some sleep.
    D. He is determined to start anew and make something of himself.

20. A. She is explaining the despair of overcoming the limitations of her handicap.
    B. They are enacting a scene in a play.
    C. She has finally turned in fury on the women who has humiliated her.
    D. She is telling the women that in spite of her handicap she knows she will succeed.

21. A. He is thinking of how quiet the big city can become in the early morning.
    B. He is watching the dark to get back at his tormentors.
    C. He is sure that some day he will be one of the successful people living in this fashionable neighbourhood.
    D. He feels that he will never beable to make the grade in the big city.

22. A. He is being awakened from a brief rest to resume work on his invention.
    B. The mand is in despair because he can do nothing to help.
    C. He is waking the other person from his sleep since it is daybreak.
    D. His meancing gesture reveals his bitterness towards the sleeping man.

23. A. The old lady is envious and resentful of this younger women.
    B. They are reminiscing about their years of happiness and success together.
    C. The old lady wishes that she had been able to help the younger women when she needed it.
    D. They are both watching the people pass on the street.

24. A. He has just completed an extremely difficult and dangerous operation.
    B. Hehas failed to save her life although he has tried his best.
    C. He is rubbing the sleep out of his eyes in an effort to keep awake.
    D. He is rejecting the women because of his disgust for her and all that she stands for.

ANSWER SHEET I.P.I.T.

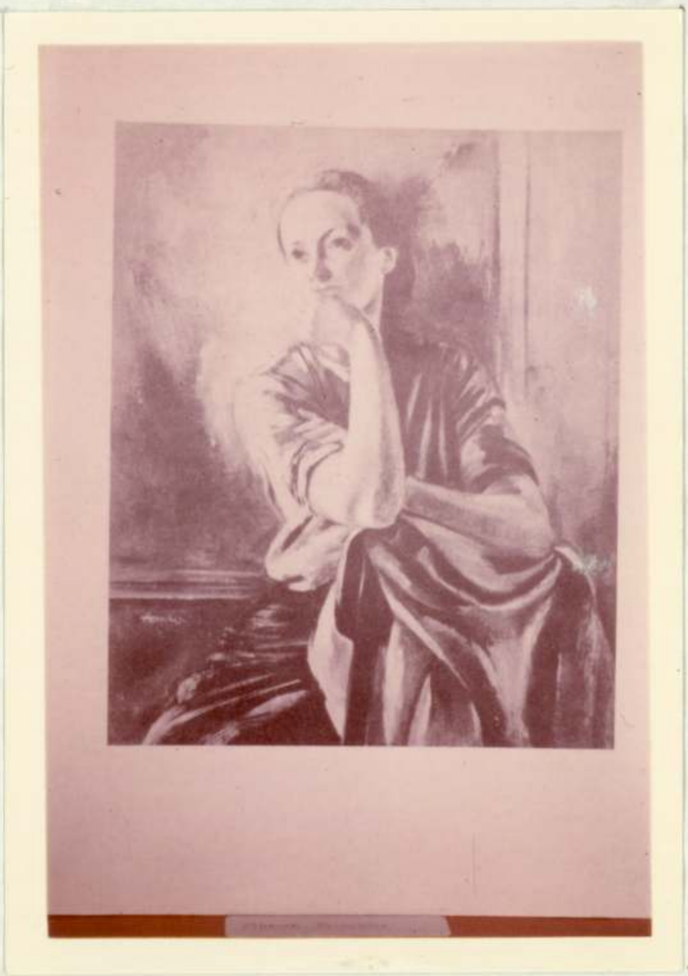
Name ________________ Sex ________ College ____________
(Block Capitals)

Exammple A ____ B ____ C ____ D ____	Card(5) A ____ B ____ C ____ D ____	Card(10) A ____ B ____ C ____ D ____	Card(15) A ____ B ____ C ____ D ____	Card(20) A ____ B ____ C ____ D ____
Card(1) A ____ B ____ C ____ D ____	Card(6) A ____ B ____ C ____ D ____	Card(11) A ____ B ____ C ____ D ____	Card(16) A ____ B ____ C ____ D ____	Card(21) A ____ B ____ C ____ D ____
Card(2) A ____ B ____ C ____ D ____	Card(7) A ____ B ____ C ____ D ____	Card(12) A ____ B ____ C ____ D ____	Card(17) A ____ B ____ C ____ D ____	Card(22) A ____ B ____ C ____ D ____
Card(3) A ____ B ____ C ____ D ____	Card(8) A ____ B ____ C ____ D ____	Card(13) A ____ B ____ C ____ D ____	Card(18) A ____ B ____ C ____ D ____	Card(23) A ____ B ____ C ____ D ____
Card(4) A ____ B ____ C ____ D ____	Card(9) A ____ B ____ C ____ D ____	Card(14) A ____ B ____ C ____ D ____	Card(19) A ____ B ____ C ____ D ____	Card(24) A ____ B ____ C ____ D ____

IOWA PICTURE INTERPRETATION TEST

The following pictures numbered 1 to 24 correspond to the questions in the test booklet.

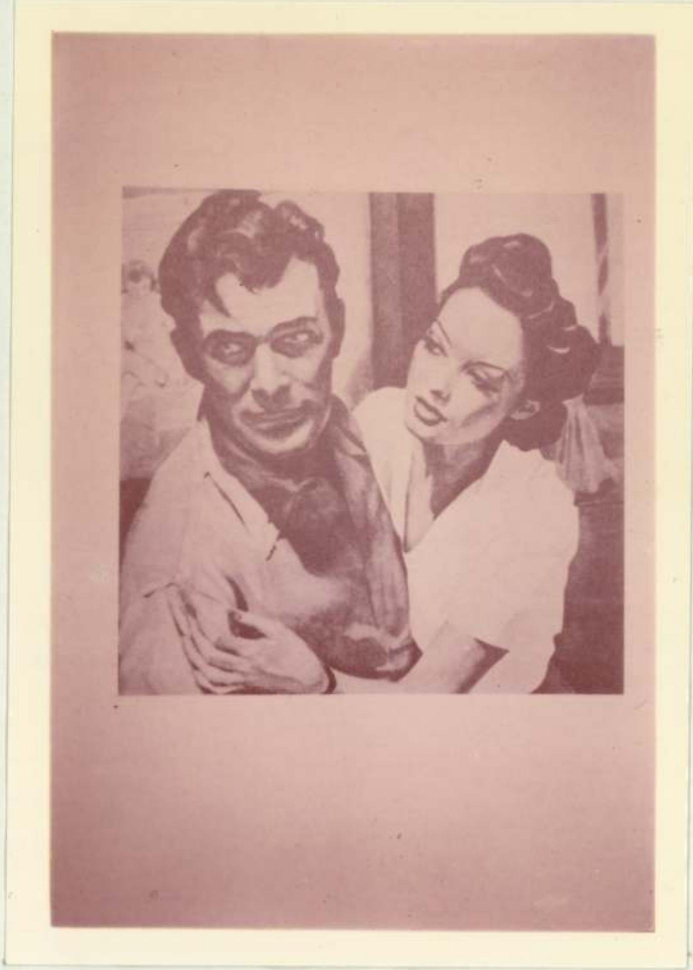
Example



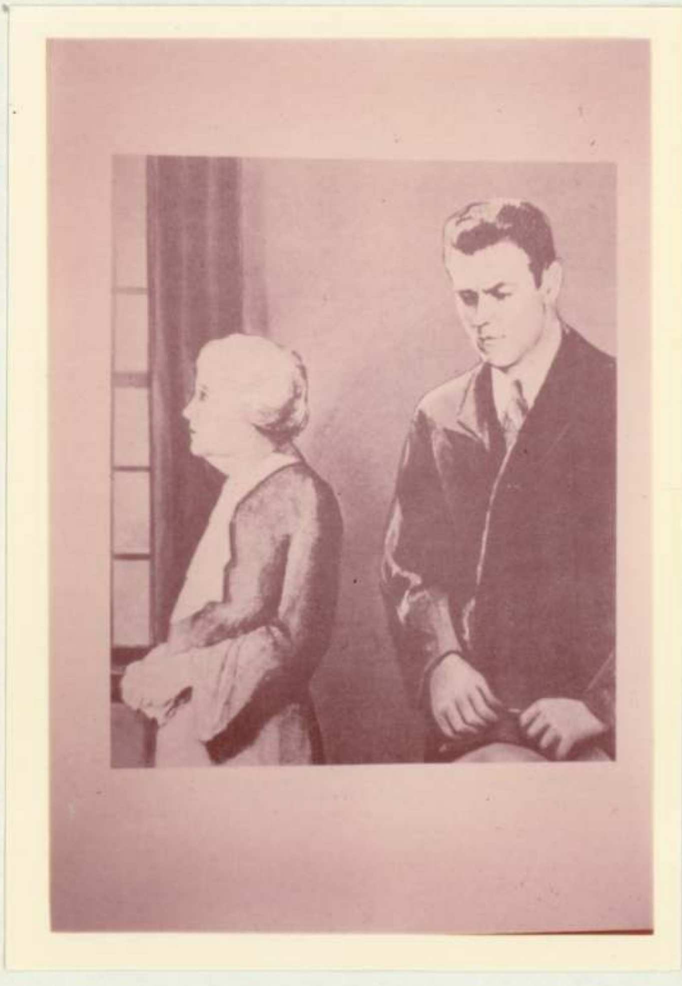
(1)

(2)

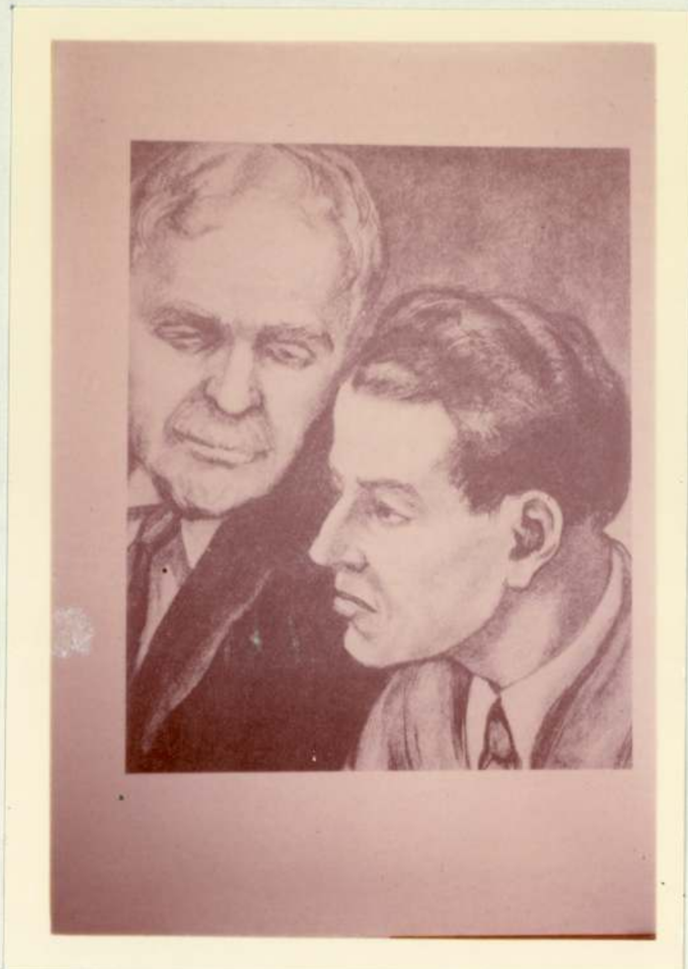
(3)



(4)



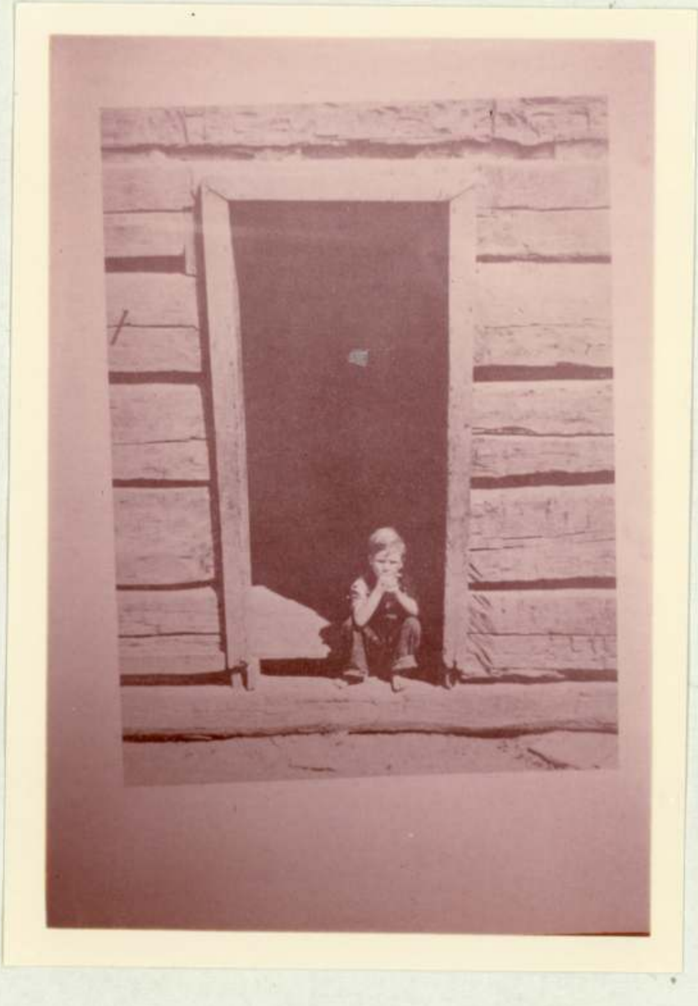
(5)



(6)

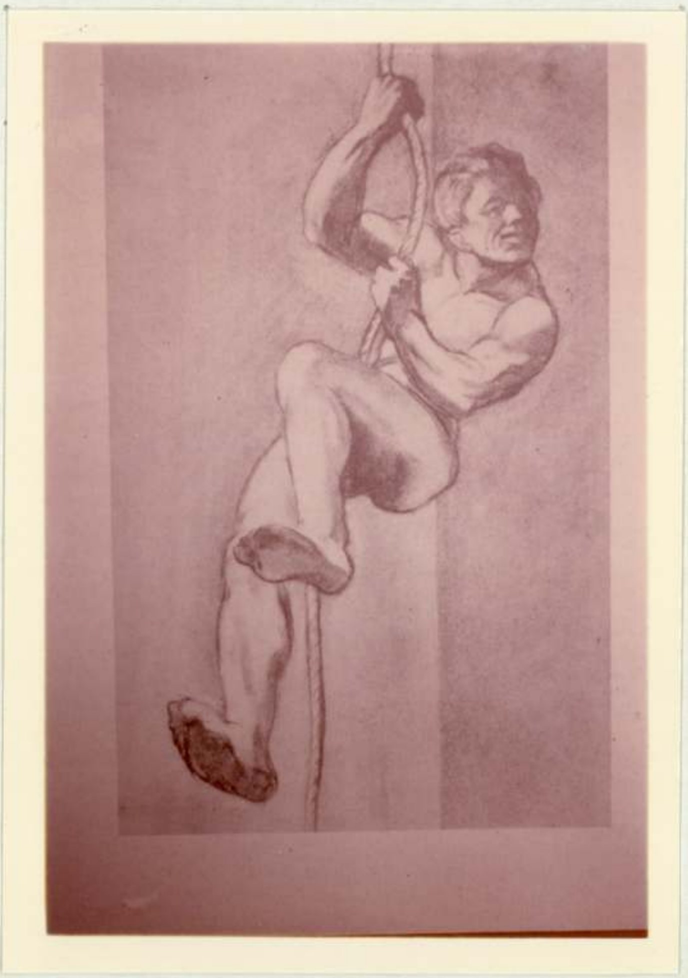
(7)

(8)



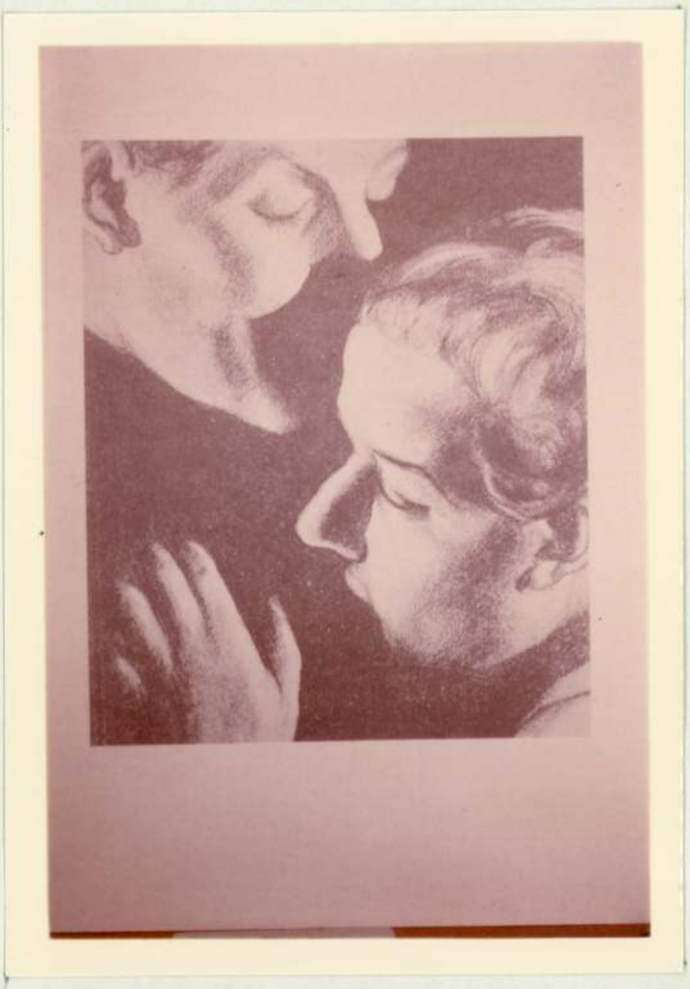
(9)

(10)

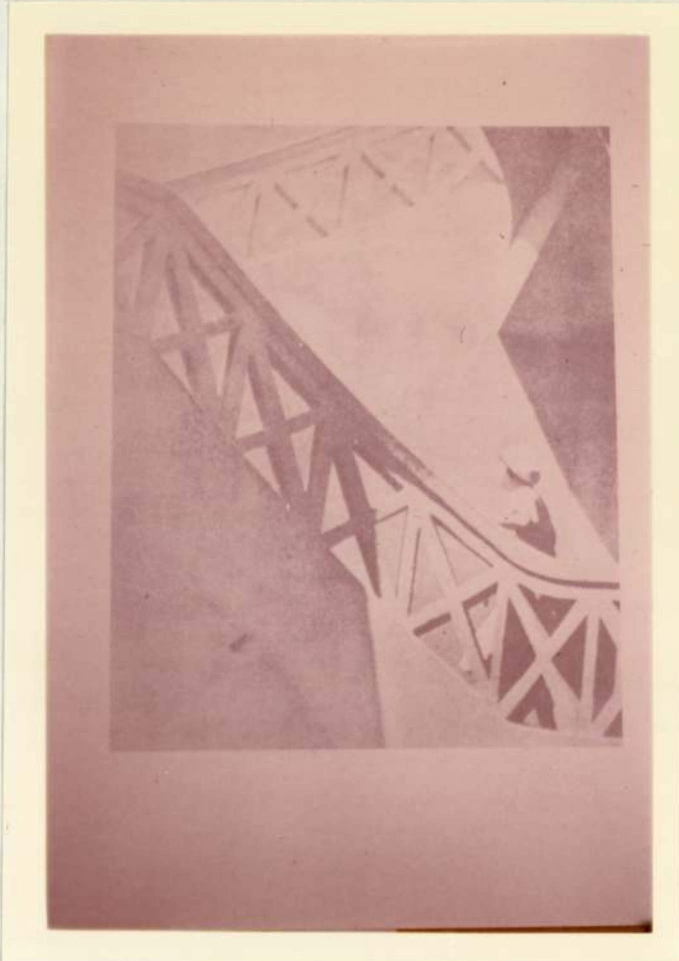


(11)

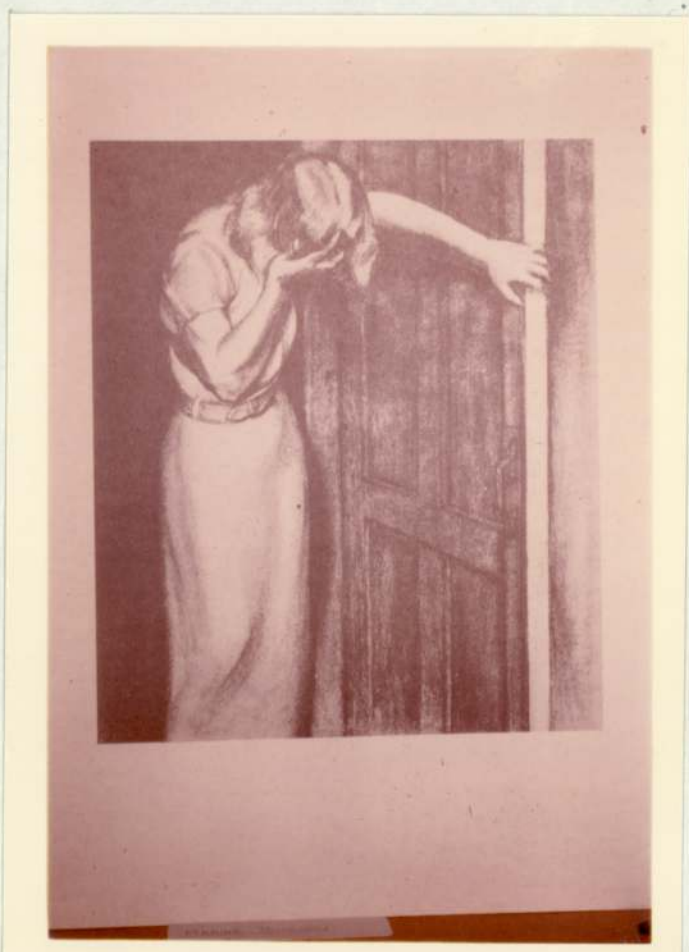
(12)



(13)



(14)



(15)

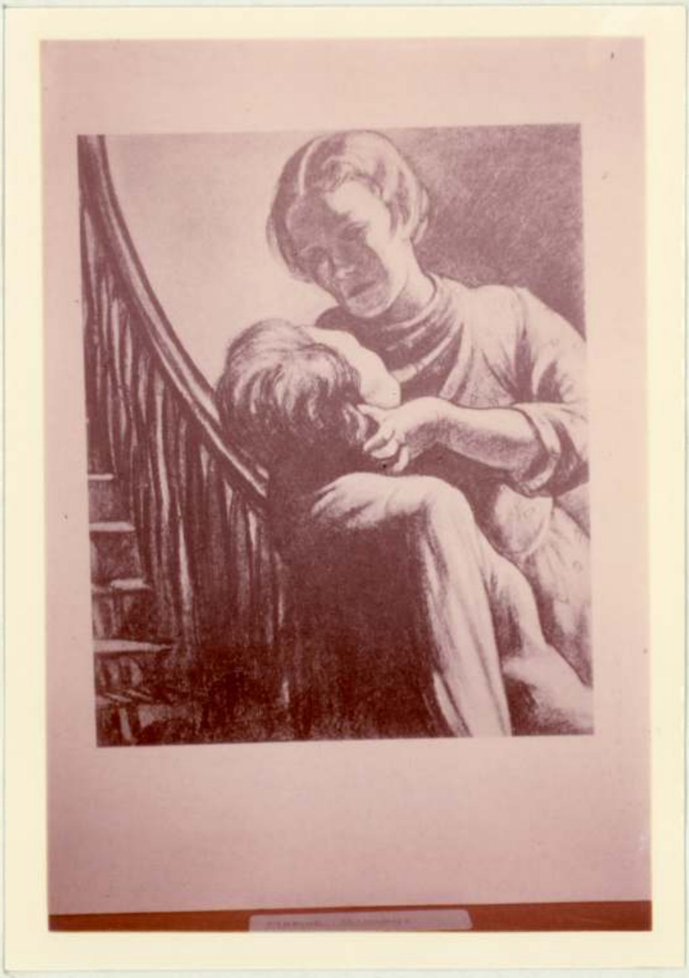
(16)

(17)

(18)

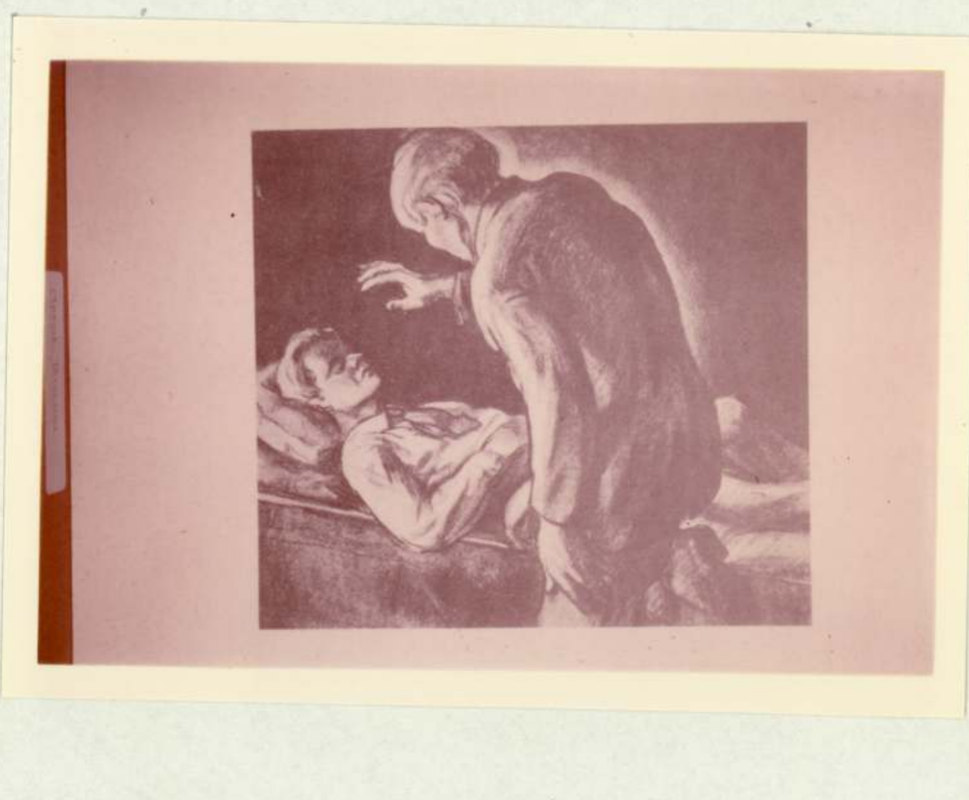
(19)

(20)

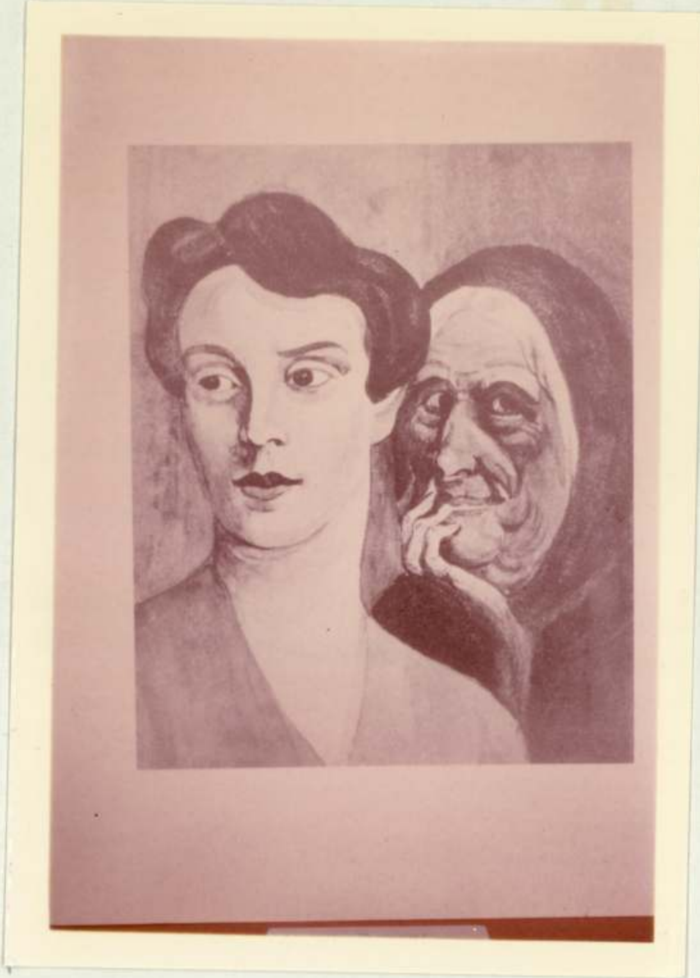


(21)

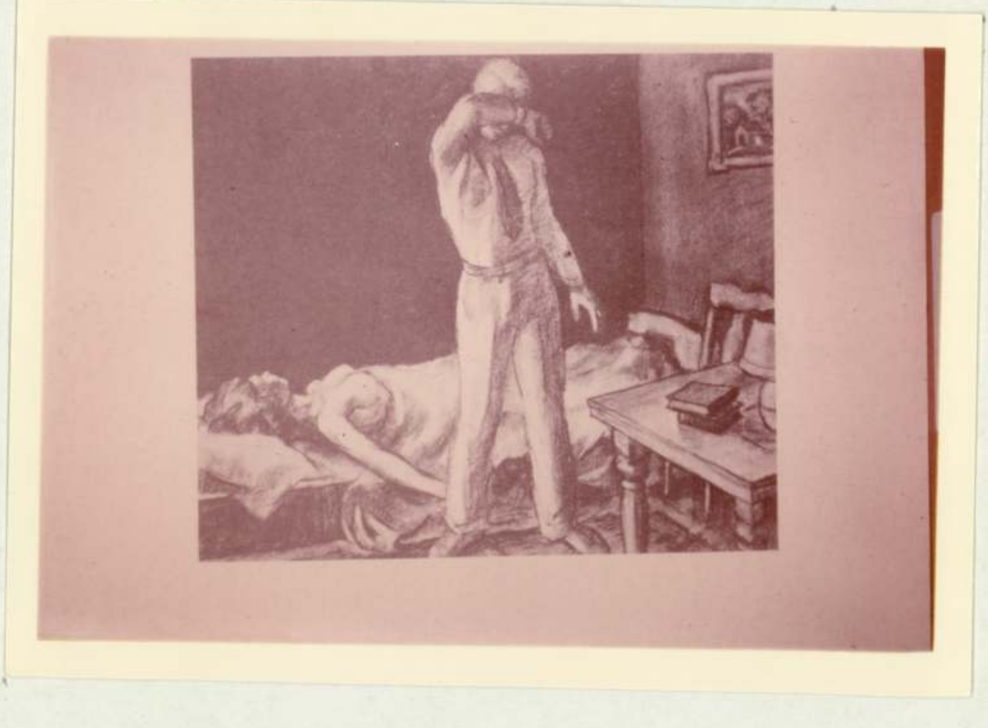
(22)



(23)



(24)



APPENDIX C.

Inductive Programme

Deductive Programme

Student Response Sheets.

CONTENTS

TO THE STUDENT...

The layout of this book is different from that of conventional books. You will immediately notice that it consists of a whole series of problems or frames. One of the reasons why this unusual format has been adopted is that it is felt that people often learn more efficiently by actively solving problems in this way rather than by just reading. You will also notice that the correct answer to each frame is given immediately underneath it. Again many people learn more effectively this way rather than if the correct answers are hidden until the end of each chapter.

However the most important reason for adopting this programmed format is that this book is being used in an educational experiment designed to find out how well people of differing abilities learn by inductive discovery i.e. a learning situation in which the student is left to discover correct general principles after trying out his own early ideas.

This new work in the field of Enzyme Kinetics is important in understanding other biological phenomena thus you are urged to do your best. Please work through the programme conscientiously paying particular attention to the following points.

1. ANSWER EACH FRAME FOR YOURSELF BEFORE LOCKING AT THE CORRECT ANSWER.

If you can visualisethe answer mentally do not feel forced to commit your answer to paper. To prevent accidental looking ahead open up the book and then cover up the page with the answer sheet. Move the sheet down to the first row of dots,answer the question, and uncover the correct answer by moving the sheet down to the next row of dots,etc.

2. KEEP AN ACCURATE RECORD OF ALL THE FRAMES YOU ANSWER INCORRECTLY BY PUTTING A CROSS IN THE CORRESPONDING SPACE ON THE ANSWER SHEET.

Please do this conscientiously and do not fake your answer sheet though this is obviously so easy to do. Remember this is an experiment and faked answer sheets will be not at all helpful. In cases where your diagram or explanation does not correspond exactly with the one given inthe text eg. where you use different wording, use your own judgement about whetheror not the wording is substantially correct.

3. DO NOT WORK THROUGH MORE THAN ONE SECTION IN ANY ONE SESSION.

If you finish a section before the session officially finishes, fill in the time doing other work of your own. If you do not finish the section by the end of the session , please complete the section before the beginning of the next session.

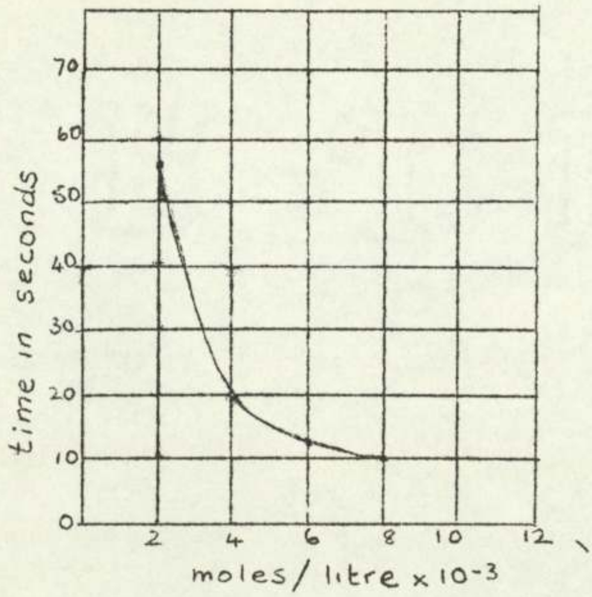
SECTION 1.

Chemical Kinetics and Equilibria.

Before you begin this section please fill in th Answer Sheet with all the information required.

1-1 Chemical reactions proceed at different speeds. For instance, a mixture of coal gas and air in a closed room remains indefinitely without reacting, but it may explode violently if so much as a glowing cigarette is brought into the room. Also, a piece of iron rusts slowly in moist air, but phosphorus bursts into flame spontaneously in air. In this first subsection we are going to examine the effect of one factor on reaction rates, namely concentration.

Here is a graph obtained from an experimentto investigate the effect of varying the concentration of potassium iodate, on the rate of production of iodine from potassium iodide.

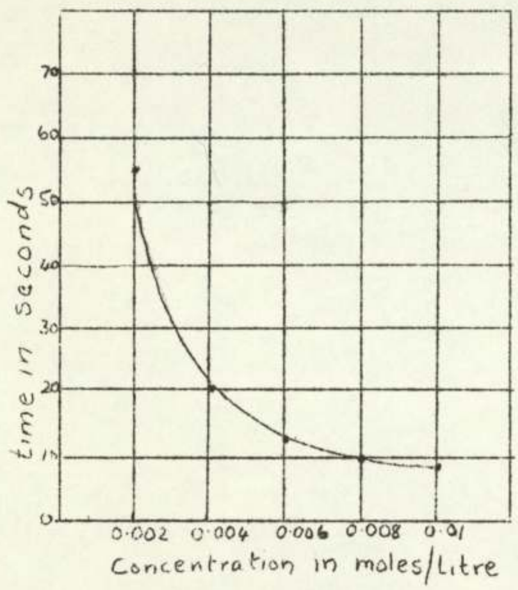


1-1 Looking at your graph, what can you say about the effect of varying the concentration on the time of the reaction?

- -

Increasing(decreasing) the concentration decreases(increases) the time.

1-2 The rate of a chemical reaction is measured by the quantity of product formed divided by the time interval, i.e. the quantity of product produced per unit time.



The graph is a repeat of the data from frame 1-1. What is the rate of reaction in the time interval?

a) 10 - 20 seconds.
b) 9 - 10 seconds.
c) 20 - 55 sconds.

- - - - - - - - - - - - - - - -

a) 0.004 moles potassium iodate per second.
b) 0.002 moles potassium iodate per second.
c) 0.000057 moles potassium iodate per second.

1-3 Referring to the graph on frame I-3, how does time appear to be related to the rate ofa reaction?

- - - - - - - - - - - - - - - -

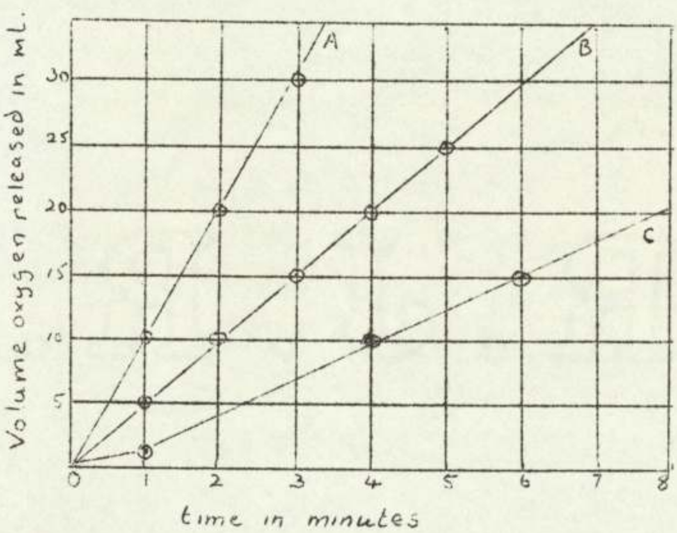
In a chemical reaction a shorter time means a faster rate.

1-4 In the reaction in which hydrogen peroxide is catalytically decomposed by manganese dioxide, 0.25 moles of hydrogen peroxide was found to be decomposed in one minute. It took two minutes to decompose the next 0.25 moles hydrogen peroxide ,and three minutes to decompose the final 0.25 moles of hydrogen peroxide. What part of the reaction has the fastest rate?

- - - - - - - - - - - - - -

The first part in which 0.25 moles are decomposed per minute.

1-5 The graph below shows the data obtained by a class of students investigating the catalytic decomposition of sodium hypochlorite. The rate of the reaction is measured by the rate at which oxygen is evolved.



Graph A shows rate of evolution of oxygen for a 10% solution of sodium hypochlorite. Graph B shows rate for a 5% solution, and graph C rate for a 2.5% solution. What happens to reaction rate

(a) on a two fold dilution.
(b) on a two fold increase in concentration.

- - - - - - - - - - - - - - -

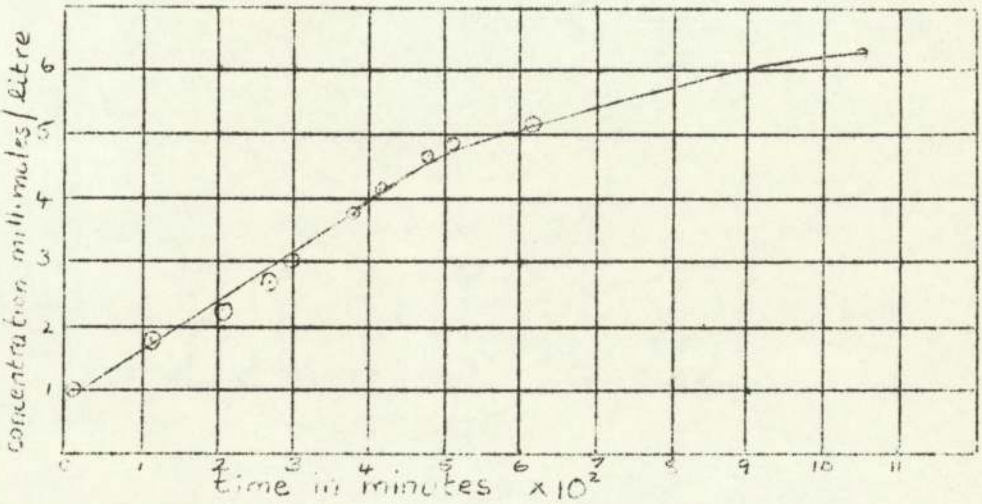
(a) two fold increases in dilution reduces rate by half.
(b) two fold increase in concentration doubles rate.

1-6 Before going on to the next frame, let us fill in with some background information which you may not know. All matter is made up of minute particles called molecules, and before a chemical reaction can occur, molecules must collide.

(No response is required to this frame, go on to frame 1-7.)

1-7 The graph below lists data for increase in concentration of bromine ions as a function of time at 79.63° C when lithium chloride reacts with isopropyl bromide in a solution of acetone.

What is the difference between reaction rate within time interval 100-200 minutes, and the reaction rate in the interval 500-600 minutes?



- - - - - - - - - - - - - - - - - -

Reaction rate in 100-200 minute interval approximately twice that in 500-600 minute interval.

1-8 Referring back to frame 1-7, in which interval do you think there are more collisions, 100-200 minute or 500-600 minute?

- - - - - - - - - - - - -

There are more collisions in 100-200 minute interval than in 500-600 minutes.

1-9 What generalisation can you make concerning the effect of varying concentration on the rate of a reaction? Explain your generalisation in terms of the collision theory.

- - - - - - - - - - - - -

A rise in concentration means a faster rate. This would be explained by the collision theory because a higher concentration would give more collisions between reactant molecules per unit time, thus increasing the reaction rate.

WARNING The above rule does not always apply to overall equations which are usually written down.

1-10 Consider two gases A and B in a container at room temperature. What effect will the following changes have on the rate of reaction between these gases?

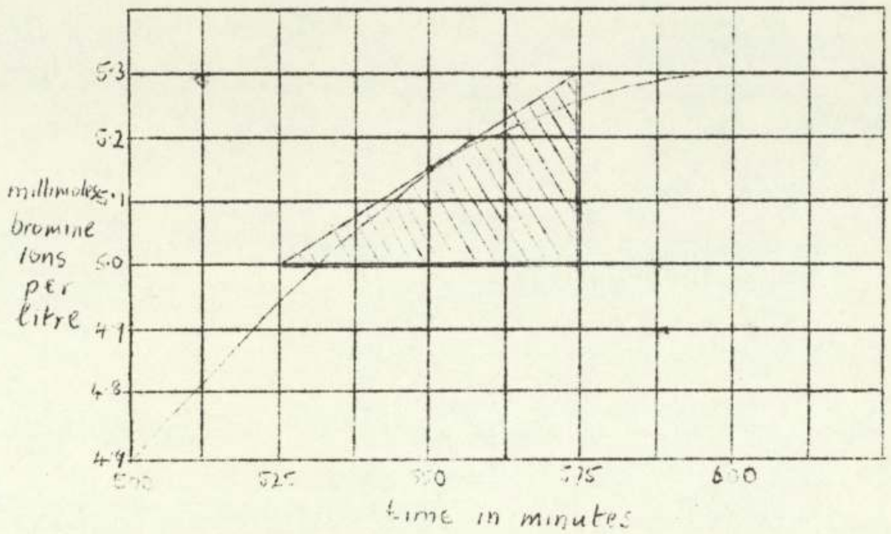
(a) the pressure is doubled.
(b) the number of molecules of gas A is doubled.
(c) the volume of the container is doubled.

- - - - - - - - - - - - -

(a) Doubling the pressure increases the concentration of both reactants, and consequently increases the rate.
(b) Doubling the number of molecules of A increases the concentration of A, and hence may result in an increase in reaction rate.
(c) Doubling the volume of the container decreases the concentration, hence slowing down the reaction rate.

1-11(cont.)

Here is a portion of the curve obtained from data in frame 1-7. It shows the production of Bromine ions over the time interval 500 - 600 minutes. The average rate of production over this time interval = 0.006 millimoles per minute. What is the average rate at the mid point of this time interval which is given by the tangent to the curve?



- - - - - - - - - - - - - -

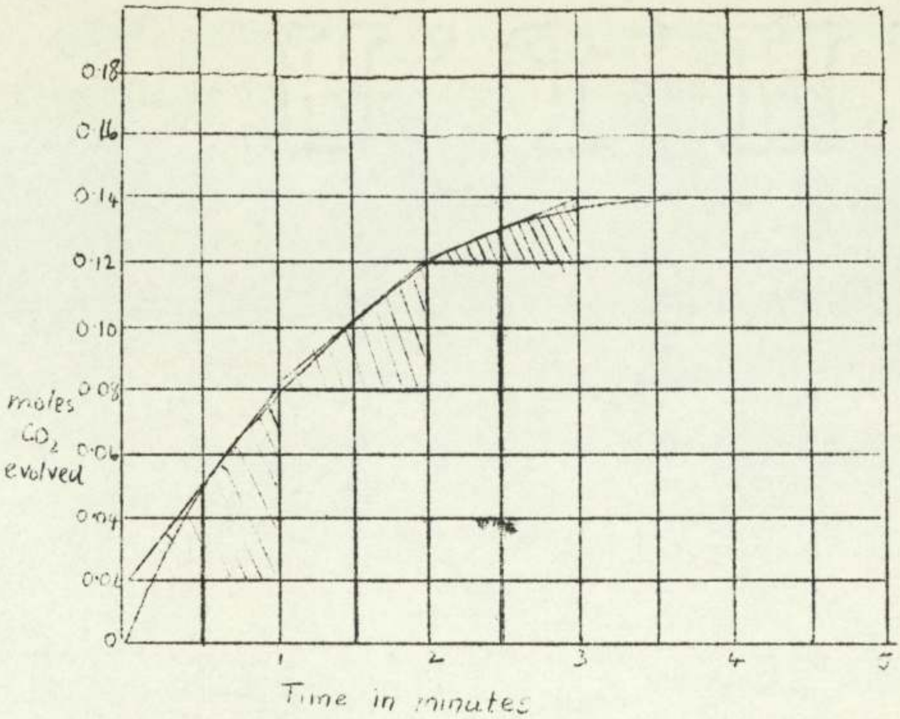
$\frac{0.3 \text{ millimoles}}{50 \text{ minutes}}$ = 0.006 millimoles per minute

---

1-12 Calcium carbonate (marble) reacts with dilute mineral acid giving calcium ions in solution, water and carbon dioxide gas. The rate of the reaction can be measured by the rate of evolution of the carbon dioxide. What is the reaction rate according to the graph at:-

i) 0.5minutes
ii) 1.5minutes
iii) 2.5minutes

1-12(cont.)

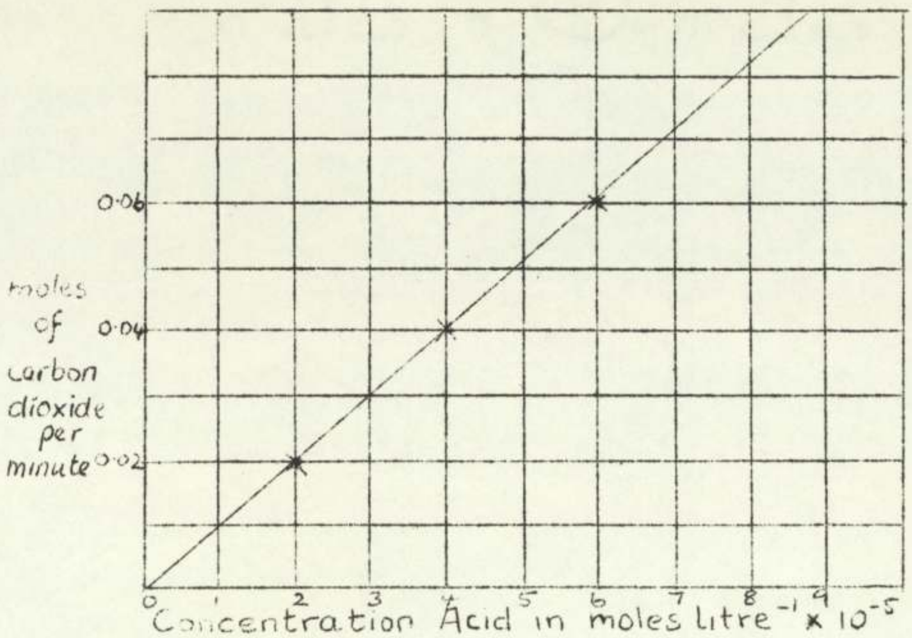


- - - - - - - - - - - - -

i) 0.06 moles per minute
ii) 0.04 moles per minute
iii) 0.02 moles per minute.

1-13 In this graph the rate data from frame 1-12 are plotted against the concentration of acid. What can you say about the relationship between the rate of the reaction and the concentration of the hydrochloric acid?

1-13(cont.)



- - - - - - - - - - -

linear relationship i.e. $\frac{\text{Rate of reaction}}{\text{concentration}}$ = k (slope of straight line)

1-14 Let us now digress for a moment to introduce some standard nomenclature and symbolism.

From the previous frame we have:-

$\frac{\text{rate}}{\text{concentration}}$ = constant (referred to as the RATE CONSTANT)

Rearranging the above we get:-

rate = constant x concentration raised to first power.

or symbolically $\frac{dx}{dt} = k[c]^{(1)}$

Where [ ] denotes concentration in moles per litre and the power to which this concentration is raised is called the ORDER OF THE REACTION.

(No response needed here, go on to next frame. Refer back to this frame if necessary)

1-15 For a first order reaction the units of the rate constant can be determined as follows

Rate = constant x concentration
in in
moles litres^{-1} seconds^{-1} = k x moles litre^{-1}

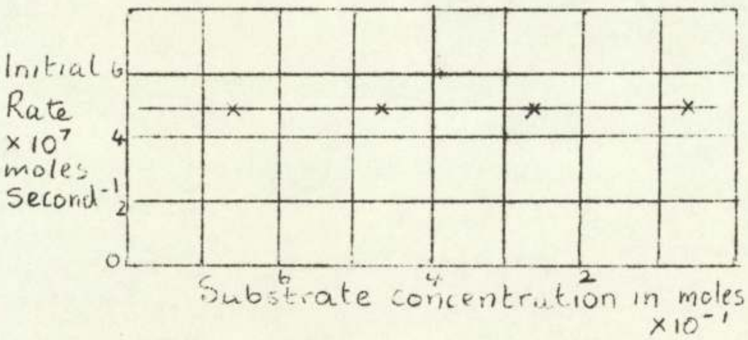
∴ The units of k = seconds^{-1}

What would be the units of the rate constant in a zero order reaction?

- - - - - - - - - - - - - -

moles litre^{-1} second^{-1}

1-16 Here are some data obtained for reaction between fumarate hydratase and fumarate:

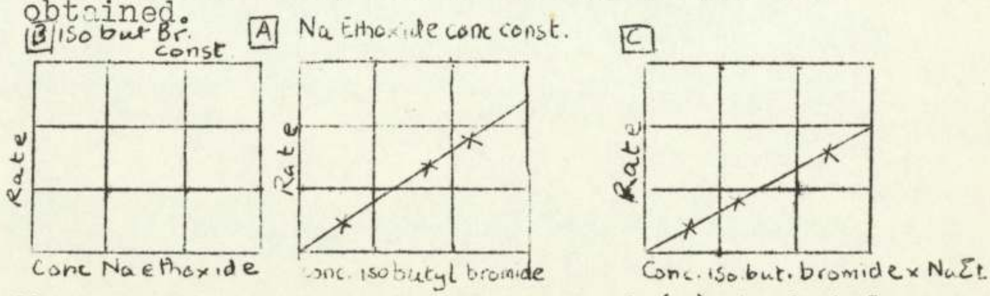


What is the order of this reaction?

- - - - - - - - - - - - - - - -

zero order.

1-17 Dostrovsky and Hughes investigated the reaction between isobutyl bromide and sodium ethoxide in absolute alcohol at 95.15 C. Using their data, the following graphs were obtained.



What is the order of reaction of (a) isobutyl bromide (b) sodium ethoxide (c) both reactants.

- - - - - - - - - - - - -

(a) First order, (b) first order, (c) second order.

1-18 Ammonium Cyanate in solution rearranges spontaneously to give urea.

$$NH_4\ CNO \longrightarrow (NH_2)_2\ CO.$$

The rate constant is found to be by experiment 5.82×10^{-2} litre $mole^{-1}$, $minute^{-1}$. What is the order of the reaction?

Second order.

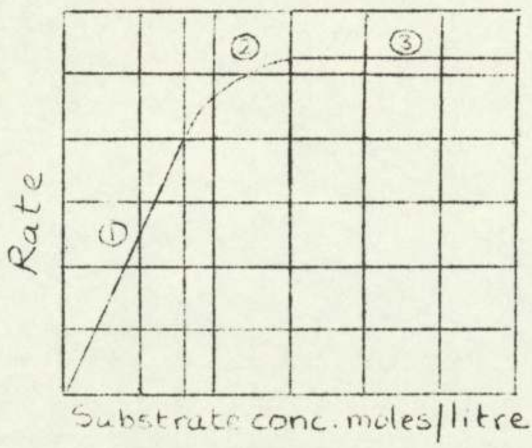
1-19 What do you think is the general law relating concentration to the rate of reaction? State the units of the rate constant.

The general rate law is empirically derived and takes the form,

$$\text{Rate} = \text{Rate constant} \times (\text{concentration in moles /litre})^n.$$

The power 'n' is <u>determined by experiment</u>
The units will be litre moles second.

1-20



Write down an expression to connect the rate with the substrate concentration in regions 1 and 3 of the above graph.

----

(1) rate = k . [Substrate]

(3) rate = k . [Substrate]

1-21. We are now going to study why very often the chemical equation cannot be used to determine the ord^r of a reaction.

Consider the reaction between ferrous ions manganate ions and hydrogen ions giving ferric ions, manganous ions and water.

$$5Fe^{+2} + MnO_4^{-} + 8H^{+} \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O.$$

According to the equation 14 ions would have to collide simultaneously if the reaction were to take place in a single step. Do you think this likely?

No, the probability of this occuring is very remote.

1-22 Consider the decomposition of hydrogen iodide, yielding hydrogen and iodine

$$2HI \longrightarrow H_2 + I_2$$

Do you consider this reaction is likely to take place in one step?

Yes - Two molecules only have to collide to yield products.

1-23 The reaction between hydrogen iodide decomposing by a one step mechanism is further supported from kinetic studies which show that the reaction is second order.

Nitrous oxide decomposes according to the following equation

$$2N_2O \longrightarrow 2N_2 + O_2$$

Is it feasible that the catalytic decomposition of nitrous oxide is a one step mechanism, if you take into account that it is found by experiment to be a first order reaction?

1-23 (Contd)
No. This suggests a mechanism other than a one stage process.

1-24. The mechanism for the catalytic decomposition of nitrous oxide has been suggested as follows:-

$$N_2O \longrightarrow N_2 + O \quad \text{(SLOW)}$$

$$O + O \longrightarrow O_2 \quad \text{(RAPID)}$$

Do you consider that the first or second step will control the rate of the process?

The **first** step will control rate of the process.

1-25 The mechanism proposed for the thermal decomposition of acetaldehyde is as follows -

$$1)\ CH_3\text{-}C(=\ddot{O})\text{-}H \longrightarrow \dot{C}H_3 + \cdot C(=\ddot{O})\text{-}H \qquad \text{FAST}$$

$$2)\ \dot{C}H_3 + H\text{-}C(=\ddot{O}) - CH_3 \longrightarrow CH_4 + \cdot C(=\ddot{O}) - CH_3 \qquad \text{SLOW}$$

$$3)\ \cdot C(=\ddot{O}) - CH_3 \longrightarrow CO + \dot{C}H_3 \qquad \text{FAST}$$

$$4)\ \dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3 \qquad \text{FAST}$$

Which of these reactions determines the rate of the reaction, and what is the order of reaction with respect to acetaldehyde.

Step (2)

First order.

1-26 The reactions between hypochlorite ions and iodide ions, in aqueous solution is represented by the following ionic equation -

$$OCl^- (aq) + I^- (aq) \rightarrow OI^- (aq) + Cl^- (aq)$$

Analytical and kinetic measurements show that the reaction mechanism involves the following steps.

(1) $OCl^- (aq) + H_2O \longrightarrow HOCl (aq) + OH^- (aq)$ FAST.

(2) $I^- (aq) + HOCl (aq) \rightarrow HOI (aq) + Cl^- (aq)$ SLOW.

(3) $OH^-(aq) + HOI(aq) \longrightarrow H_2O (l) + OI^-(aq)$ FAST.

Which of these reactions is the rate determining step?

Step (2)

1-27 Dinitrogen pentoxide is unstable in the vapour state and decomposes into nitrogen dioxide and oxygen. The following mechanism has been proposed.

(1) $N_2O_5 \longrightarrow NO_2 + NO_3$ FAST

(2) $NO_2 + NO_3 \longrightarrow N_2O_5$ FAST

(3) $NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2$ SLOW

(4) $NO + NO_3 \longrightarrow 2NO_2$ FAST

Which step determines the overall rate for the reaction?

Step (3)

1-28 In the bromoform reaction acetone reacts with bromine yielding acetate ions and bromoform. The overall reaction can be written

$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3Br_2 + 2OH^- \longrightarrow$$

$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + 2CHBr_3$$

1-28(cont.)

The reaction takes place by the following steps:-

i) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \bar{O}H \rightarrow CH_3-\overset{O}{\overset{/\!/}{C}}-\bar{C}H_2 + H_2O$ SLOW

ii) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{C}H_2 + Br_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2Br + \bar{Br}$ FAST

iii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2Br + \bar{O}H \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\ddot{C}HBr + H_2O$ FAST

iv) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{C}HBr + Br_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CHBr_2 + \bar{Br}$ FAST

v) $CH_3-\overset{O}{\overset{\|}{C}}-CHBr_2 + \bar{O}H \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\ddot{C}Br_2 + H_2O$ FAST

vi) $CH_3-\overset{O}{\overset{\|}{C}}-CBr_2 + Br_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CBr_3 + \bar{Br}$ FAST

vii) $CH_3-\overset{O}{\overset{\|}{C}}-CBr_3 + \bar{O}H \rightarrow HO-\overset{O}{\overset{\|}{C}}-CH_3 + \bar{C}Br_3$ FAST

viii) $CH_3-\overset{O}{\overset{\|}{C}}-O-H + \bar{C}Br_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\bar{O} + HCBr_3$ FAST

What is the rate determining step and order of reaction?

- - - - - - - - - - - - - - - -

1. First step.
2. First order with respect to $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

1-29 Verbalise the principle governing the rate and order of a reaction involving a mechanism of several steps.

- - - - - - - - - - - - - - - - -

Even the simplest reactions often do not proceed by one single step but by a series of steps which are referred to as the reaction mechanism. The fast steps in the mechanism occur at such a rapid rate that they do not affect the overall rate. The slowest step in any mechanism determines the rate and order of reaction and is therefore known as the <u>rate determining step</u>.

1-30 The reaction between hypochlorite and iodide ions in aqueous solution is represented by the ionic equation:-

$$O\bar{C}l + \bar{I} \longrightarrow \bar{O}I + \bar{C}l$$

The mechanism for the reaction involves three steps.

1. $O\bar{C}l + H_2O \longrightarrow HOCl + \bar{O}H$ FAST

2. $\bar{I} + HOCl \longrightarrow HOI + \bar{C}l$ SLOW

3. $\bar{O}H + HOI \longrightarrow H_2O + \bar{O}I$ FAST

What is the rate determining step and order of the reaction?

- - - - - - - - - - - - - -

a) The reaction is first order with respect to HOCl and I.

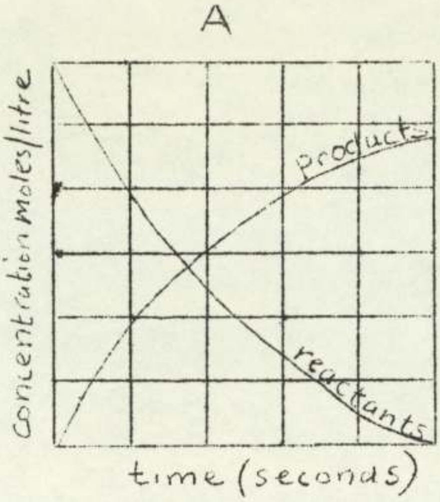
b) The rate determining step is

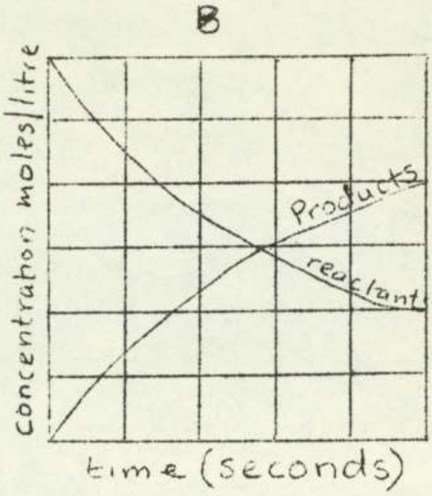
$$\bar{I} + HOCl \longrightarrow HOI + \bar{C}l$$

1-31 We often say that a chemical reaction goes "to completion". By this we mean that there is very often what appears to be a complete conversion into products. For instance, if hydrogen is sparked with $\frac{1}{2}$ its own volume of oxygen, there is apparently complete conversion to water, for no oxygen or hydrogen is detectable.

On the other hand, we say that some reactions are reversible, because both forward and reverse reactions take place to a measurable extent. For instance, ethyl alcohol forms an equilibrium mixture when added to acetic acid, giving ethyl acetate and water. The following two graphs show concentration time data for the above two reactions. Which one is which?

1-31(cont.)





- - - - - - - - - - - -

A. $2H_2 + O_2 \longrightarrow 2H_2O$

B. $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

1-32 In this section we are setting out to study the quantitative relationship which holds for concentrations of reactants and products in an equilibrium mixture.

In an experiment on the equilibrium reactions between ferric ions, thiocyanate ions and ferric thiocyanate ions, i.e.

$$Fe^{+3} + SCN^{-} \longrightarrow FeSCN^{+2}$$

the following results were obtained.

Equilibrium Conc$^{n.}$ [FeSCN]	Equilibrium Conc$^{n.}$ [Fe^{+3}]	Equilibrium Conc$^{n.}$ [SCN]	Tube No.
8.7×10^{-4}	3.9×10^{-2}	1.3×10^{-4}	1.
7.0×10^{-4}	1.5×10^{-2}	3.0×10^{-4}	2.
5.3×10^{-4}	$5;9 \times 10^{-3}$	4.7×10^{-4}	3.
2.8×10^{-4}	2.3×10^{-3}	7.2×10^{-4}	4.

1-32(cont.)

Work out the value of $[Fe^{+3}] \times [FeSCN^{+2}] \times [SCN^{-}]$ for each of the 4 tubes separately.

- - - - - - - - - - - - -

Tube No.
1. 4.4×10^{-9}.
2. 3.2×10^{-9}.
3. 1.5×10^{-10}.
4. 4.6×10^{-10}.

1-33 Using the same data as in frame 1-32, determine the value:-

$$\frac{[Fe^{+3}] \times [FeSCN^{+2}]}{[SCN^{-}]}$$

for each of the four tubes.

- - - - - - - - - - - - - -

1. 2.6×10^{-1}.
2. 3.5×10^{-2}.
3. 6.7×10^{-3}.
4. 9.0×10^{-4}.

1-34 Again using the same data as in frame 1-32, determine the value of:-

$$\frac{[FeSCN^{+2}]}{[Fe^{+3}] \times [SCN^{-}]}$$

for each of the four tubes.

- - - - - - - - - - - - -

1. 1.7×10^{2} .
2. 1.6×10^{2} .
3. 1.9×10^{2} .
4. 1.7×10^{2} .

1-35 Glance back over the answers you obtained in frames 1-32, 1-33, and 1-34. Which gave the most constant value?

a) $[Fe^{+3}] \times [FeSCN^{+2}] \times [SCN^{-}]$

b) $\frac{[Fe^{+3}] \times [FeSCN^{+2}]}{[SCN^{-}]}$

c) $\frac{[FeSCN^{+2}]}{[Fe^{+3}] \times [SCN^{-}]}$

- - - - - - - - - - - - - - - - - -

1-35(cont.)

c) $\dfrac{[FeSCN^{+2}]}{[Fe^{+3}] \times [SCN^{-}]}$

NB. In this experiment, the above expression gives <u>most</u> constant value. Variation in the constant in this case can be attributed to experimental error.

1-36 Some more accurate data have been obtained for the decomposition of hydrogen iodide at 698.6°K i.e.

hydrogen iodide ⇌ hydrogen + iodine

$2HI \rightleftharpoons H_2 + I_2$

Exp No.	H_2 moles/litre	I_2 moles/litre	HI moles/litre
1.	1.8313×10^{-3}	3.1292×10^{-3}	17.671×10^{-3}
2.	2.9070×10^{-3}	1.7069×10^{-3}	16.482×10^{-3}
3.	4.5647×10^{-3}	0.7378×10^{-3}	13.544×10^{-3}

Compute $\dfrac{[H_2] \times [I_2]}{[HI]}$ for each of these experiments

- - - - - - - - - - - - -

Expt. No.	
1.	32.429×10^{-5}
2.	30.105×10^{-5}
3.	24.866×10^{-5}

1-37 Now compute $\dfrac{[H_2] \times [I_2]}{[HI]^2}$ for each of the experiments.

Which expression:-

$\dfrac{[H_2] \times [I_2]}{[HI]}$ or $\dfrac{[H_2] \times [I_2]}{[HI]^2}$

gives the most constant value?

- - - - - - - - - - - - -

1-37(cont.)

Expt. No.

1. 1.8351×10^{-2}.
2. 1.8265×10^{-2}.
3. 1.8359×10^{-2}.

$$\frac{[H_2] \times [I_2]}{[HI]^2}$$

1-38 The data below were obtained when the equilibrium we have just examined was approached the other way i.e. by adding hydrogen and iodine vapour together at 698.6°K.

Expt No	H_2 moles/litre	I_2 moles/litre	HI moles/litre
1	0.4789×10^{-3}	0.4789×10^{-3}	3.531×10^{-3}
2	1.1409×10^{-3}	1.1409×10^{-3}	8.410×10^{-3}

Find $\frac{[H_2] \times [I_2]}{[HI]^2}$ for each of the above experiments. Do you notice anything about their constants and those obtained in frame 1-37?

- - - - - - - - - - - - - -

Expt No

1. 1.8390×10^{-2}.
2. 1.8403×10^{-2}

They are the same values almost.

1-39 What generalisation can be made about the concentration of products and reactants in an equilibrium mixture?

- - - - - - - - - - - - - -

The product of the concentrations of products each raised to the power equal to the number of moles of that substance in the chemical equation divided by concentraion of reactants raised to power equal to the number of moles of substance in chemical equation is equal to a constant.

1-40 Steam reacts with red hot iron to give ferroso ferric oxide and hydrogen.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Write down an expression for the equilibrium constant.

- - - - - - - - - - - - -

$$K = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4}$$

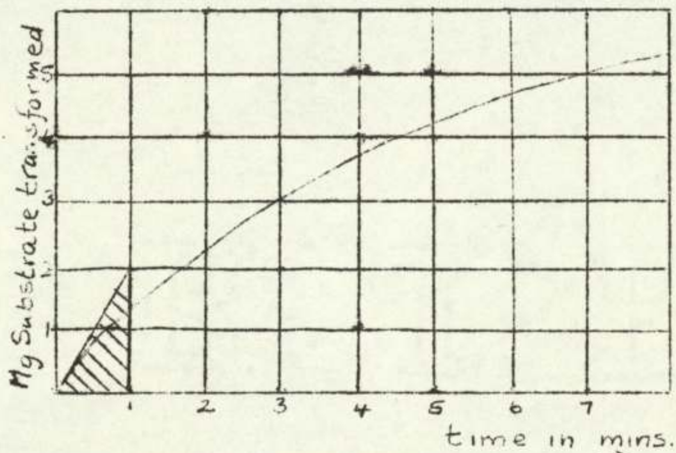
Please complete the answer sheet for this section with all the information required.

SECTION 2.

The influence of Substrate Concentration on the Rate of Enzyme Reactions.

Before you begin this section please fill in the Answer Sheet with all the information required.

2-1. Before embarking on this section let us make it clear that when we talk about the rate or velocity of an enzyme reaction we mean the <u>initial velocity</u> i.e. the velocity at the very beginning of the reaction. The procedure is essential in enzyme work because the velocity falls off with time due to such factors as product inhibition, lability of enzyme, back reactions etc. What is the initial velocity in the graph?



2mg. of substrate transformed per minute.

2-2 In the following frames the symbolism shown below will be used.

E	----	Enzyme
S	----	Substrate
ES	----	Enzyme substrate complex.
P.	----	Product.
k_{+1}	----	velocity constant fir the formation of ES from S and E.
k_{-1}	----	velocity constant for the reverse reaction of above.
k_{+2}	----	velocity constant for the breakdown of ES into P and E.

- ?

2-2 Contd.

Please refer back to this frame if you forget the symbols. There is no response needed here, go on to the next frame.

2-3 In the next few frames we go on to examine the ralationship between E, S, and ES.

In a study of the action of phosphatase on glucose 1 phosphate the following concentrations of enzyme, substrate and enzyme substrate complex were found in two separate experiments.

Expt. No.	[S]	[E]	[ES.]
1	0.5×10^{-3}	2×10^{-5}	1×10^{-5}
2.	1×10^{-3}	1×10^{-5}	1×10^{-5}

Can you see a relationship between these values?

$$\frac{[E][S]}{[ES]} = \text{constant } (10^{-3} \text{ in both experiments})$$

2-4 Kauzmann et al. have studied the luciferin / luciferase system in the luminescent ostrocod crustacean C ypridina. They obtain the following results:

	Luciferin	luciferase	luciferin/ luciferase
Exp. No,	[S]	[E]	[ES]
1	8×10^{-5}	10^{-8}	8×10^{-7}
2	4×10^{-3}	10^{-6}	4×10^{-3}

Can you see a relationship that holds between [E] [S] and [ES] ?

2-4(cont.)

In both experiments $\frac{[E][S]}{[ES]} = 10^{-6}$.

2-5 According to work by Franz and Stephenson, swine kidney pepsinase hydrolyses carbobenzoxy-1-glutamyl-tyrosine giving carbobenzoxy-1-glutamic acid and tyrosine. Results of two of their experiments are shown below.

Expt No	[E]	[S]	[ES]
1	$1x10^{-6}$	$5x10^{-3}$	$4x10^{-7}$
2	$2x10^{-8}$	$8x10^{-2}$	$1.28x10^{-7}$

What can you say about the results of these experiments?

- - - - - - - - - - - -

In both experiments $\frac{[E][S]}{[ES]}$ forms a constant which equals $1.25x10^{-2}$.

2-6 In the following three frames we are going to examine the rate constants for the various phases of the reactions we have just met.

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES \xrightarrow{k_{+2}} E + P$$

If the above represents the action between the enzyme phosphatase and glucose 1 phosphate

$k_{+1} = 10^{6}$
$k_{-1} = 10^{4}$
$k_{+2} = 18$

NB. No value is given for k since if INITIAL VELOCITIES are taken this value is assumed to be negligible.

What do you notice about k_{+1} and k_{-1} compared to k_{+2}? What does this show about reaction rates?

- - - - - - - - - - - -

k_{+1} and k_{-1} are very much larger than k_{+2} showing that first two reactions are very much quicker.

2-7 In the luciferin/luciferase system of Cypridinia, $k_{+1}=10^6$, $k_{-1}= 10^5$; $k_{+2}=26$. What is the rate determining step above?

- - - - - - - - - - - - - - -

The breakdown of the enzyme-substrate complex into products is the rate determining step.

2-8 In the hydrolysis of carbobenzoxy-l-glutamyl tyrosine by pepsin, the following rate constants were found: $k_{+1}= 10^4$, $k_{-1}= 10^3$, $k_{+2}= 10$. What do you notice about the rate of formation of the enzyme substrate complex and its reverse reaction compared to the rate of decomposition of the enzyme substrate complex into products?

- - - - - - - - - - - - - - -

Both the rate of the formation of the enzyme substrate complex and its reverse reaction are <u>much</u> fasterthan the rate of decomposition of the enzyme substrate complex into products

---

2-9 What model would you postulate for enzyme reactions taking all these experimental results into consideration

- - - - - - - - - - - - - - -

The enzyme and substrate are at equilibrium with the enzyme substrate complex, because the equilibrium is formed at a much faster rate than the breakdown of the enzyme substrate complex into products.

Symbolically,

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES \xrightarrow{k_{+2}} E + P$$

2-10 (a). What is the velocity of the overall enzyme reaction in terms of the concentration of the enzyme substrate complex?

(b). What is the concentration of the enzyme substrate complex in terms of the substrate and enzyme concentration

(c). What is the velocity of the reaction in terms of the enzyme and substrate concentration.

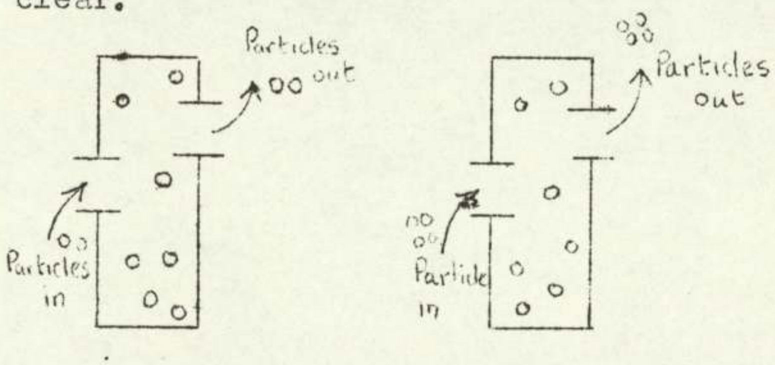
- - - - - - - - - - - - -

(a). $V = k_{+2}[ES]$ (b). $[ES] = K[E][S]$

(c). $V = k_{+2}K[E][S]$

2-11 Let us digress for one moment to considerthe difference between equilibrium and steady state.

Equilibrium is characterised by the constancy of macroscopic properties, that is to say that when the equilibrium is established no changes appear to be taking place visually. This cannot be the only characteristic of equilibrium. Consider a bunsen flame, the structure of the flame, rate of the gas flow to the flame, temperature in various zones does not change but the flame is not in equilibrium, since gaseous products of combustion are continuouslyleaving the system. Such a system is said to be in a steady state. The diagram below will help tp make this clear.



Why does a steady state exist in the above two diagrams?

- - - - - - - - - - - - - - - - -

A steady state exists because the rate at which matter is entering the system equals the rate at whic matter is leaving the system, thus ensuring that the amount of matter within the system remains constant.

2-12. Which of the following systems constitute steady state situations and which are at equilibrium? For each one a constant property is indicated.
(a). An open pan of water boiling on a stove. The temperature of the water is constant.
(b). A balloon contains air and a few drops of water. The pressure in the balloon is constant.
(c). An ant hill follows its daily life. The populationof the ant hill is constant.

- - - - - - - - - - - - - - -

(a). Steady state (a). Equilibrium
(c). Steady state.

2-13

Here are some concentrations for enzyme, substrate and enzyme substrate complex. The second set of readings was taken on the same system a little while after the first set.

	[Enzyme]	[Substrate]	[Enzyme/Substrate Complex]
Expt 1	trypsin	benzoyl-1-arginine	benzoyl-1-arginine trypsin
1st Reading	10^{-5} x1	0.1	$1 x 10^{-3}$
2nd Reading	10^{-5} x0.9	0.099	$1 x 10^{-3}$
Expt 2			
1st Reading	10^{-6} x 0.25	0.05	$0.25 x 10^{-5}$
2nd Reading	10^{-6} x0.223	0.049	$0.25 x 10^{-5}$

Does equilibrium exist between E, S, And ES in any of the above systems?

- - - - - - - - - - - - - - - - -

$\frac{[ES]}{[E] \times [S]}$ does not form a constant in either of the above systems, therefore they are not at equilibrium.

2-14 Refer back to frame 2-13. Does the enzyme, substrate, or enzyme substrate complex appear to exist in steady state in any of the above systems?

- - - - - - - - - - - - - - - - -

Enzyme substrate complex exists in a steady state in both systems.

2-15 Gut freund has carried out a number of measurements on various enzyme substrate systems to determine the velocity constants for different stages of the reaction. This frame and those immediately following show some of

2-15(cont.)
his results.

For the hydrolysis of benzoyl -l-arginine ethyl ester by trypsin $k_{+1} = 4x10^{6}$, $k_{-1} = 25$, $k_{+2} = 15$.

(a). What is the fastest reaction here?

(b). What do you notice about the rate of breakdown of the enzyme substrate complex into reactants and products?

- - - - - - - - - - - - - - - - - -

(a). The fastest reaction is the rate of formation of the Enzyme substrate complex.

(b). The rate of breakdown of the enzyme substrate complex into products and reactants are approximately of the same order of magnitude.

2-16 For the hydrolysis of benzoyl-l-arginine ethyl ester by ficin, $k_{+1} = 5x10^{7}$, $k_{-1} = 6$, $k_{+2} = 1.5$.

(a). What is the slowest reaction?

(b). What reaction determines the speed of the enzyme reaction?

(c). What do you notice about the rate of the breakdown of the enzyme substrate complex into products and reactants?

- - - - - - - - - - - - - - - - -

(a). The breakdown of the enzyme substrate complex into products.

(b). The breakdown of the enzyme substrate Complex.

(c). They are both of the same magnitude approximately.

2-17 In the hydrolysis of acetyl-l-phenyl-alanine ethyl ester by chymotrypsin, $k_{+1} > 10$, $k_{+2} \simeq 10$, $k_{-1} > 90$.

(a). what is the rate determining step?

(b). What do you notice about the size of the rate constants for the breakdown of the enzyme substrate conplex?

- - - - - - - - - - - - - - - - - -

(a) The breakdown of the enzyme substrate complex into product and enzyme.

(b). They are approximately of the same size compared to the formation of the enzyme substrae complex which takes place more rapidly.

2-18 Do you notice any major differences between the rate constants in frames 2-6 - 2-8, and those just given in frames 2-15 - 2-17?

- - - - - - - - - - - - - - - - - -

In the first set of rate constants k_{+2} is very much smaller than k_{-1} but in the second set they are approximately the same size.

2-19 In frame 2-9 you proposed a model for enzyme action which is referred to as the Michaelis Menten model. What modifications to this michaelis Menten model do you think are necessary in the light of results given in this subsection?

- - - - - - - - - - - - - - - -

It cannot be assumed for all enzyme reactions that the enzyme, substrate, and the enzyme substrate complex exist in equilibrium, because very often the rate of breakdown of the enzyme substrate complex back into reactants approximates the rate at which it gives the products. A more valid assumption is that the enzyme substrate complex exists in a steady state, i.e. its concentration is steady (fixed) over the period of time taken to measure the initial velocity.

2-20 $$\underset{e-c}{E} + \underset{s}{S} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \underset{c}{ES} \xrightarrow{k_{+2}} E + P$$

concentration in moles/litre.

(a). What is the rate of formation of the enzyme substrate complex ES?

(b). What is the rate of decomposition of the enzyme substrate complex ES?

(c). What can you say about the rate of formation and the rate of decompostion of the enzyme substrate complex?

- - - - - - - - - - - - - - - -

(a) Rate of formation of ES = $k_{+1}(e-c)x(s)$.

(b). Rate of decomposition of ES = $k_{-1}(c) + k_{+2}(c)$.

(c). Rate of formation of ES = rate of decomposition of ES.

2-21 The model which we have just proposed for enzyme action which assumes that the enzyme sustrate complex exists in a steady state is referred to as the Briggs Haldane model. No response needed go to next frame.

2-22 Examine once more the process

$E + S \rightleftharpoons ES \rightarrow E + P$

and complete the following algebraic equivalents of the two verbal statements of what is assumed for each of our two kinetic models:

Verbal Statement	Algebraic Statement
ES is formed from E and S essentially as fast as it is consum -ed, either by conver -sion back to E and S or on to E and P.	$k_{+1}[E][S] = k_{-1}[\_\_] + \_\_[ES]$
ES is formed from E and S essetially as fast as it redissoc-iates to them.	$k_{+1}[E][S] = k_{-1}[\_\_]$

- - - - - - - - - - - - - - - - -

ES, k_{+2}, ES

2-23 Rearranging the first algebraic statement from frame 2-23 we get

$$\frac{k_{-1} + k_{+2}}{k_{+1}} = K_m = \frac{[E][S]}{[ES]}$$

Rearranging the second statement we get

$$\frac{k_{-1}}{k_{+1}} = K_S = \frac{[E][S]}{[ES]}$$

What do you notice that is unusual about the two equilibrium constants given above?

- - - - - - - - - - - - - - -

The fraction is inverted one to that you would expect from the work we have done on equilibrium, i.e. $\frac{[E][S]}{[ES]}$ not $\frac{[ES]}{[E][S]}$

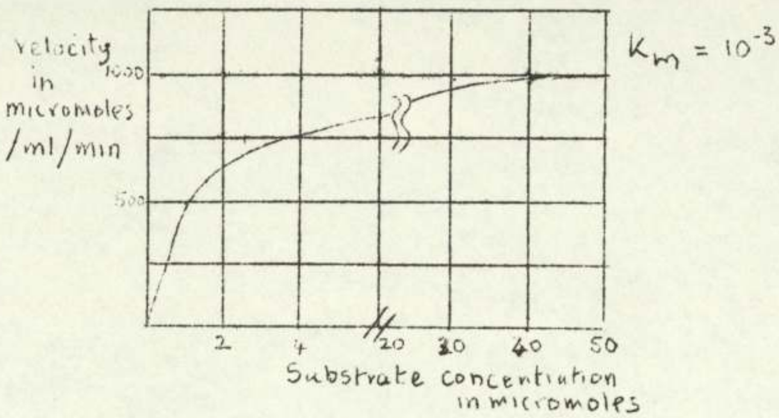
2-24 The following graph shows how the velocity of enzyme reactions characteristically increase with substrate concentration. The curve has been interrupted to permit examination over a wide range of concentrations From the curve you can see that at higher concentrations the rate can no longer be increased by further addition of substrate.

2-24(cont.)

The rate can no longer be made to rise because the substrate has saturated the the enzyme process. The rate observed under these conditions the maximum velocity and is indicated by V_{max}.

K_m(orK_s) is numerically equal to the substrate concentration that gives half maximum velocity.

What is the maximum velocity according to the graph?



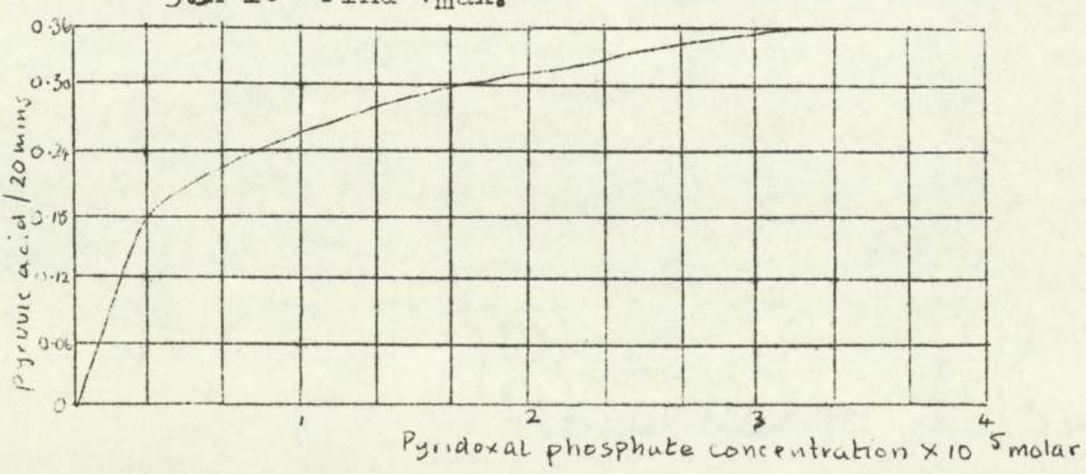
- -

V_{max} = 1000 micrmoles/ml/min.
NB. The definition of maximum velocity does not say that this is the highest rate that can be reached under any conditions whatever, eg. by higher temperature.

2-25 Yanofsky has shown that D-serine hydratase of Neurospore crassa requires pyridoxal phosphate as a coenzyme. The enzyme catalysesthe reaction

$CH_2OHCHCOOH \longrightarrow CH_3COCOOH + NH_3$

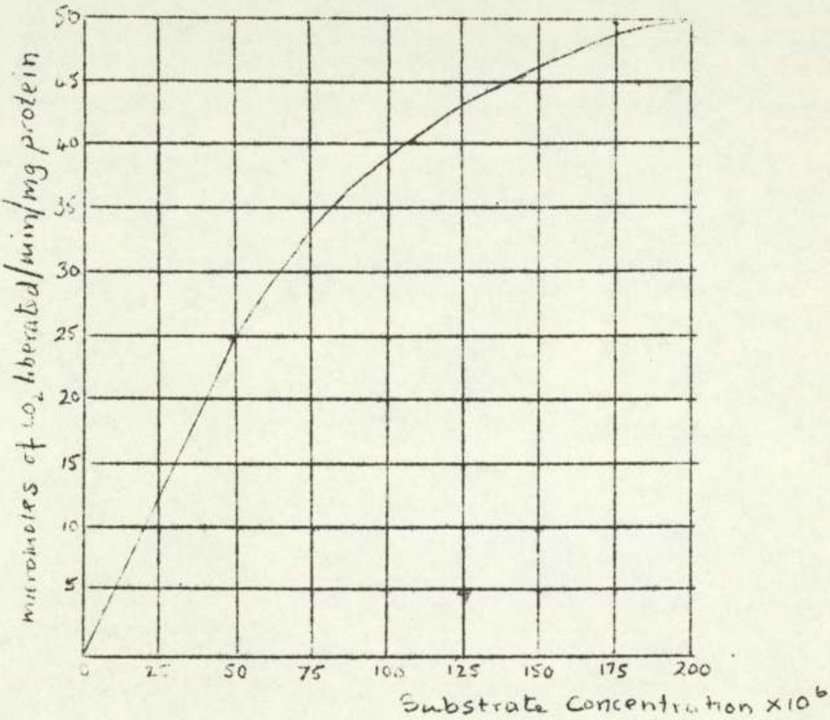
The graph below shows the pyridoxal phosphate saturation curve for the enzyme. K_m for the serine hydratase pyridoxal phosphate complex $=3.3 \times 10^{-6}$ Find V_{max}.



2-25 (cont.)

V_{max} = 0.36micromoles of pyruvic acid per 20 mins.

2-26 The activity of l-aspartate 4 carboxylase can be assayed manometrically by following the rate of evolution of carbon dioxide from l-aspartate. Here is a graph showing the results from this experiment. What isthe maximum velocity? $K_m = 10^{-6} x\ 50$



- - - - - - - - - - - - - - - - -

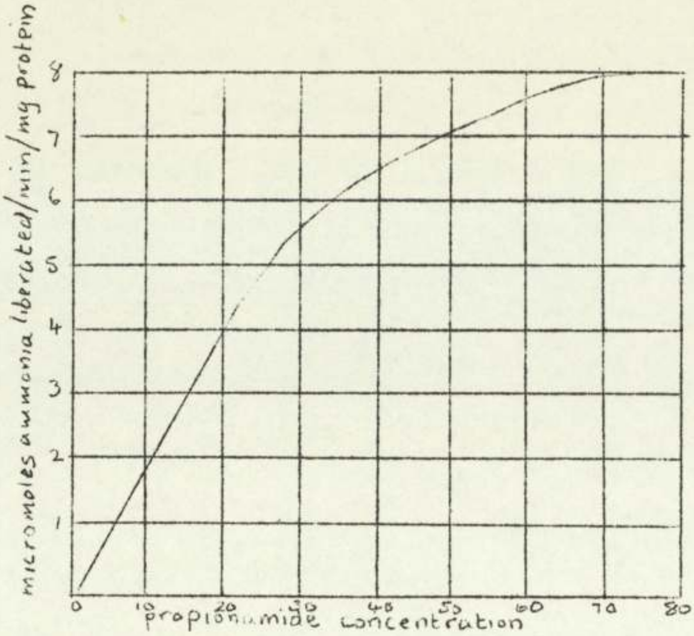
V_{max} = 50 micromoles of carbon dioxide /min./mg. of protein.

2-27 The organism Pseudomonas aeruginosa is capable of hydrolysing propionamide.

$$CH_3CH_2CONH_2 + H_2O \rightleftharpoons CH_3CH_2COOH + NH_3$$

What is V_{max} and K_m?

2-27(cont.)

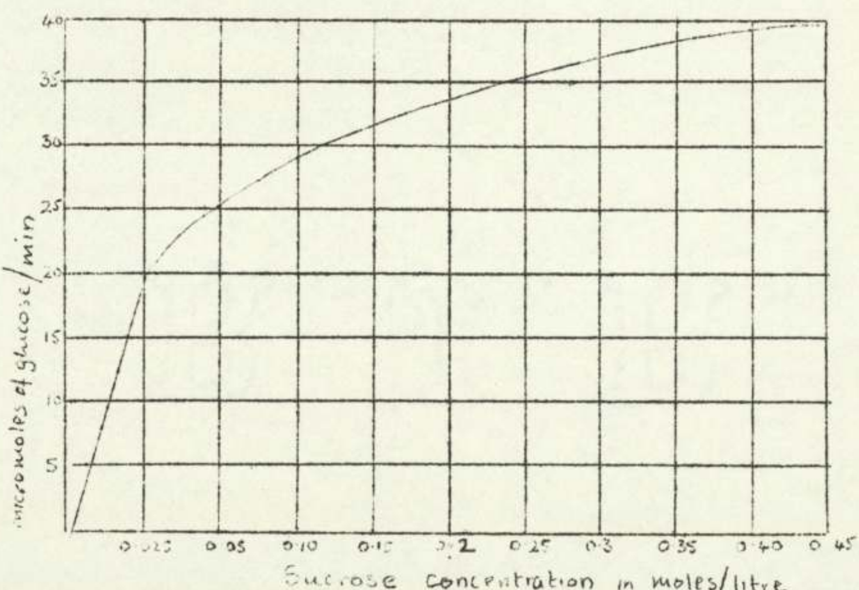


- - - - - - - - - - - - - - -

V_{max} = 8micromoles NH_3/min/mg. of prottein

K_m = $20x\ 10^{-3}$

2-28 The graph below shows the rate of hydrolysis of sucrose by yeast saccharase. Find V_{max} and K_m.



- - - - - - - - - - - - - - - -

V_{max} = 40 micromoles of glucose/minute

K_m = 0.025.

2-29 What generalisation can you make about the relationship between K_m and the substrate concentration?

- - - - - - - - - - - - - - - -

K_m (or K_s) is numerically equal to the substrate concentration that gives half maximum velocity.

2-30 The influence of A.T.P. concentration on the rate of dephosphorylation of A.T.P. by myosin which catalyses the reaction:

A.T.P.⟶ A.D.P. + inorganic phosphate

has been studied at 25°C and pH =7. The following data were obtained.

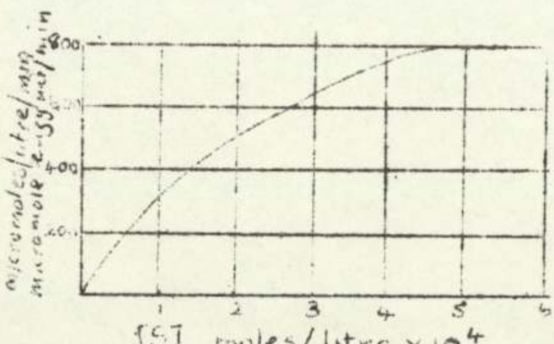
Velocity of reaction micromoles of phosphate produced/litre/sec.	A.T.P. concentration micromoles
0.067	7.5
0.095	12.5
0.119	20
0.149	32.5
0.185	62.5
0.195	320
0.195	450

Find K_m for the reaction by plotting the data on the grid provided.

- - - - - - - - - - - - - - - - - - - -

$K_m = 15 \times 10^{-3}$.

2-31 So far in this programme we have assumed that the maximum velocity can easily be read off a graph in the form shown below.



What does the maximum velocity appear to be?

- - - - - - - - - - - - - -

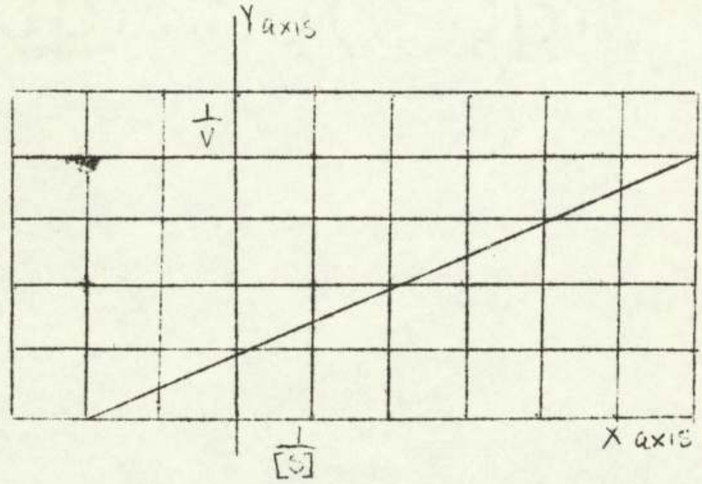
2-31(cont)

800 micromoles/min/micromole of enzyme /litre.

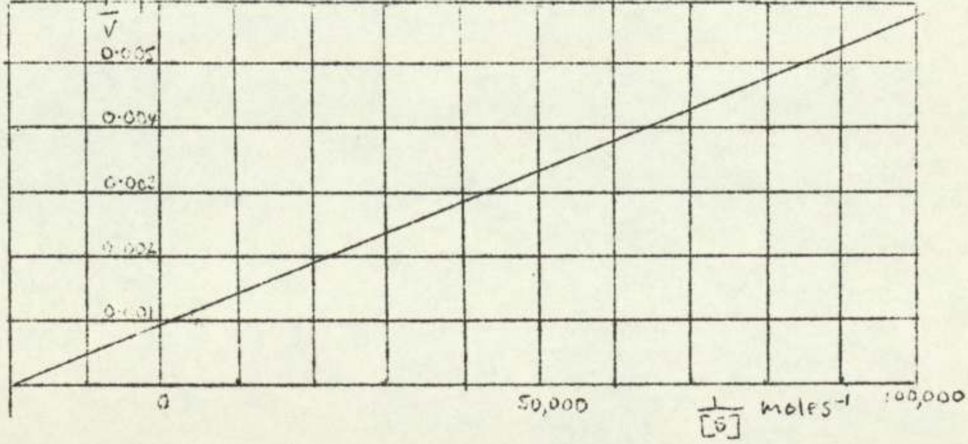
2-32 Actually the true maximum velocity for the enzyme reaction shown in frame 2-31 is 900 micromoles per litre per minute per micromoles of enzyme. The difficulty is that the human eye has very little ability to estimate how high a plateau will be reached by the curve.

To overcome this difficulty Lineweaver and Burke have proposed plotting reciprocals of velocity and substrate concentration which yields a straight line graph as shown.

No response is required here pass on to the next frame.



2-33 The graph below shows the rate of conversion of glucose into glucose-6-phosphate by the enzyme hexokinase.



2-33(cont)
Vmax is 1000(min^{-1}); what is the value of intercept on the y axis?

- - - - - - - - - - - - - - - -

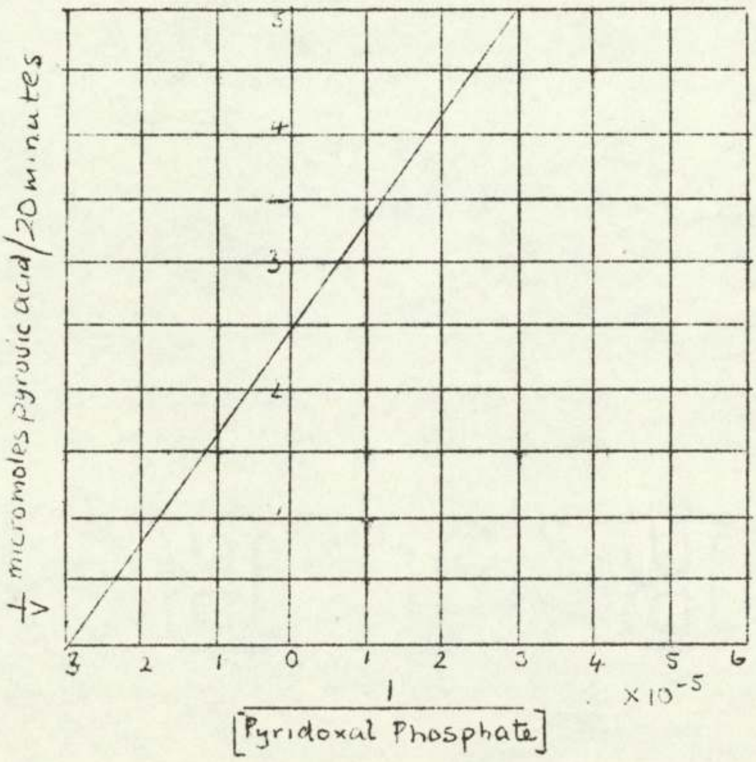
$\frac{1}{0.001}$

2-34 In the reaction whose results are shown in the previous frame $K_m = 5 \times 10^{-5}$. What is the value of the intercept on the x axis?

- - - - - - - - - - - -

-20,000.

2-35 D-Serine hydratase of Neurospora Crassa requires pyridoxal phosphate as a co-enzyme. The graph shows the rate at which pyruvic acid is formed from serine in varying concentrations of pyridoxal phosphate. Vmax is 0.4 micromoles pyruvic acid/20 mins. What is the intercept on the y axis?



- - - - - - - - - - - - - -

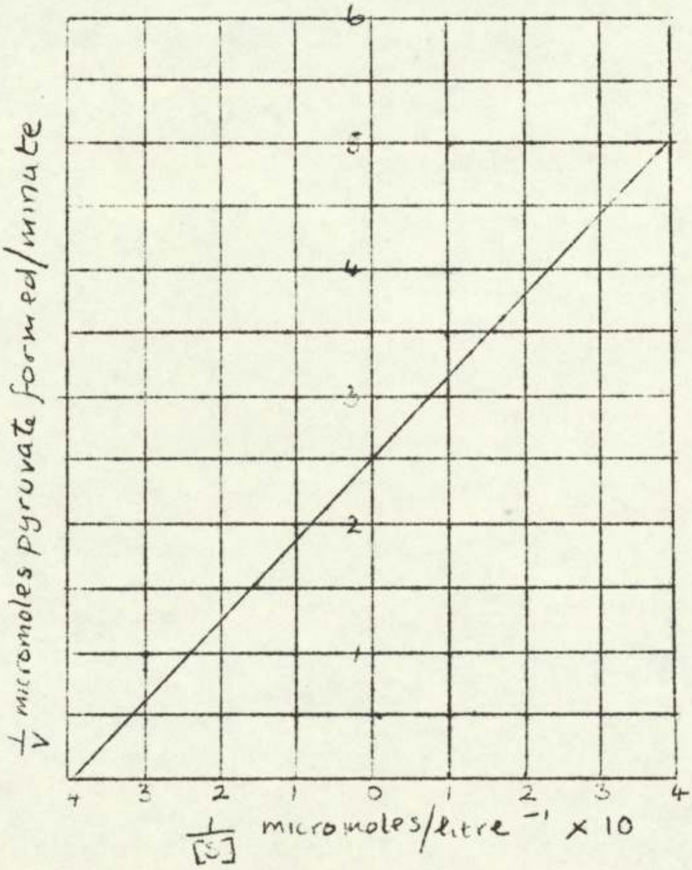
$\frac{1}{2.5}$

2-36 For the reaction whose graph is shown in frame 2-35 $K_m = 3 \cdot 3 \times 10^{-6}$ What is the intercept on the x axis?

- - - - - - - - - - - - -

$-3x10^5$

2-37 The enzyme hydroxyaspartate aldolase catayses the cleavage of erythro-β-methylhydroxy aspartate to pyruvic acid and glycine. The accompanying graph shows the results from this experiment plotted by the Lineweaver Burke method. V_{max} =0.4miro moles of pyruvate/nimute. What is the value of the intercept on the y axis?



- - - - - - - - - - - - -

1/2·5 micromoles of pyruvate /minute.

2-38 Referring back to frame 2-37, $K_m = 2{\cdot}5$. What is the intercept on the x axis?

- - - - - - - - - - - - -

$-1/0{\cdot}4$

2-39 What genralisation can you make about the intercept of the graph on the x and y axis in the Lineweaver Burke plot?

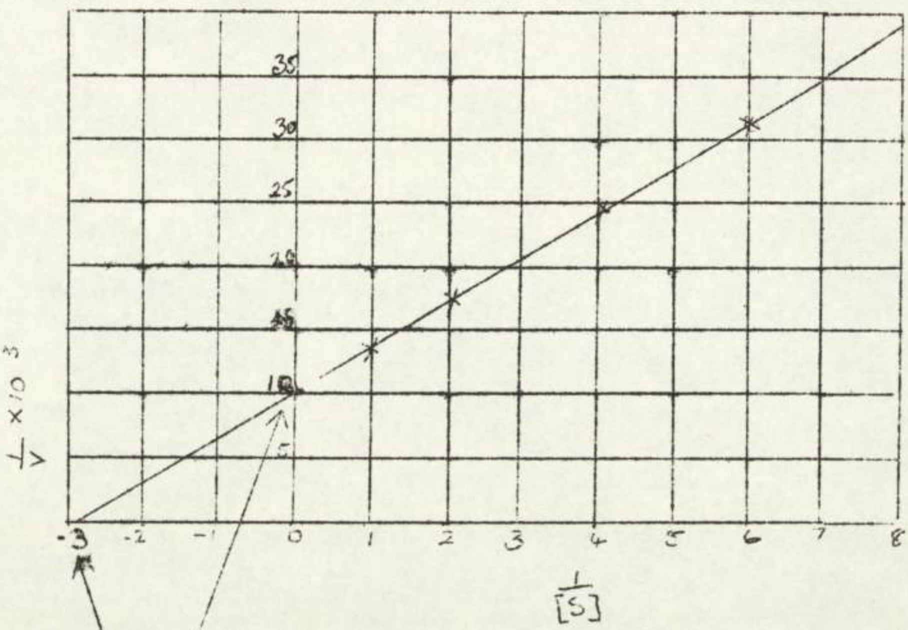
- - - - - - - - - - - -

The intercept on the y axis = $1/V_{max}$. and the intercept on the x axis = $-1/K_m$.

2-40 On the grid provided plot the following data. Find from the graph the value of V_{max} and K_m

1/ S moles	1/V minutes
1000	0·014
2000	0·018
4000	0·025
6000	0·033
8000	0·040

- - - - - - - - - - - - - - -



$1/V = 1/0{\cdot}01$ therefore $V_{max} = 100$.

$-1/K_m = -1/3x10^3$ " $K_m = 10^{-4} x\ 3{\cdot}3$

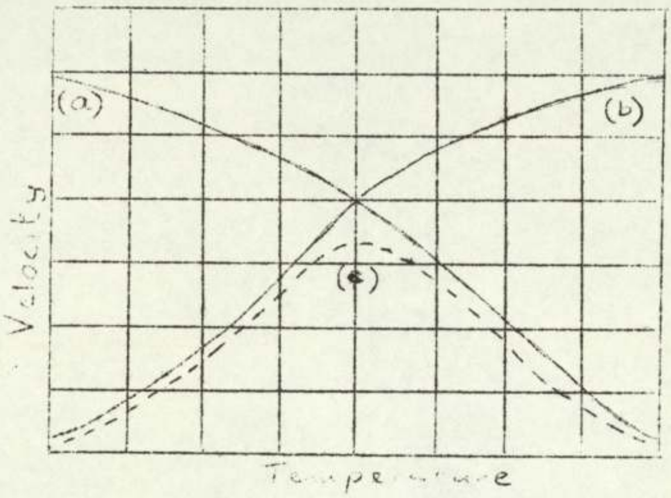
Please complete the answer sheet for this section with all the information required.

SECTION 3.

The effect of Temperature and pH on the rate of Enzyme Reactions.

Before you begin on this section please fill in the answer sheet with all the information required.

3-1 Inthis section we are going to examine separately the effect of temperature and pH on the effect of enzyme reactions. The graph below shows a typical curve which is obtained when the velocity of an enzyme reaction is plotted against the temperature.



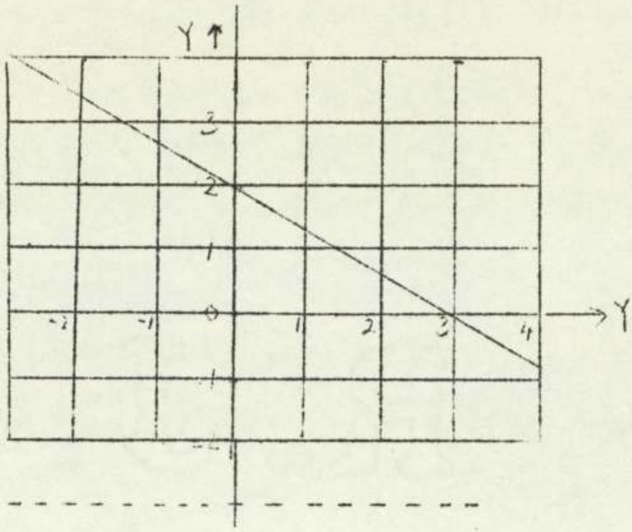
As you can see two processes seem to be influencing the reaction rate; one speeding up the reaction (b) and one slowing down the rate(a). The optimum temperature occurring where there is a balance between these two processes, shown on the **resultant** dotted curve by(c). No response is needed here go to 3-2.

3-2 Before trying to establish a law which relates increase in the rate with the temperature, let us revise some elementary mathematics.

The equation for a straight line is $y = mx + c$, Where m is the slope of the line and c is a constant equal to the intercept on the y axis when $x = 0$. If x increases as y increases then the slope of the line is positive, whereas if y decreases while x increases then the slope of the line is negative.

What is the slope and value of c in the following graph?

3-2(cont.)

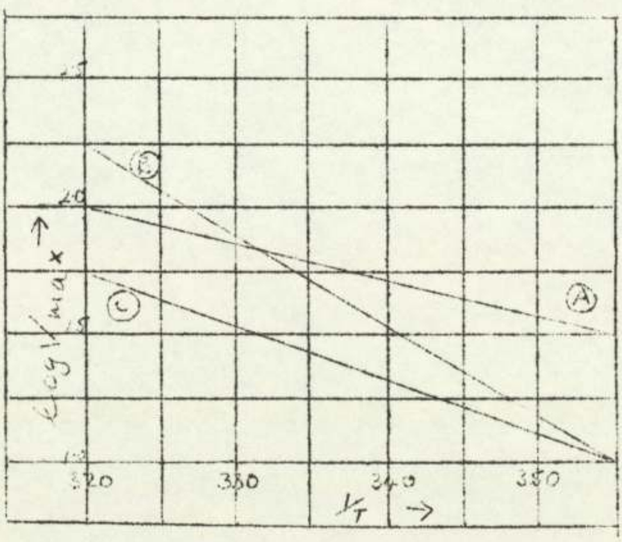


- - - - - - - - - - - - - - - - -

-2/3 and +2.

3-3. We are now going to look more closely at the relationship beween maximum velocity and temperature.

For the next few frames you will need to refer back to the graph shown below. Line (A) shows how the enzyme fumaric hydratase which acts on fumaric acid is influenced by temperature. How does Log V_{max} vary with the temperature?



- - - - - - - - - - - - - - - - - -

log V_{max} varies inversely with 1/T

3-4 What is the slope of the line showing how log V_{max} for fumarate hydratase varies with temperature?

- - - - - - - - - - - - - -

-0.5/0·035

3-5 Line (B) shows how $\log V_{max}$ for malic acid dehydrogenase acting on malic acid varies with temperature. What do you notice about this variation?

- - - - - - - - - - - -

Log V_{max} varies inversely with 1/T

3-6 What is the slope of this line which shows how log V_{max} for malic acid dehydrogenase varies with temperature?

- - - - - - - - - - - -

- 1·25/0·035.

3-7 Line (C) shows how log V_{max} for the action of choline esterase on acetyl choline varies with the temperature. How is $\log V_{max}$ related to the temperature and the slope?

- - - - - - - - - - - - - -

$\log V_{max}$ varies as -0.75/0.035 x 1/T

3-8 What other empirical constant do you notice in the graph on frame 3-3, besides the slope of each line?

- - - - - - - - - - - -

The intersection of each line with the y axis. (K)

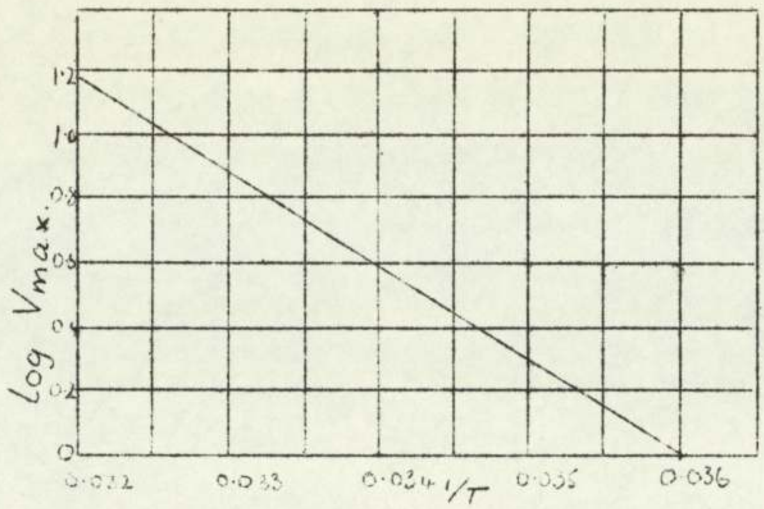
3-9 What empirical relationship appears to hold between $\log V_{max}$ and the absolute temperature?

- - - - - - - - - - - -

$\log V_{max} = K - E/T$

3-10 The following graph shows how the hydrolysis of adenosine triphosphate by myosin varies with the temperature.

3-10(cont).



(a) What happens to $\log V_{max}$ as the temperature increases?
(b) What happens to the slope E as the temperature increases?

- - - - - - - - - - - - - -

(a) $\log V_{max}$ increases (b) E remains constant.

Ex2·3 R(Where E is the slope obtained when $\log V_{max}$ is plotted against 1/T and R is the universal gas constant) equals the Activation Energy. This activation energy is the minimum energy reacting molecules must have in order to form the products.

3-11 Having considered the process which is responsible for speeding up enzyme reactions when heat is applied, we now examine the opposite process which is serving to slow a reaction down when heat is applied.

The thermal inactivation of enzymes has been shown to be due to their protein nature. Enzyme inactivation by heat has been shown to be due to protein denaturation.

Let us briefly go on to consider the various thermodynamic parameters governing protein denaturation.

No response is needed here go on to frame 3-12.

3-12 A specified chemical system has a fixed heat content(H). When one system(reactants) is converted into another(products), the change in heat content(ΔH), is given by H(products)-H(reactants).

3-11(cont.)

Ifthe heat content of the products is less than that of the reactants i.e. ΔH is negative, the surplus energy is transferred from the system to the surroundings and the reaction is exothermic; conversely if the reaction is endothermic ΔH is positive.

The change from ordered to disordered energy in a system is represented by the change in free energy (ΔG). This is made up of two terms, ΔH which measures change from ordered energy inside the system to disordered heat energy given to the surroundings and $T\Delta S$ which measures change in disordered energy inside the system, where T is temperature in °K and ΔS is the increase in entropy or disorder inside the system resulting from changes in molecular structure.

The terms are connected by the equation

$$\Delta G = \Delta H - T\Delta S$$

and a negative value for ΔG indicates that the reaction can theoretically take place spontaneously.

Which of the following reactions is spontaneous :

Reaction A ΔH= +ve. and ΔS = -ve.

Reaction B ΔH= -ve. and ΔS = +ve.

- - - - - - - - - - - - - -

Reaction B.

3-13 $\Delta G = \Delta H - T\Delta S$

For the action of pepsin on carbobenzoxy-l-glutamyl-l-tyrosyl methyl ester at 37°C(310°K) ΔH= +2400 cals/mole and ΔS = + 20·6 cals/deg/mole. What is the value of ΔG?

- - - - - - - - - - - - - - - - - -

-3986 cals.

3-14 $\Delta G = \Delta H - T\Delta S$

In the reaction between the enzyme chymotrypsin and the substrate benzoyl-1 -tyrosinamide at 40°C (313°K) ΔH = +14400 cal/mole and ΔS = + 438 cals/deg/mole. What is the value of ΔG?

- - - - - - - - - - - - -

-122694 cals

3-15 $\Delta G = \Delta H - T\Delta S$

When urease acts on urea at a temperature of 25°C (298°K) ΔH is found to be + 3300cals /mole and ΔS is+13·3 cals/deg/mole. What is the value of ΔG?

- - - - - - - - - - - - -

-663·4 cals

3-16 For the reaction between ribonuclease and ribonucleic acid at 25°C(298°K) ΔH = + 3710 cals/mole and ΔS =+110 cals/deg /mole. Find ΔG.

- - - - - - - - - - - - -

-29070 cals

3-17 $\Delta G = \Delta H - T\Delta S$

In the reaction between trypsin and benzoyl-1-arginimide ΔH = +6800 cals/mole and ΔS =+213cals/deg/mole at a temperature of 25°C (298°K). What is the value of ΔG?

- - - - - - - - - - - - -

-56674cals

3-18 $\Delta G = \Delta H - T\Delta S$

In the reaction where lactic dehydrogenase acts on lactic acid ΔH = + 800cals/mole and ΔS =+20 cals/deg/mole at a temperature of 37°C (310°K) Find ΔG

- - - - - - - - - - - - -

-5400cals

3-19 What relationship appears to hold between the thermodynamic parameters ΔG, ΔH, and ΔS for the reaction in which enzymes are inactivated by heat?

- - - - - - - - - - - - -

3-19(cont.)

In the case of heat inactivation of enzymes the reaction is endothermic(ie. ΔH Is positive) but there is a large accompanying increase in entropy (ie. ΔS is positive). This means that even at relatively low temperatures ΔG is negative and hence the reaction is spontaneous.

3-20 Whichof the following reactions do you think represents heat inactivation of an enzyme;

Reaction	ΔHcals	T°K	ΔScals/dg/mole
A	-1000	300	+ 24
B	+1000	300	+ 24
C	-1000	300	- 24
D	+1000	300	-24

- - - - - - - - - - - - -

B

3-21 In this subsection we are going to examine the effect of varying the pH upon the velocity of enzyme reactions. Before doing this it will be necessary toreview a few basic concepts about pH. Acidity can be measured interms of hydrogen ion concentration H^+, in a solution. The concentration of H^+ is usually very small, thus to avoid the inconvenience of working with negative indices the pH scale has been devised, which defines pH as -log$[H^+]$ What would the pH of a solution be whose $[H^+] = 10^{-4}$gramions/litre?

- - - - - - - - - - - -

4

3-22 According to the Bronsted Lowery definition an acid is a substance which yields $H^+$and a base is a substance which accepts H^+.

Consider the system,

Conjugate acid $\rightleftharpoons$ Conjugate base + hydrogen ions

$$HA \rightleftharpoons A^- + H^+$$

3-22(cont.)

The equilibrium constant (K) for the reaction = $\frac{[\bar{\text{Conjugate base}}][\overset{+}{H}]}{[\text{Conjugate acid}]}$

like the hydrogen ion concentration K is usually very small so again the negative logarithm of K, referred to as pK , is taken

What is the pK expression for the following reaction

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

- - - - - - - - - - - - -

$$\frac{-\log[\overset{+}{H}][CH_3C\bar{O}O]}{[CH_3COOH]}$$

3-23 Here is the data from three separate experiments to determine the relationship beween pH and pK value. In the first experiment the pK value is given, can you predict what it will be for the second and third experiment?

Expt. 1

pH	[Conjugate acid] / [Conjugate base]
2	7
4	4
6	1
8	0·3
10	0·02

pK = 6

Expt. 2.

pH	[Conjugate acid] / [conjugate base]
3	5
5	2
7	1
9	0·5
11	0·1

Expt. 3.

pH	[Conjugate acid] / [conjugate base]
2·5	6
4·5	2
6·5	1
7·5	0·5
8·5	0·01

- - - - - - - - - - - - - - -

Expt. 2 pK = 7; Expt. 3 pk = 6·5.

3-24 What is the relationship between pH and pK value?

- - - - - - - - - - - - - -

When the concentration of conjugate acid = concentration of conjugate base, pH = -logK

3-25 The concentration of the conjugate acid H_2PO_4 eqals the concentration of its conjugate base HPO_4 when the pH = 6. What is the pK value of the system

$$H_2PO_4^- \rightleftharpoons HPO_4^{-2} + H^+ \quad ?$$

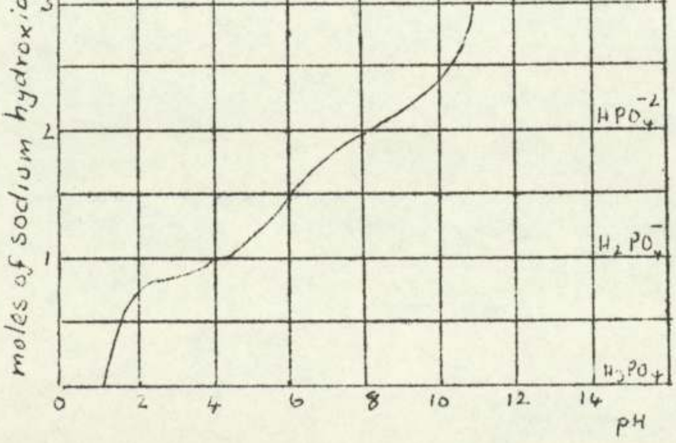
- - - - - - - - - - - - - - -

pK = 6

3-26 The curve below is called a titration curve. This particular curve shows the change in pH which is observed when 0·1 molar sodium hydroxide is titrated against 0·1 molar phosphoric acid at 25°C

When the first titration is complete H_3PO_4 has split completely into H^+ and $H_2PO_4^-$. When the second dissociation is complete $H_2PO_4^-$ has split completely into H^+ and HPO_4^{-2}. When the third dissociation is complete, HPO_4^{-2} has split completely into H^+ and PO_4^{-3}.

In the graph below what conjugate acid and base would you expect to find at pH 6, which is also the pK value?

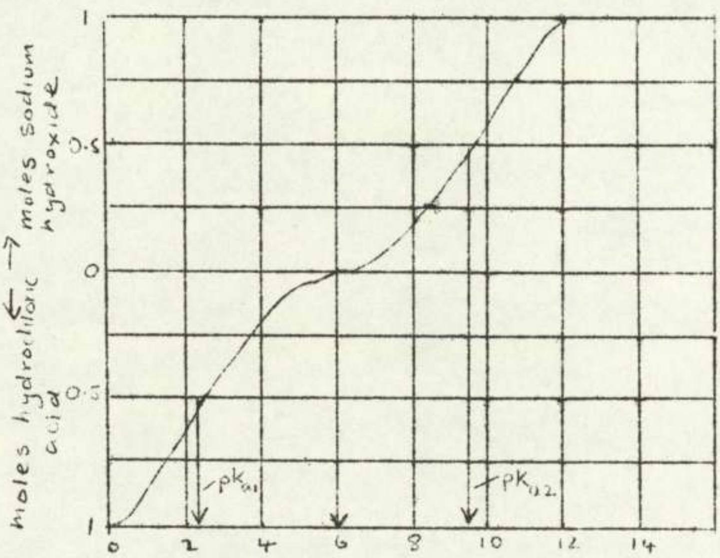


3-26(cont.)
A mixture of HPO_4^{-2} and $H_2PO_4^-$

3-27 The titration curve below shows the results obtained when 0·1 molar glycine is titrated against 0·1 molar hydrochloric acid and 0·1molar sodium hydroxide.

At pH = 2·4 ie. pK_{a_1} equimolar proportions of $\underset{COOH}{CH_2NH_3^+}$ and $\underset{COO^-}{CH_2NH_3^+}$ are present.

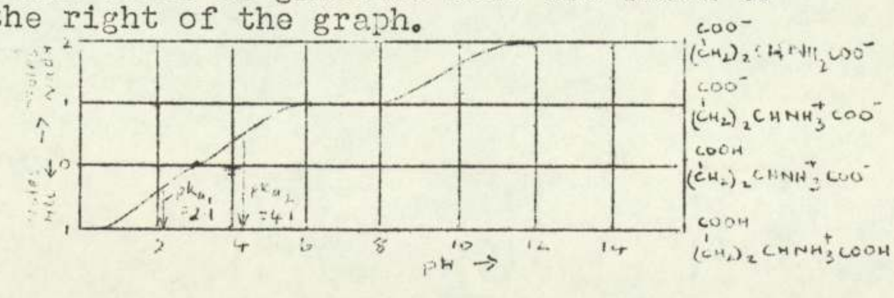
At pH = 9·8 ie. pK_{a_2} equimolar proportions of $\underset{COO^-}{CH_2NH_3^+}$ and $\underset{COO^-}{CH_2NH_2}$ are present. What would expect to find present at pH = 6 ?



- - - - - - - - - - - - -

$\underset{COO^-}{CH_2NH_3^+}$

3-28 The graph following shows the titration curve obtaied when 0·1 molar glutamic acid is titrated against 0·1 molar hydrochloric acid and against 0·1 molar sodium hydroxide. The ionic forms of glutamic acid are shown to the right of the graph.

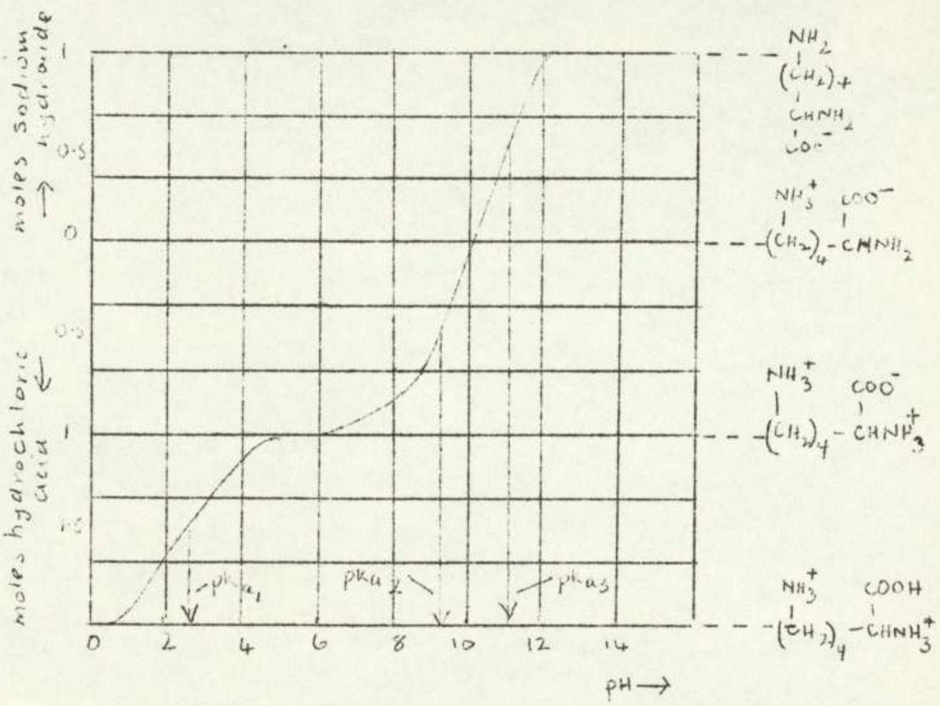


3-28(cont.)
What form would you expect to find present at pH = 3·1?

- - - - - - - - - - - - -

COOH
|
$CH_2-CH_2-CHNH_3^+COO^-$

3-29 Here is the titration curve obtained when 0·1 molar lysine is titrated against 0·1 molar hydrochloric acid and 0·1 molar sodium hydroxide. What forms are present at pK_{a_2}?



- - - - - - - - - - - - -

NH_3^+ COO^-
|
$CH_2-CH_2-CH_2-CH_2-CHNH_2$

and

NH_3^+ COO^-
|
$CH_2-CH_2-CH_2-CH_2-CHNH_3^+$

3-30 What is the principle that seems to govern the breakdown of a polyprotic weak acid?

- - - - - - - - - - -

At a point halfway between the pK values only one ionic form of a polyprotic weak acid exists in solution.

3-31 At pK = 4 $R - CH\overset{+}{N}H_3COOH$ and $R - CH\overset{+}{N}H_3COO^-$ exist in solution and at pK = 8 $R- CH\overset{+}{N}H_3COO^-$ and $R - CHNH_2COO^-$ exist in solution. What form(s) of the amino acid would you expect to find in solution at pH = 6?

(Assume that at each pK there are equal molar quantities of the appropriate ionic forms.)

- - - - - - - - - - - -

$R - CH\overset{+}{N}H_3COO^-$ only.

3-32 In the following group of frames we are not going to concern ourselves with the irreversible effects of extremes of pH on protein structure of enzymes, or with effects of pH on ionization of substrate. We are only going to consider effects on binding of enzyme to substrate.

The effect of pH on the affinity of enzyme for substrate is readily eliminated by the use of substrate concentrations high enough to saturate the enzyme at all pH's being investigated. One major source of error in this work has been the assumption, usually without experimental verification, that a substrate concentration adequate to saturate an enzyme at one particular pH also does so at all other pH's.

By ensuring that the substrate concentration used is high enough to saturate the enzyme at all pH values listed, then the effect of pH on maximum velocity will be established.

3-32(cont.)

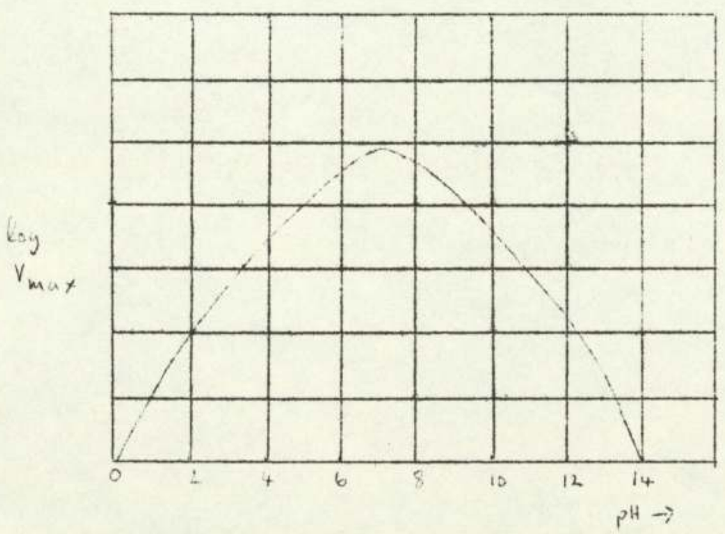
In the following frames these conditions are assumed to be operating, thus ensuring that all the enzyme will be in the form of enzyme substrate complex. Thus we shall be exam ining solely the effect of pH on the enzyme substrate complex.

No response is required here, go to frame 3-33.

3-33 The bell-shaped curve shown below is a typical curve which is obtained by plotting the pH of an enzyme reaction against log V_{max}

The optimumpH is that which gives the greatest maximum velocity.

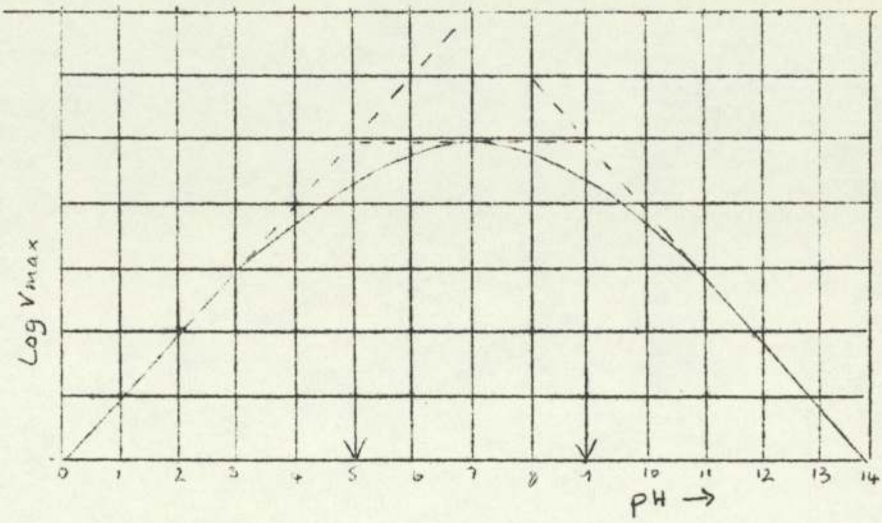
What is the optimum pH in the reaction given below which shows results obtained from the enzyme peroxidase on hydrogen peroxide.



\- - - - - - - - - - -

pH = 7 optimum.

3-34 Dixon has shown that by extrapolation of linear portions of the curves to the point of intersection the two pK values can be ascertained. What are the two pK values inthe graph below?



- - - - - - - - - - - - -

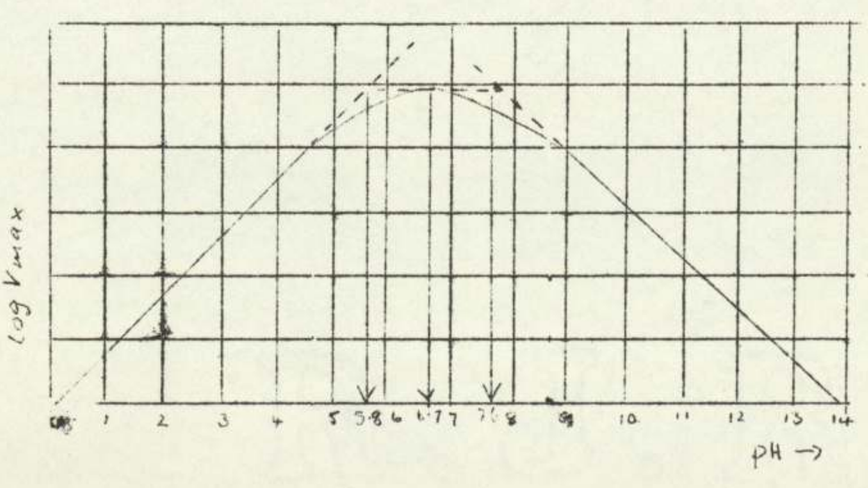
5 and 9

3-35 The optimum pH in frame 3-34 = 6·7 ie. $\frac{pk_1 + pk_2}{2}$. How many ionic forms ofthe enzyme substrate complex will be present at pH = 6·7 which gives the maximum velocity?

- - - - - - - - - - - - - - - - - -

1 ionic form.

3-36 Massey and Alberty have investigated the action of the enzyme fumarate hydratase on the substrate fumarate at a number of different pHs Their results are shown below.



3-36(cont.)
At what pH is the maximum velocity greatest? How does this relate to the pK values of the of the enzyme substrate complex?

\- - - - - - - - - - - - -

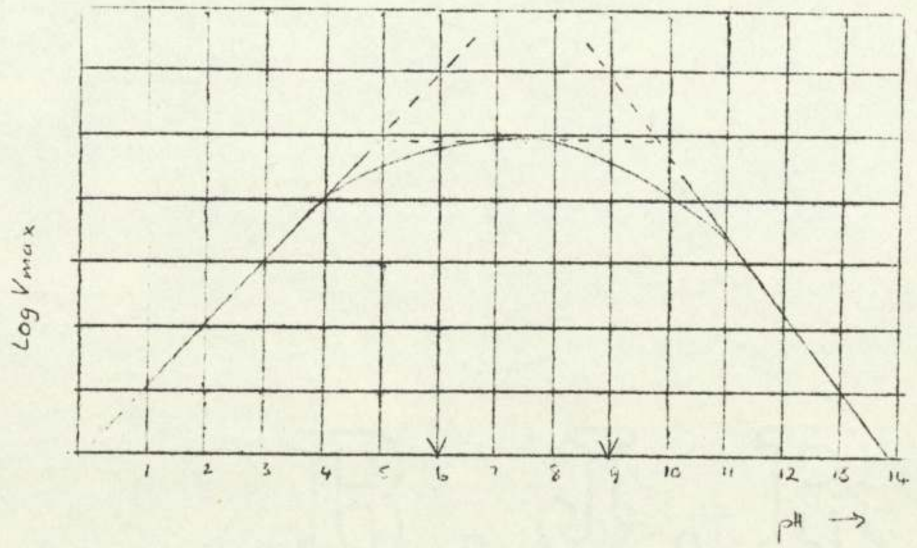
V_{max} is greatest at pH 6·7. This is half way between the two pK values of the enzyme substrate complex.

3-37 Referringback to frame 3-36 determine how many forms of the enzyme substrate complex are present at pH 5·8, pH 6·7 and pH 7·6?

\- - - - - - - - - - -

At pH 5·8 2forms of the enzyme substrate complex.
At pH 6·7 1 form of the enzyme substrate complex.
At pH 7·6 2 forms of the enzyme substrate complex.

3-38 The graph below was obtained by Laidlerr for the action of cholinesterase on acetyl choline. What is the optimum pH and how many forms of the enzyme substrate complex are present at this point?



3-38(cont.)

7.5 is the optimum pH, and only one form of enzyme-substrate complex is present at this point.

3-39 What principle do you think is responsible for causing an enzyme to exhibit an optimum velocity of reaction at a particular pH?

\- - - - - - - - - - - -

An enzyme has an optimum pH because only one ionic form of enzyme substrate complex breaks down into products, and this is mainly present at the optimum pH.

3-40 Alberty and Massey have suggested the following mechanism to explain the effects of pH on enzyme.

(1) Substrate + Enzyme + $2\overset{+}{H}$ $\rightleftharpoons$ Enzyme Substrate → Products

$\updownarrow$

(2) Substrate + Enzyme-H + $\overset{+}{H}$ $\rightleftharpoons$ Enzyme-hydrogen-substrate → Products

$\updownarrow$

(3) Substrate + Enzyme-H_2 $\rightleftharpoons$ Enzyme 2hydrogen substrate → Products

Which of these enzyme substrate complexes would you expect to break down into products? 1,2,or 3?

\- - - - - - - - - -

2 Enzyme-hydrogen substrate.

Please complete the answer sheet for this section with all the information required.

CONTENTS

TO THE STUDENT-----

The layout of this book is different from that of conventional books. You will immediately notice that it consists of a whole series of problems or "frames". One of the reasons why this unusual format has been adopted is that it is felt that people often learn more efficiently by actively solving problems in this way rather than by just reading. You will also notice that the correct answer to each frame is given immediately underneath it. Again, many people learn more effectively this way rather than if the correct answers are hidden until the end of each chapter.

However,the most important reason for adopting this programmed format is that this book is being used in an educational experiment designed to find out how different ways of teaching suit different kinds of people. By analysing the answers which people give for each frame, we can see if and how the two methods do work differently.

The two different methods to be compared are respectively in the deductive and inductive versions of thisprogramme. In the deductive version, each of the general principles to be taught is given to the student before he is given a series of frames to practise applying the principle. In the inductive version the student is left to think up his own theories first, and to discover the correct general principles after trying out his own early ideas. Many people believe that this 'learning by discovery' is more effective than the deductive method of teaching, but unfortunately, there is little experimental evidence to support this point of view. Furthermore, it seems most unlikely that any one method of teaching is better for all kinds of students, and that different students do better with different teaching methods. Previously, you have worked through a number of different tests and this experiment will we hope be able to discover which method is more suitable for people who score differently on each of these tests.

Obviously, the success of an experiment such as this is entirely dependent upon the co-operation of the students participating, and you are asked to work through the programmecarefully and conscientiously,paying pariculiar attention tothe following points.

1. ANSWER EACH FRAME FOR YOURSELF BEFORE LOOKING AT THE CORRECT ANSWER.

If you find that drawing diagrams and writing explanations is too time consuming or tedious, and that you can visualise the diagrams mentally for yourself, do not feel forced to commit your answer to paper. To prevent accidental looking ahead open up the book and then cover up the page with the answer sheet. Move the sheet down to the first row of dots, answer the question, and uncover the correct answer by moving the sheet down to the next row of dots,etc.

2. KEEP AN ACCURATE RECORD OF ALL THE FRAMES YOU ANSWER INCORRECTLY BY PUTTING A CROSS IN THE CORRESPONDING CIRCLE ON THE ANSWER SHEET.

Please do this conscientiously and do not fake your answer sheet though this is obviously so easy to do. Remember this is an experiment and faked answer sheets will not be at all helpful. In cases where your diagram or explanation does not correspond exactly with the one given in the text eg. where you use different wording, use your own judgement about whether or not the wording is substatially correct.

3. DO NOT WORK THROUGH MORE THAN ONE SECTION IN ANY ONE SESSION.

If you finish a section before the session officially finishes, fill in the time doing some other work of your own. If you do not finish the section by the end of the session please complete the section before the beginning of the next session.

People are sometimes worried about being used as guinea pigs in educational experiments and that they may have been given an inferior teaching method. In this case we definitely do not know in advance which is the better teaching method, and in any case it almost certainly depends on the individual student. Thus there is no need to worry about being "used"for this experiment.

SECTION I.

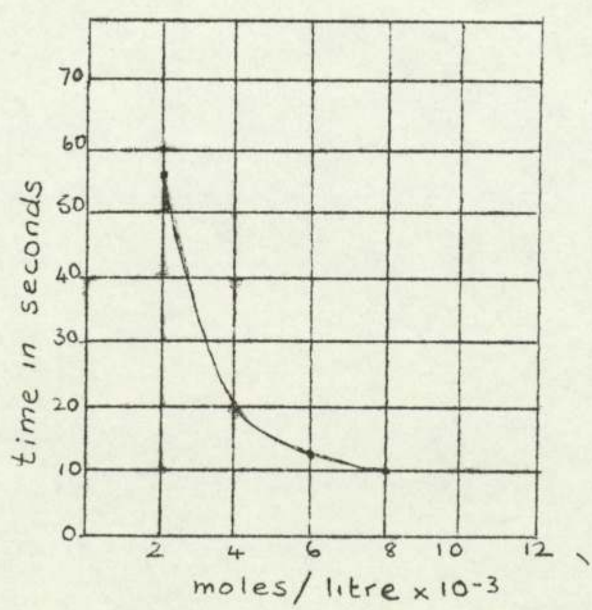
Chemical Kinetics and Equilibria.

Before you begin this section please fill in th Answer Sheet with all the information required.

1-1 Chemical reactions proceed at different speeds. For instance, a mixture of coal gas and air in a closed room remains indefinitely without reacting, but it may explode violently if so much as a glowing cigarette is brought into the room. Also, a piece of iron rusts slowly in moist air, but phosphorus bursts into flame spontaneously in air. In this first subsection we are going to examine the effect of one factor on reaction rates, namely concentration.

A rise in concentration means a faster rate. This would be explained by the collision theory, because a higher concentration would give more collisions between reactant molecules per unit time, thus increasing the reaction rate.

Here is a graph obtained from an experimentto investigate the effect of varying the concentration of potassium iodate, on the rate of production of iodine from potassium iodide.

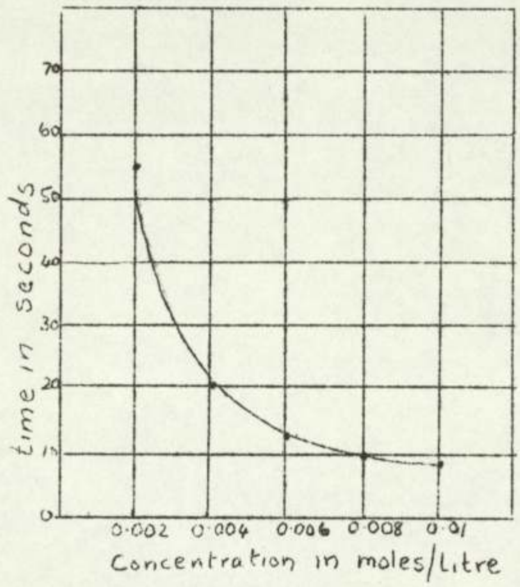


1-1 Looking at your graph, what can you say about the effect of varying the concentration on the time of the reaction?

- -

Increasing(decreasing) the concentration decreases(increases) the time.

1-2 The rate of a chemical reaction is measured by the quantity of product formed divided by the time interval, i.e. the quantity of product produced per unit time.



The graph is a repeat of the data from frame 1-1. What is the rate of reaction in the time interval?

a) 10 - 20 seconds.
b) 9 - 10 seconds.
c) 20 - 55 sconds.

- - - - - - - - - - - - - - -

a) 0.004 moles potassium iodate per second.
b) 0.002 moles potassium iodate per second.
c) 0.000057 moles potassium iodate per second.

1-3 Referring to the graph on frame I-3, how does time appear to be related to the rate ofa reaction?

- - - - - - - - - - - - - - -

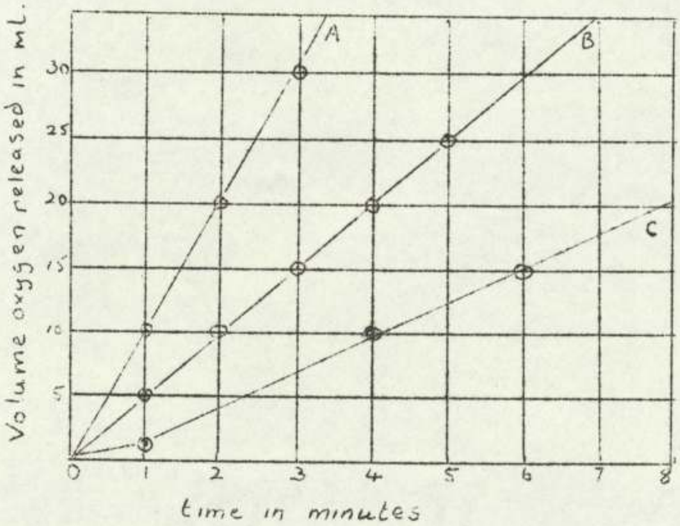
In a chemical reaction a shorter time means a faster rate.

1-4 In the reaction in which hydrogen peroxide is catalytically decomposed by manganese dioxide, 0.25 moles of hydrogen peroxide was found to be decomposed in one minute. It took two minutes to decompose the next 0.25 moles hydrogen peroxide, and three minutes to decompose the final 0.25 moles of hydrogen peroxide. What part of the reaction has the fastest rate?

- - - - - - - - - - - - - - -

The first part in which 0.25 moles are decomposed per minute.

1-5 The graph below shows the data obtained by a class of students investigating the catalytic decomposition of sodium hypochlorite. The rate of the reaction is measured by the rate at which oxygen is evolved.



Graph A shows rate of evolution of oxygen for a 10% solution of sodium hypochlorite. Graph B shows rate for a 5% solution, and graph C rate for a 2.5% solution. What happens to reaction rate

(a) on a two fold dilution.
(b) on a two fold increase in concentration.

- - - - - - - - - - - - - - -

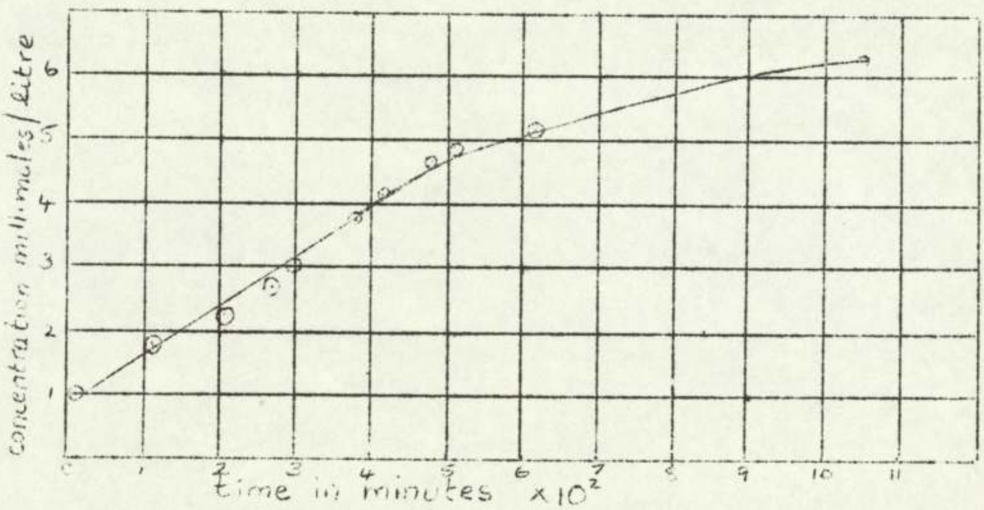
(a) two fold increases in dilution reduces rate by half.
(b) two fold increase in concentration doubles rate.

1-6 Before going on to the next frame, let us fill in with some background information which you may not know. All matter is made up of minute particles called molecules, and before a chemical reaction can occur, molecules must collide.

(No response is required to this frame, go on to frame 1-7.)

1-7 The graph below lists data for increase in concentration of bromine ions as a function of time at 79.63°C when lithium chloride reacts with isopropyl bromide in a solution of acetone.

What is the difference between reaction rate within time interval 100-200 minutes, and the reaction rate in the interval 500-600 minutes?



- - - - - - - - - - - - - - - - - -

Reaction rate in 100-200 minute interval approximately twice that in 500-600 minute interval.

1-8 Referring back to frame 1-7, in which interval do you think there are more collisions, 100-200 minute or 500-600 minute?

- - - - - - - - - - - -

There are more collisions in 100-200 minute interval than in 500-600 minutes.

1-9 What generalisation can you make concerning the effect of varying concentration on the rate of a reaction? Explain your generalisation in terms of the collision theory.

- - - - - - - - - - - - -

A rise in concentration means a faster rate. This would be explained by the collision theory because a higher concentration would give more collisions between reactant molecules per unit time, thus increasing the reaction rate.

WARNING The above rule does not always apply to overall equations which are usually written down.

1-10 Consider two gases A and B in a container at room temperature. What effect will the following changes have on the rate of reaction between these gases?

(a) the pressure is doubled.
(b) the number of molecules of gas A is doubled.
(c) the volume of the container is doubled.

- - - - - - - - - - - - -

(a) Doubling the pressure increases the concentration of both reactants, and consequently increases the rate.
(b) Doubling the number of molecules of A increases the concentration of A, and hence may result in an increase in reaction rate.
(c) Doubling the volume of the container decreases the concentration, hence slowing down the reaction rate.

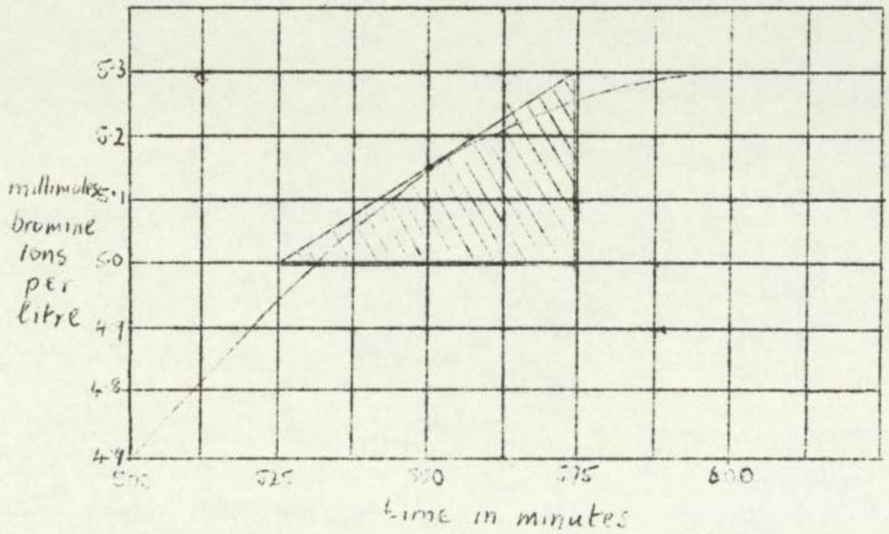
1-11 The general lwa relating concentration to the rate of a reaction is empirically derived and takes thisform:-

$$\text{rate} = \text{rate constant} \times \begin{pmatrix}\text{concentration} \\ \text{in moles litre}\end{pmatrix}^n$$

The power n is determined by experiment
The units will be litre^{n-1} moles^{1-n} second^{-1}

1-11(cont.)

Here is a portion of the curve obtained from data in frame 1-7. It shows the production of Bromine ions over the time interval 500 - 600 minutes. The average rate of production over this time interval = 0.006 millimoles per minute. What is the average rate at the mid point of this time interval which is given by the tangent to the curve?



- - - - - - - - - - - - -

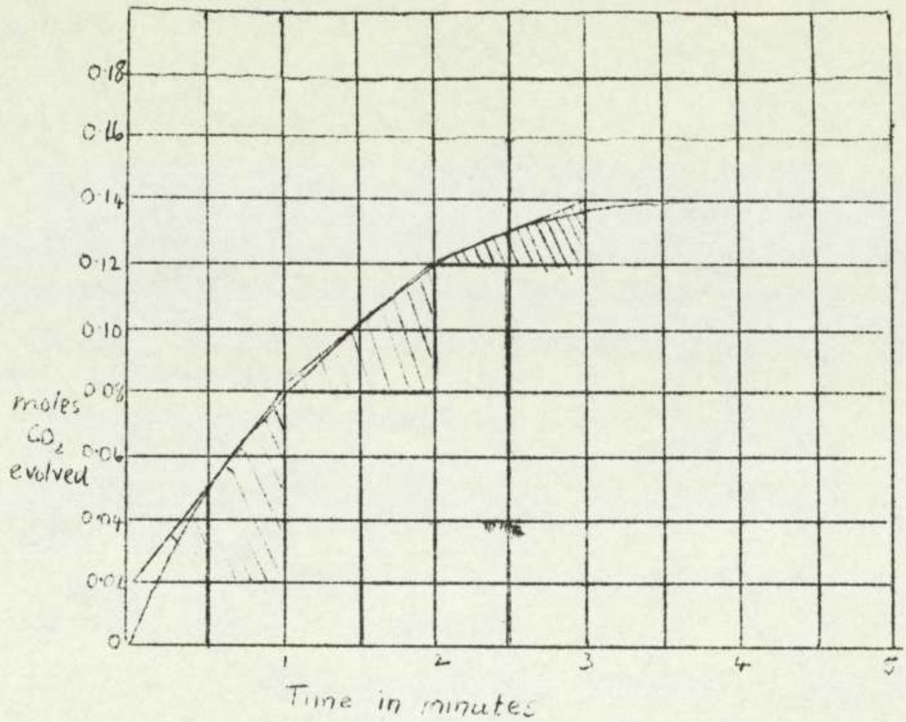
$\frac{0.3 \text{ millimoles}}{50 \text{ minutes}}$ = 0.006 millimoles per minute

---

1-12 Calcium carbonate (marble) reacts with dilute mineral acid giving calcium ions in solution, water and carbon dioxide gas. The rate of the reaction can be measured by the rate of evolution of the carbon dioxide. What is the reaction rate according to the graph at:-

i) 0.5minutes
ii) 1.5minutes
iii) 2.5minutes

1-12(cont.)

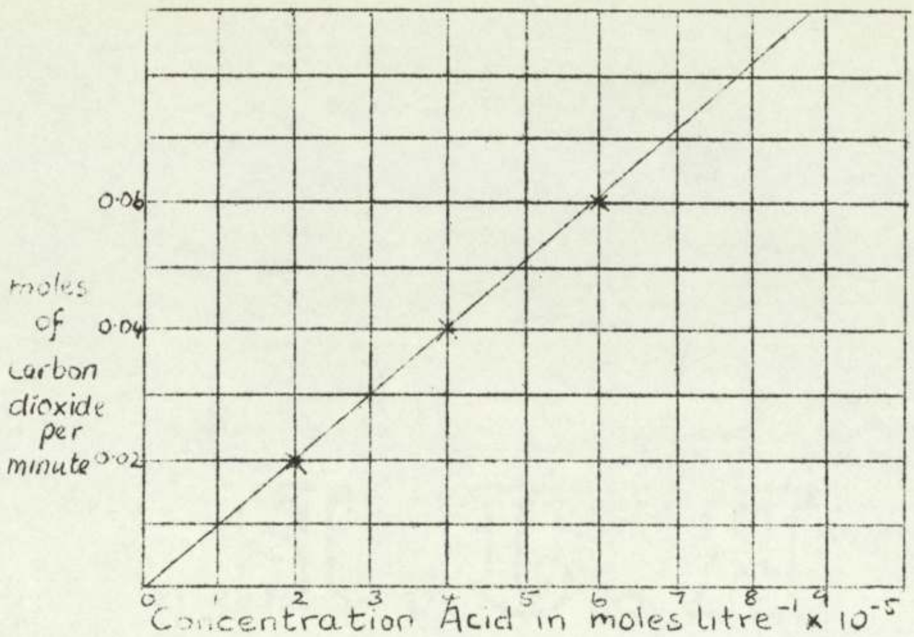


- - - - - - - - - - - - - -

i) 0.06 moles per minute
ii) 0.04 moles per minute
iii) 0.02 moles per minute.

1-13 In this graph the rate data from frame 1-12 are plotted against the concentration of acid. What can you say about the relationship between the rate of the reaction and the concentration of the hydrochloric acid?

1-13(cont.)



- - - - - - - - - - -

linear relationship i.e. $\frac{\text{Rate of reaction}}{\text{concentration}}$ = k (slope of straight line)

1-14 Let us now digress for a moment to introduce some standard nomenclature and symbolism.

From the previous frame we have:-

$\frac{\text{rate}}{\text{concentration}}$ = constant (referred to as the RATE CONSTANT)

Rearranging the above we get:-

rate = constant x concentration raised to first power.

or symbolically $\frac{dx}{dt} = k[c]^{(1)}$

Where [ ] denotes concentration in moles per litre and the power to which this concentration is raised is called the ORDER OF THE REACTION.

(No response needed here, go on to next frame. Refer back to this frame if necessary)

1-15 For a first order reaction the units of the rate constant can be determined as follows

Rate in = constant x concentration in

moles litres^{-1} seconds^{-1} = k x moles litre^{-1}

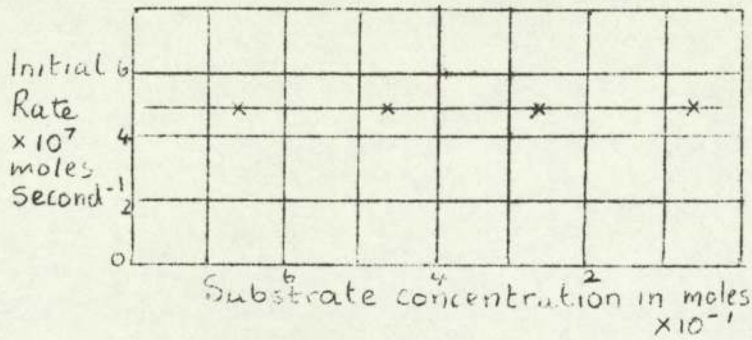
∴ The units of k = seconds^{-1}

What would be the units of the rate constant in a zero order reaction?

- - - - - - - - - - - - - -

moles litre^{-1} second^{-1}

1-16 Here are some data obtained for reaction between fumarate hydratase and fumarate:

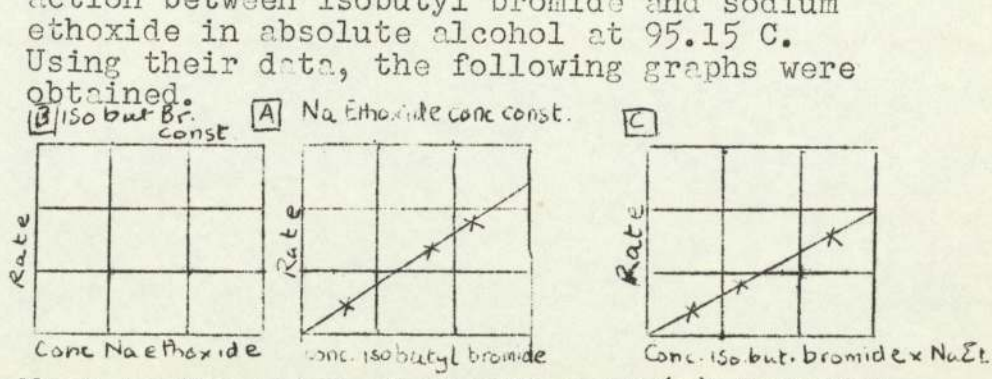


What is the order of this reaction?

- - - - - - - - - - - - - - -

zero order.

1-17 Dostrovsky and Hughes investigated the reaction between isobutyl bromide and sodium ethoxide in absolute alcohol at 95.15 C. Using their data, the following graphs were obtained.



What is the order of reaction of (a) isobutyl bromide (b) sodium ethoxide (c) both reactants.

- - - - - - - - - - - - -

(a) First order, (b) first order, (c) second order.

1-18 Ammonium Cyanate in solution rearranges spontaneously to give urea.

$NH_4\ CNO \longrightarrow (NH_2)_2\ CO.$

The rate constant is found to be by experiment 5.82×10^{-2} litre $mole^{-1}$, $minute^{-1}$. What is the order of the reaction?

Second order.

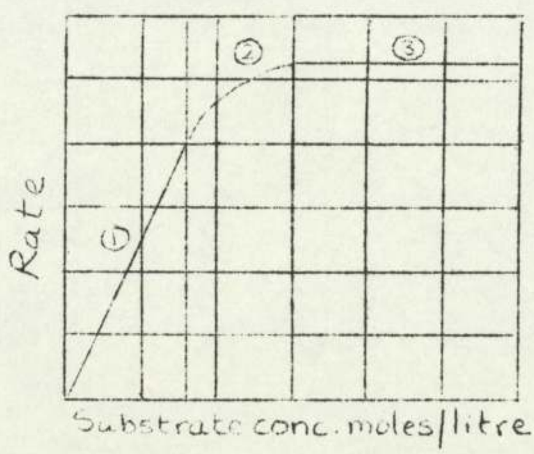
1-19 What do you think is the general law relating concentration to the rate of reaction? State the units of the rate constant.

The general rate law is empirically derived and takes the form,

Rate = Rate constant x (concentration in moles /litre $)^{n}$.

The power 'n' is <u>determined by experiment</u>
The units will be litre moles second.

1-20



Write down an expression to connect the rate with the substrate concentration in regions 1 and 3 of the above graph.

----

(1) rate = k . [Substrate]

(3) rate = k . [Substrate]

1-21. We are now going to study why very often the chemical equation cannot be used to determine the order of a reaction.

Even the simplest reactions often do not proceed by one single step but by a series of steps which are referred to as the reaction mechanism. The fast steps in the mechanism occur at such a rapid rate that they do not affect the overall rate. The slowest step in any mechanism determines the rate and order of reaction and is therefore known as the <u>rate determining step.</u>

Consider the reaction between ferrous ions manganate ions and hydrogen ions giving ferric ions, manganous ions and water.

$$5Fe^{+2} + MnO_4^{-} + 8H^{+} \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O.$$

According to the equation 14 ions would have to collide simultaneously if the reaction were to take place in a single step.
Do you think this likely?

No, the probability of this occuring is very remote.

1-22 Consider the decomposition of hydrogen iodide, yielding hydrogen and iodine

$$2HI \longrightarrow H_2 + I_2$$

Do you consider this reaction is likely to take place in one step?

Yes - Two molecules only have to collide to yield products.

1-23 The reaction between hydrogen iodide decomposing by a one step mechanism is further supported from kinetic studies which show that the reaction is second order. . . .

Nitrous oxide decomposes according to the following equation

$$2N_2O \longrightarrow 2N_2 + O_2$$

Is it feasible that the catalytic decomposition of nitrous oxide is a one step mechanism, if you take into account that it is found by experiment to be a first order reaction?

1-23 (Contd)
No. This suggests a mechanism other than a one stage process.

1-24. The mechanism for the catalytic decomposition of nitrous oxide has been suggested as follows:-

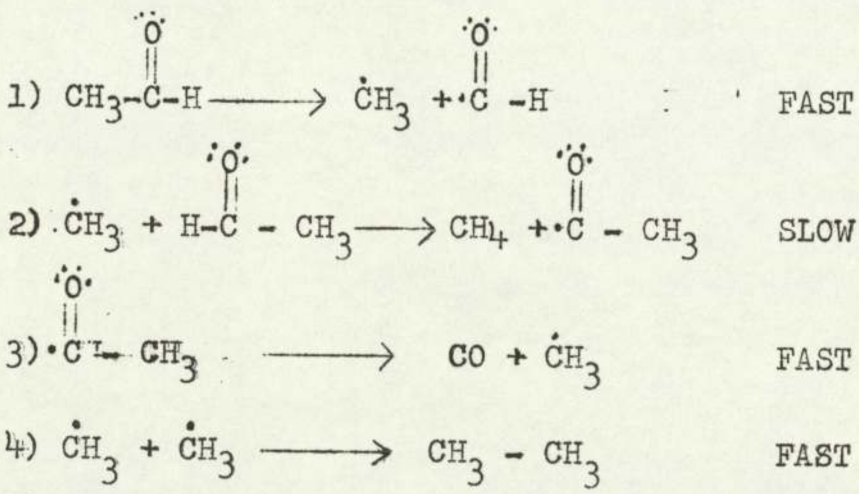
$$N_2O \longrightarrow N_2 + O \quad \text{(SLOW)}$$

$$O + O \longrightarrow O_2 \quad \text{(RAPID)}$$

Do you consider that the first or second step will control the rate of the process?

The **first** step will control rate of the process.

1-25 The mechanism proposed for the thermal decomposition of acetaldehyde is as follows -



Which of these reactions determines the rate of the reaction, and what is the order of reaction with respect to acetaldehyde.

Step (2)

First order.

1-26 The reactions between hypochlorite ions and iodide ions, in aqueous solution is represented by the following ionic equation -

$$OCl^-(aq) + I^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$$

Analytical and kinetic measurements show that the reaction mechanism involves the following steps.

(1) $OCl^-(aq) + H_2O \longrightarrow HOCl(aq) + OH^-(aq)$ FAST.

(2) $I^-(aq) + HOCl(aq) \longrightarrow HOI(aq) + Cl^-(aq)$ SLOW.

(3) $OH^-(aq) + HOI(aq) \longrightarrow H_2O(l) + OI^-(aq)$ FAST.

Which of these reactions is the rate determining step?

Step (2)

1-27 Dinitrogen pentoxide is unstable in the vapour state and decomposes into nitrogen dioxide and oxygen. The following mechanism has been proposed.

(1) $N_2O_5 \longrightarrow NO_2 + NO_3$ FAST

(2) $NO_2 + NO_3 \longrightarrow N_2O_5$ FAST

(3) $NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2$ SLOW

(4) $NO + NO_3 \longrightarrow 2NO_2$ FAST

Which step determines the overall rate for the reaction?

Step (3)

1-28 In the bromoform reaction acetone reacts with bromine yielding acetate ions and bromoform. The overall reaction can be written

$$2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3Br_2 + 2OH^- \longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-O^- + 2CHBr_3$$

1-28(cont.)

The reaction takes place by the following steps:-

i) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \bar{O}H \rightarrow CH_3-\overset{\overset{O}{/\!/}}{C}-\bar{C}H_2 + H_2O$ SLOW

ii) $CH_3-\overset{\overset{O}{\|}}{C}-\ddot{C}H_2 + Br_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2Br + \bar{B}r$ FAST

iii) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2Br + \bar{O}H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\ddot{C}HBr + H_2O$ FAST

iv) $CH_3-\overset{\overset{O}{\|}}{C}-\ddot{C}HBr + Br_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CHBr_2 + \bar{B}r$ FAST

v) $CH_3-\overset{\overset{O}{\|}}{C}-CHBr_2 + \bar{O}H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\ddot{C}Br_2 + H_2O$ FAST

vi) $CH_3-\overset{\overset{O}{\|}}{C}-\ddot{C}Br_2 + Br_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CBr_3 + \bar{B}r$ FAST

vii) $CH_3-\overset{\overset{O}{\|}}{C}-CBr_3 + \bar{O}H \longrightarrow HO-\overset{\overset{O}{\|}}{C}-CH_3 + \bar{C}Br_3$ FAST

viii) $CH_3-\overset{\overset{O}{\|}}{C}-O-H + \bar{C}Br_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\bar{O} + HCBr_3$ FAST

What is the rate determining step and order of reaction?

- - - - - - - - - - - - - - -

1. First step.
2. First order with respect to $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

1-29 Verbalise the principle governing the rate and order of a reaction involving a mechanism of several steps.

- - - - - - - - - - - - - - - -

Even the simplest reactions often do not proceed by one single step but by a series of steps which are referred to as the reaction mechanism. The fast steps in the mechanism occur at such a rapid rate that they do not affect the overall rate. The slowest step in any mechanism determines the rate and order of reaction and is therefore known as the <u>rate determining step</u>.

1-30 The reaction between hypochlorite and iodide ions in aqueous solution is represented by the ionic equation:-

$$\bar{OCl} + \bar{I} \longrightarrow \bar{OI} + \bar{Cl}$$

The mechanism for the reaction involves three steps.

1. $\bar{OCl} + H_2O \longrightarrow HOCl + \bar{OH}$ FAST

2. $\bar{I} + HOCl \longrightarrow HOI + \bar{Cl}$ SLOW

3. $\bar{OH} + HOI \longrightarrow H_2O + \bar{OI}$ FAST

What is the rate determining step and order of the reaction?

- - - - - - - - - - - - - - -

a) The reaction is first order with respect to HOCl and I.

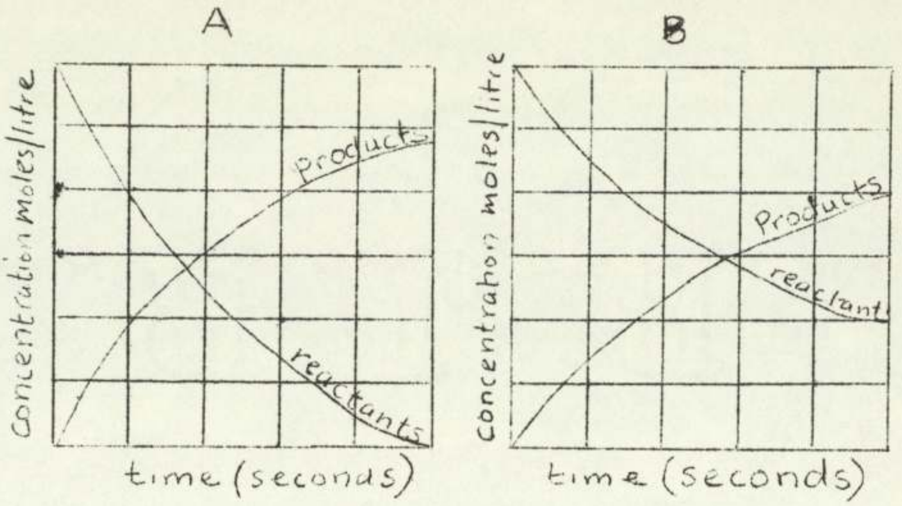
b) The rate determining step is

$$\bar{I} + HOCl \longrightarrow HOI + \bar{Cl}$$

1-31 We often say that a chemical reaction goes "to completion". By this we mean that there is very often what appears to be a complete conversion into products. For instance, if hydrogen is sparked with $\frac{1}{2}$ its own volume of oxygen, there is apparently complete conversion to water, for no oxygen or hydrogen is detectable.

On the other hand, we say that some reactions are reversible, because both forward and reverse reactions take place to a measurable extent. For instance, ethyl alcohol forms an equilibrium mixture when added to acetic acid, giving ethyl acetate and water. The following two graphs show concentration time data for the above two reactions. Which one is which?

1-31(cont.)



- - - - - - - - ---- - - -

A. $2H_2 + O_2 \longrightarrow 2H_2O$

B. $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

1-32 In this section we are setting out to study the quantitative relationship which holds for concentrations of reactants and products in an equilibrium mixture.

The product of concentrations of products each raised to the power equal to the number of moles of that substance in the chemical equation divided by concentration of reactants raised to the power equal to the number of moles ~~of~~ substance in the chemical equation is equal to a constant.

In an experiment on the equilibrium reactions between ferric ions, thiocyanate ions and ferric thiocyanate ions, i.e.

$$Fe^{+3} + SCN^{-} \longrightarrow FeSCN^{+2}$$

the following results were obtained.

Equilibrium Conc$^{n.}$ $[FeSCN^{++}]$	Equilibrium Conc$^{n.}$ $[Fe^{+3}]$	Equilibrium Conc$^{n.}$ $[SCN^{-}]$	Tube No.
8.7×10^{-4}	3.9×10^{-2}	1.3×10^{-4}	1.
7.0×10^{-4}	1.5×10^{-2}	3.0×10^{-4}	2.
5.3×10^{-4}	5;9 $\times 10^{-3}$	4.7×10^{-4}	3.
2.8×10^{-4}	2.3×10^{-3}	7.2×10^{-4}	4.

1-32(cont.)

Work out the value of $[Fe^{+3}] \times [FeSCN^{+2}] \times [SCN^-]$ for each of the 4 tubes separately.

- - - - - - - - - - - -

Tube No.
1. 4.4×10^{-9}.
2. 3.2×10^{-9}.
3. 1.5×10^{-10}.
4. 4.6×10^{-10}.

1-33 Using the same data as in frame 1-32, determine the value:-

$$\frac{[Fe^{+3}] \times [FeSCN^{+2}]}{[SCN^-]}$$

for each of the four tubes.

- - - - - - - - - - - - -

1. 2.6×10^{-1}.
2. 3.5×10^{-2}.
3. 6.7×10^{-3}.
4. 9.0×10^{-4}.

1-34 Again using the same data as in frame 1-32, determine the value of:-

$$\frac{[FeSCN^{+2}]}{[Fe^{+3}] \times [SCN^-]}$$

for each of the four tubes.

- - - - - - - - - - - -

1. 1.7×10^2 .
2. 1.6×10^2 .
3. 1.9×10^2 .
4. 1.7×10^2 .

1-35 Glance back over the answers you obtained in frames 1-32, 1-33, and 1-34. Which gave the most constant value?

a) $[Fe^{+3}] \times [FeSCN^{+2}] \times [SCN^-]$

b) $\frac{[Fe^{+3}] \times [FeSCN^{+2}]}{[SCN^-]}$

c) $\frac{[FeSCN^{+2}]}{[Fe^{+3}] \times [SCN^-]}$

- - - - - - - - - - - - - - - - - -

1-35(cont.)

c) $\dfrac{[FeSCN^{+2}]}{[Fe^{+3}] \times [SCN^{-}]}$

NB. In this experiment, the above expression gives most constant value. Variation in the constant in this case can be attributed to experimental error.

1-36 Some more accurate data have been obtained for the decomposition of hydrogen iodide at 698.6°K i.e.

hydrogen iodide ⇌ hydrogen + iodine

$$2HI \rightleftharpoons H_2 + I_2$$

Exp No.	H_2 moles/litre	I_2 moles/litre	HI moles/litre
1.	1.8313×10^{-3}	3.1292×10^{-3}	17.671×10^{-3}
2.	2.9070×10^{-3}	1.7069×10^{-3}	16.482×10^{-3}
3.	4.5647×10^{-3}	0.7378×10^{-3}	13.544×10^{-3}

Compute $\dfrac{[H_2] \times [I_2]}{[HI]}$ for each of these experiments

- - - - - - - - - - - - -

Expt. No.	
1.	32.429×10^{-5}
2.	30.105×10^{-5}
3.	24.866×10^{-5}

1-37 Now compute $\dfrac{[H_2] \times [I_2]}{[HI]^2}$ for each of the experiments.

Which expression:-

$\dfrac{[H_2] \times [I_2]}{[HI]}$ or $\dfrac{[H_2] \times [I_2]}{[HI]^2}$

gives the most constant value?

- - - - - - - - - - - - -

1-37(cont.)

Expt. No.
1. 1.8351×10^{-2}.
2. 1.8265×10^{-2}.
3. 1.8359×10^{-2}.

$$\frac{[H_2] \times [I_2]}{[HI]^2}$$

1-38 The data below were obtained when the equilibrium we have just examined was approached the other way i.e. by adding hydrogen and iodine vapour together at 698.6°K.

Expt No	H_2 moles/litre	I_2 moles/litre	HI moles/litre
1	0.4789×10^{-3}	0.4789×10^{-3}	3.531×10^{-3}
2	1.1409×10^{-3}	1.1409×10^{-3}	8.410×10^{-3}

Find $\frac{[H_2] \times [I_2]}{[HI]^2}$ for each of the above experiments. Do you notice anything about their constants and those obtained in frame 1-37?

- - - - - - - - - - - - -

Expt No
1. 1.8390×10^{-2}.
2. 1.8403×10^{-2}

They are the same values almost.

1-39 What generalisation can be made about the concentration of products and reactants in an equilibrium mixture?

- - - - - - - - - - - - -

The product of the concentrations of products each raised to the power equal to the number of moles of that substance in the chemical equation divided by concentraion of reactants raised to power equal to the number of moles of substance in chemical equation is equal to a constant.

1-40 Steam reacts with red hot iron to give ferroso ferric oxide and hydrogen.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Write down an expression for the equilibrium constant.

- - - - - - - - - - - - -

$$K = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4}$$

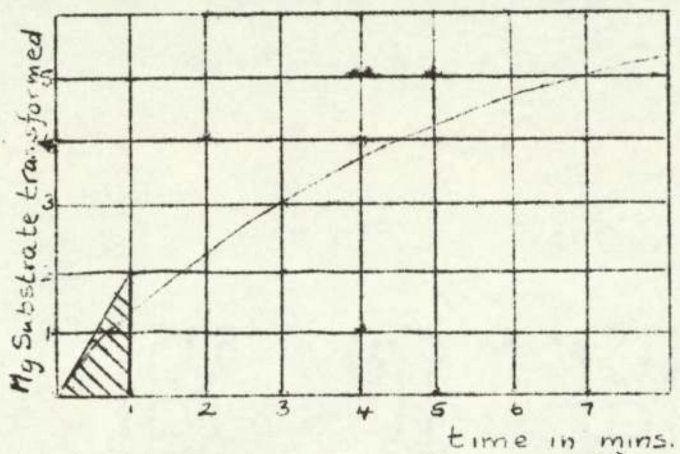
Please complete the answer sheet for this section with all the information required.

SECTION 2.

The influence of Substrate Concentration on the Rate of Enzyme Reactions.

Before you begin this section please fill in the Answer Sheet with all the information required.

2-1. Before embarking on this section let us make it clear that when we talk about the rate or velocity of an enzyme reaction we mean the <u>initial velocity</u> i.e. the velocity at the very beginning of the reaction. The procedure is essential in enzyme work because the velocity falls off with time due to such factors as product inhibition, lability of enzyme, back reactions etc. What is the initial velocity in the graph?



2mg. of substrate transformed per minute.

2-2 In the following frames the symbolism shown below will be used.

E	----	Enzyme
S	----	Substrate
ES	----	Enzyme substrate complex.
P.	----	Product.
k_{+1}	----	velocity constant fir the formation of ES from S and E.
k_{-1}	----	velocity constant for the reverse reaction of above.
k_{+2}	----	velocity constant for the breakdown of ES into P and E.

2-2 Contd.

Please refer back to this frame if you forget the symbols. There is no response needed here, go on to the next frame.

2-3 In the next few frames we go on to examine the ralationship between E, S, and ES.

The enzyme and substrate are at equilibrium with the enzyme substrate complex; because this equilibrium is formed at a much faster rate than the breakdown of the enzyme substrate complex into products,

Symbolically,

$$E + S \rightleftharpoons ES \longrightarrow E + P$$

In a study of the action of phosphatase on glucose 1 phosphate the following concentrations of enzyme, substrate and enzyme substrate complex were found in two separate experiments.

Expt. No.	[S]	[E]	[ES.]
1	0.5×10^{-3}	2×10^{-5}	1×10^{-5}
2.	1×10^{-3}	1×10^{-5}	1×10^{-5}

Can you see a relationship between these values?

$$\frac{[E]\,[S]}{[ES]} = \text{constant } (10^{-3} \text{ in both experiments})$$

2-4 Kauzmann et al. have studied the luciferin / luciferase system in the luminescent ostrocod crustacean C ypridina. They obtain the following results:

	Luciferin	luciferase	luciferin/ luciferase
Exp. No,	[S]	[E]	[ES]
1	8×10^{-5}	10^{-8}	8×10^{-7}
2	4×10^{-3}	10^{-6}	4×10^{-3}

Can you see a relationship that holds between [E] [S] and [ES] ?

2-4(cont.)

In both experiments $\frac{[E][S]}{[ES]} = 10^{-6}$.

2-5 According to work by Franz and Stephenson, swine kidney pepsinase hydrolyses carbobenzoxy-l-glutamyl-tyrosine giving carbobenzoxy-l-glutamic acid and tyrosine. Results of two of their experiments are shown below.

Expt No	[E]	[S]	[ES]
1	1×10^{-6}	5×10^{-3}	4×10^{-7}
2	2×10^{-3}	8×10^{-2}	1.28×10^{-7}

What can you say about the results of these experiments?

- - - - - - - - - - -

In both experiments $\frac{[E][S]}{[ES]}$ forms a constant which equals 1.25×10^{-4}.

2-6 In the following three frames we are going to examine the rate constants for the various phases of the reactions we have just met.

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES \xrightarrow{k_{+2}} E + P$$

If the above represents the action between the enzyme phosphatase and glucose 1 phosphate

$$k_{+1} = 10^6$$
$$k_{-1} = 10^4$$
$$k_{+2} = 18$$

NB. No value is given for k since if INITIAL VELOCITIES are taken this value is assumed to be negligible.

What do you notice about k_{+1} and k_{-1} compared to k_{+2}? What does this show about reaction rates?

- - - - - - - - - - -

k_{+1} and k_{-1} are very much larger than k_{+2} showing that first two reactions are very much quicker.

2-7 In the luciferin/luciferase system of Cypridinia, $k_{+1}=10^6$, $k_{-1}=10^5$, $k_{+2}=26$. What is the rate determining step above?

- - - - - - - - - - - - - - -

The breakdown of the enzyme-substrate complex into products is the rate determining step.

2-8 In the hydrolysis of carbobenzoxy-l-glutamyl tyrosine by pepsin, the following rate constants were found: $k_{+1}= 10^4$, $k_{-1}= 10^3$, $k_{+2}= 10$. What do you notice about the rate of formation of the enzyme substrate complex and its reverse reaction compared to the rate of decomposition of the enzyme substrate complex into products?

- - - - - - - - - - - - - - - -

Both the rate of the formation of the enzyme substrate complex and its reverse reaction are <u>much</u> fasterthan the rate of decomposition of the enzyme substrate complex into products

---

2-9 What model would you postulate for enzyme reactions taking all these experimental results into consideration

- - - - - - - - - - - - - - - -

The enzyme and substrate are at equilibrium with the enzyme substrate complex, because the equilibrium is formed at a much faster rate than the breakdown of the enzyme substrate complex into products. Symbolically,

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES \overset{k_{+2}}{\rightarrow} E + P$$

2-10 (a). What is the velocity of the overall enzyme reaction in terms of the concentration of the enzyme substrate complex?

(b). What is the concentration of the enzyme substrate complex in terms of the substrate and enzyme concentration

(c). What is the velocity of the reaction in terms of the enzyme and substrate concentration.

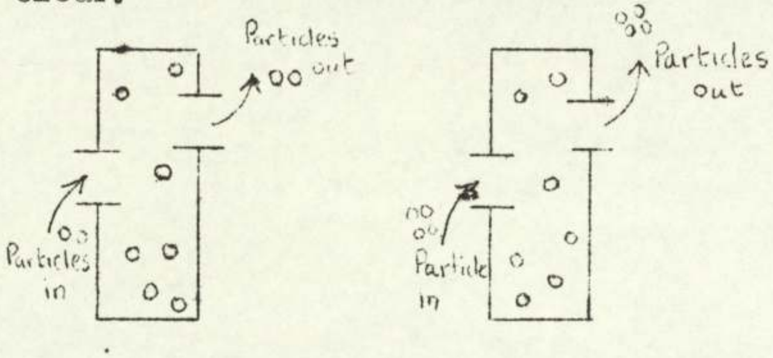
- - - - - - - - - - - - - -

(a). $V = k_{+2}[ES]$ (b). $[ES] = K[E][S]$

(c). $V = k_{+2}K[E][S]$

2-11 Let us digress for one moment to considerthe difference between equilibrium and steady state.

Equilibrium is characterised by the constancy of macroscopic properties, that is to say that when the equilibrium is established no changes appear to be taking place visually. This cannot be the only characteristic of equilibrium. Consider a bunsen flame, the structure of the flame, rate of the gas flow to the flame, temperature in various zones does not change but the flame is not in equilibrium, since gaseous products of combustion are continuouslyleaving the system. Such a system is said to be in a steady state. The diagram below will help tp make this clear.



Why does a steady state exist in the above two diagrams?

- - - - - - - - - - - - - - - - -

A steady state exists because the rate at which matter is entering the system equals the rate at which matter is leaving the system, thus ensuring that the amount of matter within the system remains constant.

2-12. Which of the following systems constitute steady state situations and which are at equilibrium? For each one a constant property is indicated.
(a). An open pan of water boiling on a stove. The temperature of the water is constant.
(b). A balloon contains air and a few drops of water. The pressure in the balloon is constant.
(c). An ant hill follows its daily life. The populationof the ant hill is constant.

- - - - - - - - - - - - - - -

(a). Steady state (a). Equilibrium
(c). Steady state.

2-13 It cannot be assumed for all enzyme reactions that enzyme substrate and enzyme substrate complex exist in equilibrium, because very often the rate of breakdown of enzyme substrate complex back into reactants approximates the rate at which it gives products. A more valid assumption is that enzyme substrate complex exists in a steady state i.e. its concentration is steady (fixed), over a period of time taken to measure initial velocity.

Here are some concentrations for enzyme, substrate and enzyme substrate complex. The second set of readings was taken on the same system a little while after the first set.

	[Enzyme]	[Substrate]	[Enzyme/ Substrate Complex]
Expt 1	trypsin	benzoyl-1-arginine	benzoyl-1-arginine trypsin
1st Reading	$10^{-5} \times 1$	0.1	1×10^{-3}
2nd Reading	$10^{-5} \times 0.9$	0.099	1×10^{-3}
Expt 2			
1st Reading	$10^{-6} \times 0.25$	0.05	0.25×10^{-5}
2nd Reading	$10^{-6} \times 0.223$	0.049	0.25×10^{-5}

Does equilibrium exist between E, S, And ES in any of the above systems?

- - - - - - - - - - - - - - - - - -

$\frac{[ES]}{[E] \times [S]}$ does not form a constant in either of the above systems, therefore they are not at equilibrium.

2-14 Refer back to frame 2-13. Does the enzyme, substrate, or enzyme substrate complex appear to exist in steady state in any of the above systems?

- - - - - - - - - - - - - - - - - -

Enzyme substrate complex exists in a steady state in both systems.

2-15 Gut freund has carried out a number of measurements on various enzyme substrate systems to determine the velocity constants for different stages of the reaction. This frame and those immediately following show some of

2-15(cont.)
his results.

For the hydrolysis of benzoyl -1-arginine ethyl ester by trypsin
$k_{+1} = 4\times10^{6}$, $k_{-1} = 25$, $k_{+2} = 15$.
(a). What is the fastest reaction here?
(b). What do you notice about the rate of breakdown of the enzyme substrate complex into reactants and products?

- - - - - - - - - - - - - - - - - -

(a). The fastest reaction is the rate of formation of the Enzyme substrate complex.

(b). The rate of breakdown of the enzyme substrate complex into products and reactants are approximately of the same order of magnitude.

2-16 For the hydrolysis of benzoyl-1-arginine ethyl ester by ficin, $k_{+1} = 5\times10^{3}$, $k_{-1} = 6$, $k_{+2} = 1.5$.
(a). What is the slowest reaction?
(b). What reaction determines the speed of the enzyme reaction?
(c). What do you notice about the rate of the breakdown of the enzyme substrate complex into products and reactants?

- - - - - - - - - - - - - - - - - -

(a). The breakdown of the enzyme substrate complex into products.

(b). The breakdown of the enzyme substrate Complex.

(c). They are both of the same magnitude approximately.

2-17 In the hydrolysis of acetyl-1-phenylalanine ethyl ester by chymotrypsin,
$k_{+} > 10$, $k_{++} \simeq 10$, $k_{-} > 90$.
(a). what is the rate determining step?
(b). What do you notice about the size of the rate constants for the breakdown of the enzyme substrate complex?

- - - - - - - - - - - - - - - - - -

(a) The breakdown of the enzyme substrate complex into product and enzyme.

(b). They are approximately of the same size compared to the formation of the enzyme substrae complex which takes place more rapidly.

2-18 Do you notice any major differences between the rate constants in frames 2-6 - 2-8, and those just given in frames 2-15 - 2-17?

- - - - - - - - - - - - - - - - - -

In the first set of rate constants k_{+2} is very much smaller than k_{-1} but in the second set they are approximately the same size.

2-19 In frame 2-9 you proposed a model for enzyme action which is referred to as the Michaelis Menten model. What modifications to this michaelis Menten model do you think are necessary in the light of results given in this subsection?

- - - - - - - - - - - - - - -

It cannot be assumed for all enzyme reactions that the enzyme, substrate, and the enzyme substrate complex exist in equilibrium,because very often the rate of breakdown of the enzyme substrate complex back into reactants approximates the rate at which it gives the products. A more valid assumption is that the enzyme substrate complex exists in a steady state, i.e. its concentration is steady (fixed) over the period of time taken to measure the initial velocity.

2-20 $$\underset{e-c}{E} + \underset{s}{S} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \underset{c}{ES} \overset{k_{+2}}{\longrightarrow} E + P$$

concentrationin moles/litre.

(a). What is the rate of formation of the enzyme substrate complex ES?
(b). What is the rate of decomposition of the enzyme substrate complex ES?
(c). What can you say about the rate of formation and the rate of decompostion of the enzyme substrate complex?

- - - - - - - - - - - - - - - - - -

(a) Rate of formation of ES = $k_{+1}(e-c)x(s)$.
(b). Rate of decomposition of ES = $k_{-1}(c) + k_{+2}(c)$.
(c). Rate of formation of ES = rate of decomposition of ES.

2-21 The model which we have just proposed for enzyme action which assumes that the enzyme sustrate complex exists in a steady state is referred to as the Briggs Haldane model.No response needed go to next frame.

2-22 Examine once more the process

$$E + S \rightleftharpoons ES \longrightarrow E + P$$

and complete the following algebraic equivalents of the two verbal statements of what is assumed for each of our two kinetic models:

Verbal Statement	Algebraic Statement
ES is formed from E and S essentially as fast as it is consum -ed, either by conver -sion back to E and S or on to E and P.	$k_{+1}[E][S] = k_{-1}[\_\_] + \_\_[ES]$
ES is formed from E and S essetially as fast as it redissoc- iates to them.	$k_{+1}[E][S] = k_{-1}[\_\_]$

- - - - - - - - - - - - - - - - -

ES, k_{+2}, ES

2-23 Rearranging the first algebraic statement from frame 2-23 we get

$$\frac{k_{-1} + k_{+2}}{k_{+1}} = K_m = \frac{[E][S]}{[ES]}$$

Rearranging the second statement we get

$$\frac{k_{-1}}{k_{+1}} = K_S = \frac{[E][S]}{[ES]}$$

What do you notice that is unusual about the two equilibrium constants given above?

- - - - - - - - - - - - - - - -

The fraction is inverted one to that you would expect from the work we have done on equilibrium, i.e. $\frac{[E][S]}{[ES]}$ not $\frac{[ES]}{[E][S]}$

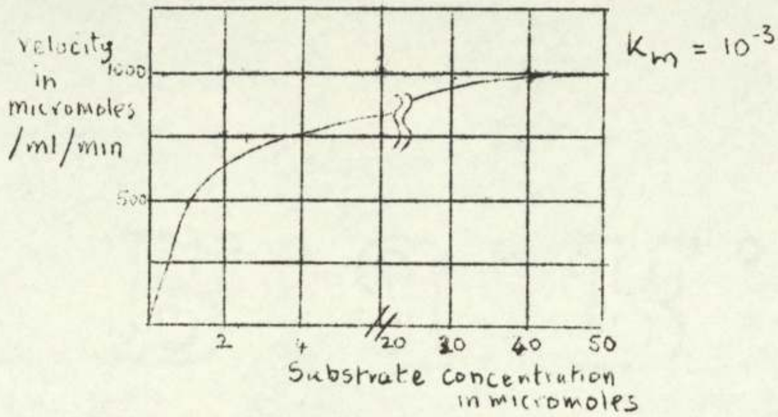
2-24 The following graph shows how the velocity of enzyme reactions characteristically increase with substrate concentration.
The curve has been interrupted to permit examination over a wide range of concentrations
From the curve you can see that at higher concentrations the rate can no longer be increased by further addition of substrate.

2-24(cont.)

The rate can no longer be made to rise because the substrate has saturated the the enzyme process. The rate observed under these conditions the maximum velocity and is indicated by V_{max}.

K_m(orK_s) is numerically equal to the substrate concentration that gives half maximum velocity.

What is the maximum velocity according to the graph?

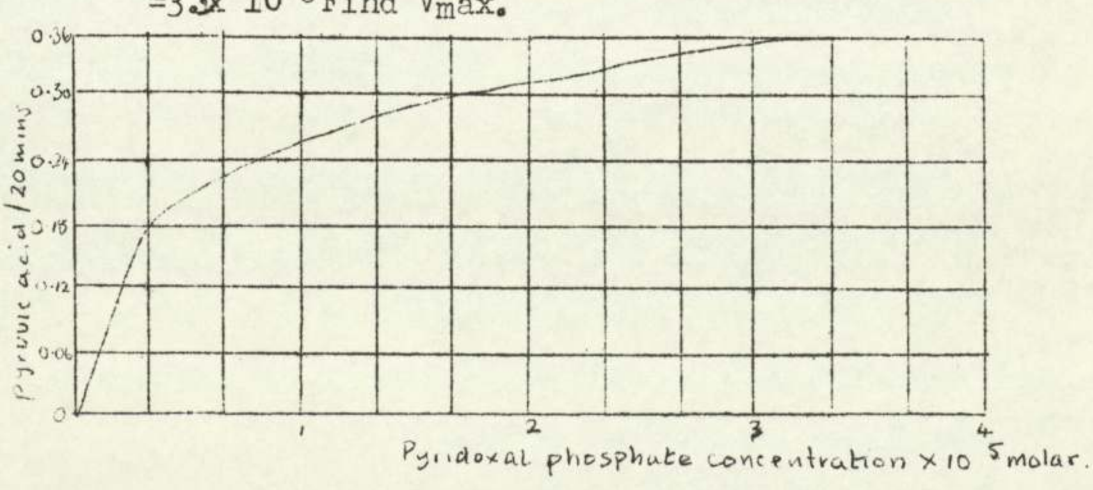


V_{max} = 1000 micrmoles/ml/min.
NB. The definition of maximum velocity does not say that this is the highest rate that can be reached under any conditions whatever, eg. by higher temperature.

2-25 Yanofsky has shown that D-serine hydratase of Neurospore crassa requires pyridoxal phosphate as a coenzyme. The enzyme catalysesthe reaction

$CH_2OHCHCOOH \longrightarrow CH_3COCOOH + NH_3$

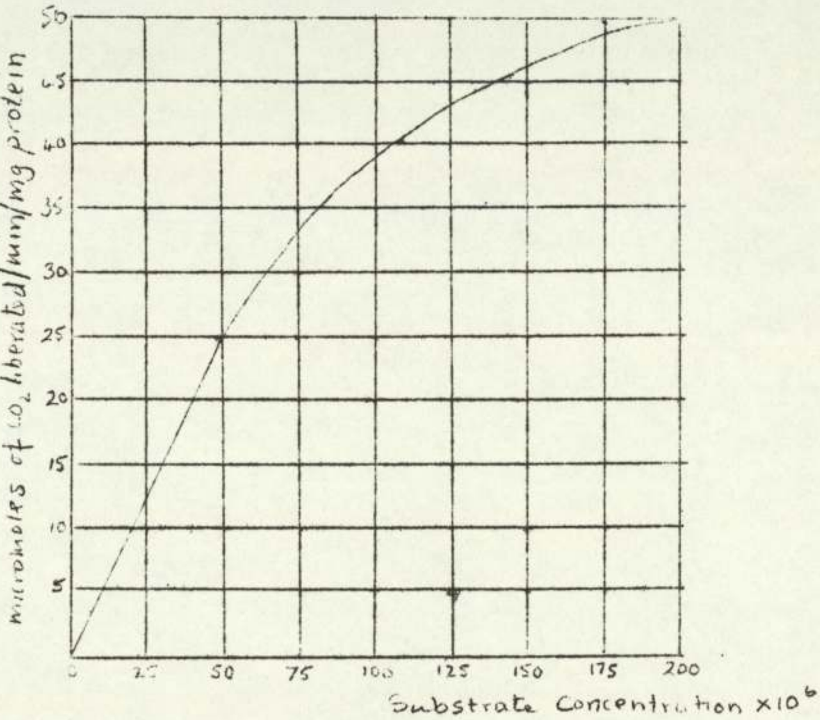
The graph below shows the pyridoxal phosphate saturation curve for the enzyme. K_m for the serine hydratase pyridoxal phosphate complex $=3.3 \times 10^{-6}$ Find V_{max}.



2-25 (cont.)

V_{max} = 0.36micromoles of pyruvic acid per 20 mins.

2-26 The activity of l-aspartate 4 carboxylase can be assayed manometrically by following the rate of evolution of carbon dioxide from l-aspartate. Here is a graph showing the results from this experiment. What isthe maximum velocity? $K_m = 10^{-6} x 50$



- - - - - - - - - - - - - - - - -

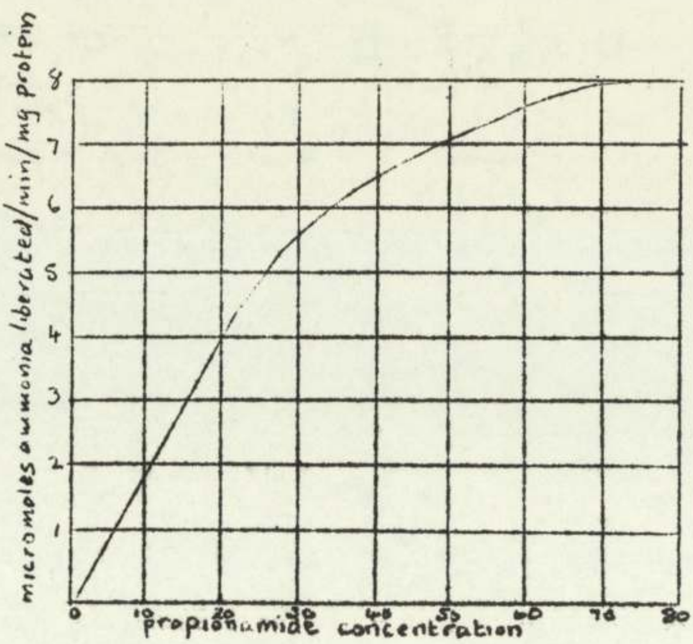
V_{max} = 50 micromoles of carbon dioxide /min./mg. of protein.

2-27 The organism Pseudomonas aeruginosa is capable of hydrolysing propionamide.

$$CH_3CH_2CONH_2 + H_2O \rightleftharpoons CH_3CH_2COOH + NH_3$$

What is V_{max} and K_m?

2-27(cont.)

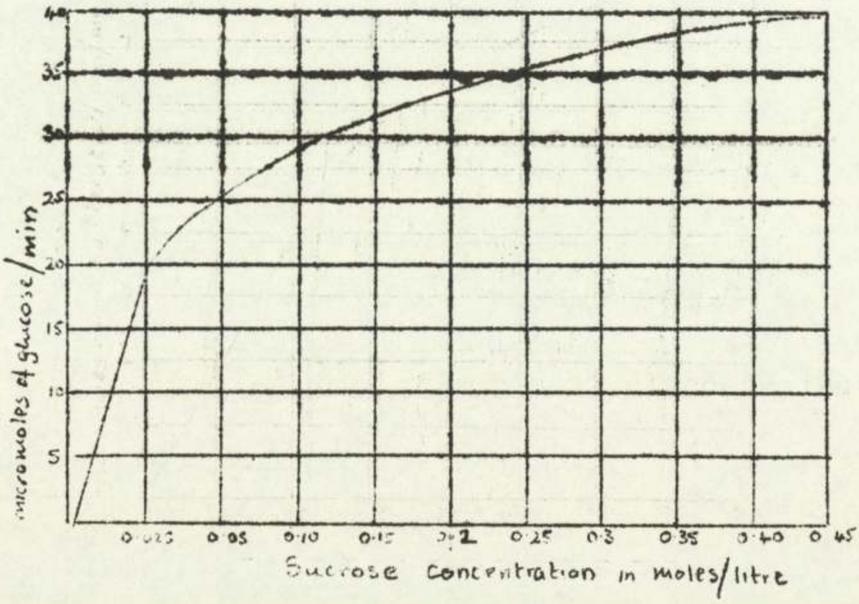


- - - - - - - - - - - - - - - -

V_{max} = 8micromoles NH_3/min/mg. of prottein

K_m = 20×10^{-3}

2-28 The graph below shows the rate of hydrolysis of sucrose by yeast saccharase. Find V_{max} and K_m.



- - - - - - - - - - - - - - - - -

V_{max} = 40 micromoles of glucose/minute

K_m = 0.025.

2-29 What generalisation can you make about the relationship between K_m and the substrate concentration?

- - - - - - - - - - - - - - - - - -

K_m (or K_s) is numerically equal to the substrate concentration that gives half maximum velocity.

2-30 The influence of A.T.P. concentration on the rate of dephosphorylation of A.T.P. by myosin which catalyses the reaction:

A.T.P.⟶ A.D.P. + inorganic phosphate

has been studied at 25°C and pH =7. The following data were obtained.

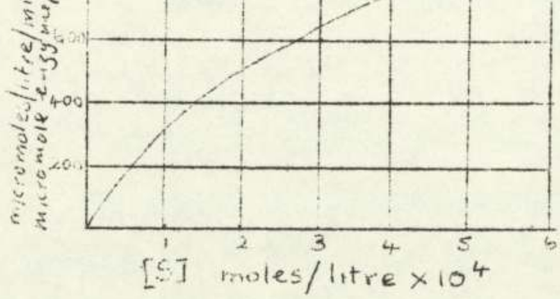
Velocity of reaction micromoles of phosphate produced/litre/sec.	A.T.P. concentration micromoles
0.067	7.5
0.095	12.5
0.119	20
0.149	32.5
0.185	62.5
0.195	320
0.195	450

Find K_m for the reaction by plotting the data on the grid provided.

- - - - - - - - - - - - - - - - - - - -

$K_m = 15 \times 10^{-3}$.

2-31 So far in this programme we have assumed that the maximum velocity can easily be read off a graph in the form shown below.



What does the maximum velocity appear to be?

- - - - - - - - - - - - - -

2-31(cont)

800 micromoles/min/micromole of enzyme /litre.

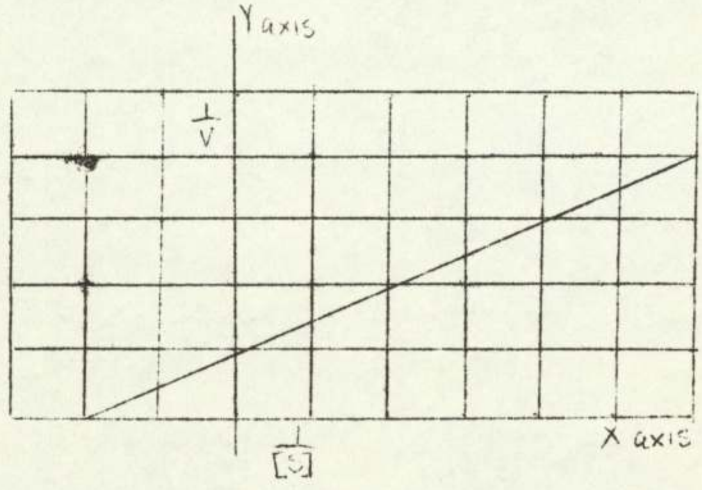
2-32 Actually the true maximum velocity for the enzyme reaction shown in frame 2-31 is 900 micromoles per litre per minute per micromoles of enzyme. The difficulty is that the human eye has very little ability to estimate how high a plateau will be reached by the curve.

To overcome this difficulty Lineweaver and Burke have proposed plotting reciprocals of velocity and substrate concentration which yields a straight line graph as shown.

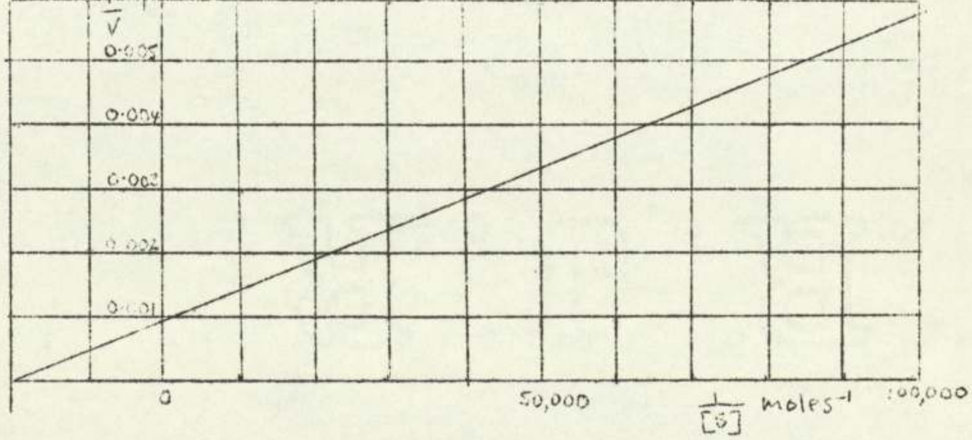
Intercept on the y axis = $\frac{1}{V_{max}}$

Intercept on the x axis = $\frac{-1}{K_m}$

No response is required here pass on to the next frame.



2-33 The graph below shows the rate of conversion of glucose into glucose-6-phosphate by the enzyme hexokinase.



2-33(cont)

Vmax is 1000(min^{-1}); what is the value of intercept on the y axis?

- - - - - - - - - - - - - - - -

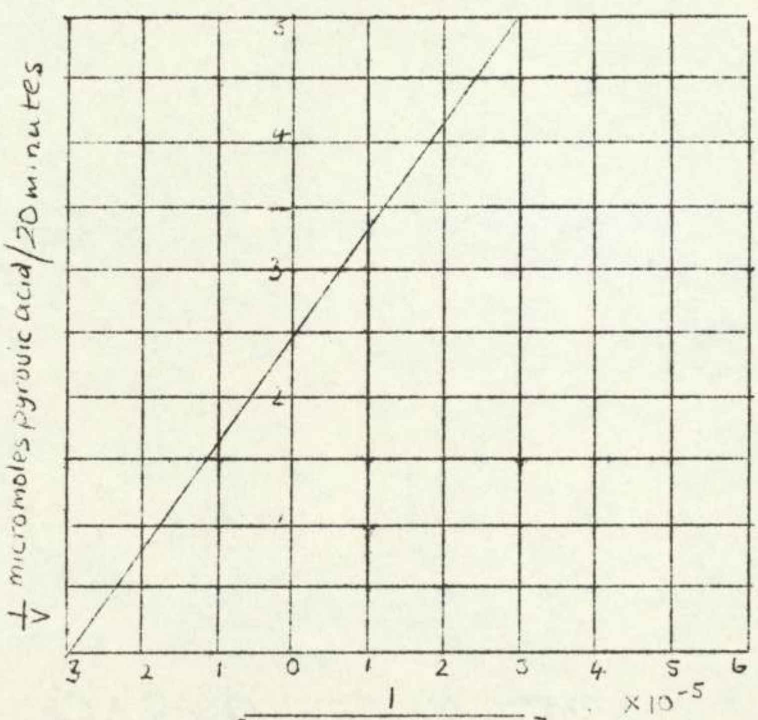
$$\frac{1}{0.001}$$

2-34 In the reaction whose results are shown in the previous frame $K_m = 5 \times 10^{-5}$. What is the value of the intercept on the x axis?

- - - - - - - - - - - - - -

-20,000.

2-35 D-Serine hydratase of Neurospora Crassa requires pyridoxal phosphate as a co-enzyme. The graph shows the rate at which pyruvic acid is formed from serine in varying concentrations of pyridoxal phosphate. Vmax is 0.4 micromoles pyruvic acid/20 mins. What is the intercept on the y axis?



- - - - - - - - - - - - - - - -

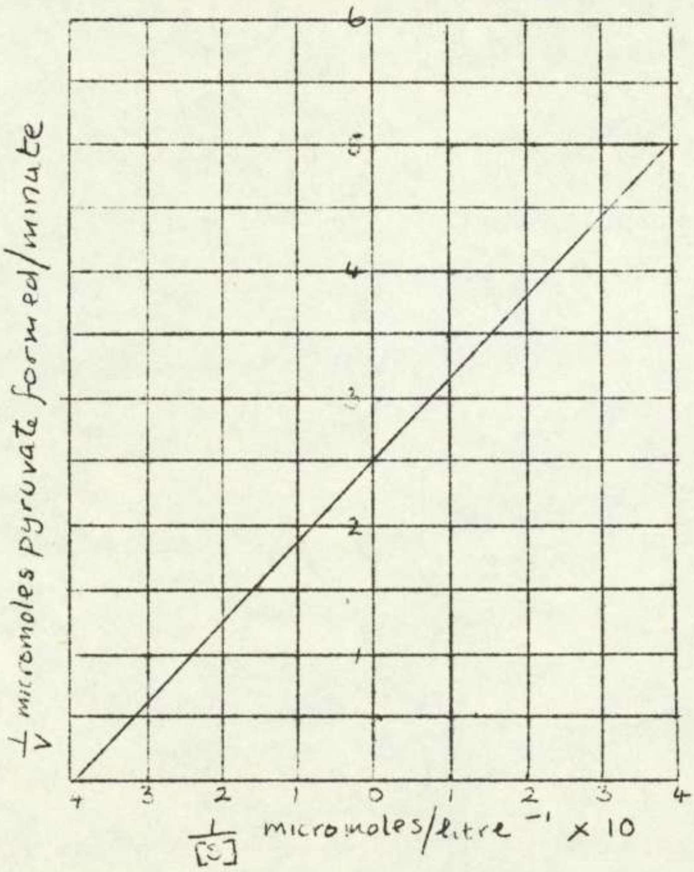
$$\frac{1}{2.5}$$

2-36 For the reaction whose graph is shown in frame 2-35 $K_m = 3{\cdot}3 \times 10^{-6}$ What is the intercept on the x axis?

- - - - - - - - - - - - - -

$-3x10^{5}$

2-37 The enzyme hydroxyaspartate aldolase catayses the cleavage of erythro-β-methyl-hydroxy aspartate to pyruvic acid and glycine. The accompanying graph shows the results from this experiment plotted by the Lineweaver Burke method. V_{max} =0.4miro moles of pyruvate/minute. What is the value of the intercept on the y axis?



- - - - - - - - - - - - - -

1/2·5 micromoles of pyruvate /minute.

2-38 Referring back to frame 2-37, K_m = 2·5. What is the intercept on the x axis?

- - - - - - - - - - - - - -

-1/0·4

2-39 What genralisation can you make about the intercept of the graph on the x and y axis in the Lineweaver Burke plot?

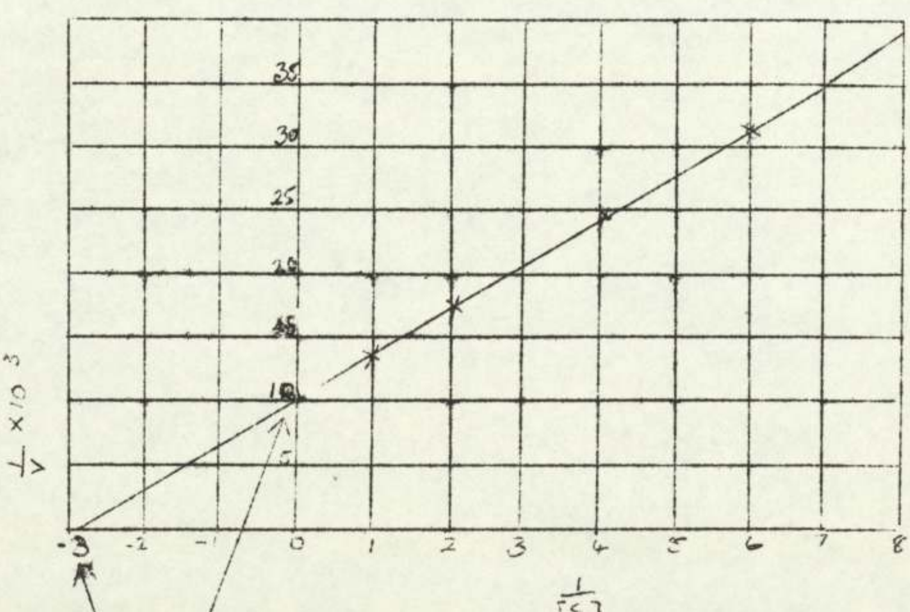
- - - - - - - - - - - -

The intercept on the y axis = $1/V_{max}$. and the intercept on the x axis = $-1/K_m$.

2-40 On the grid provided plot the following data. Find from the graph the value of V_{max} and K_m

1/ S moles	1/V minutes
1000	0·014
2000	0·018
4000	0·025
6000	0·033
8000	0·040

- - - - - - - - - - - - - - -



1/V = 1/0·01 therêfore V_{max} = 100.

$-1/K_m = -1/3x10^3$ " $K_m = 10^{-4}x\ 3{\cdot}3$

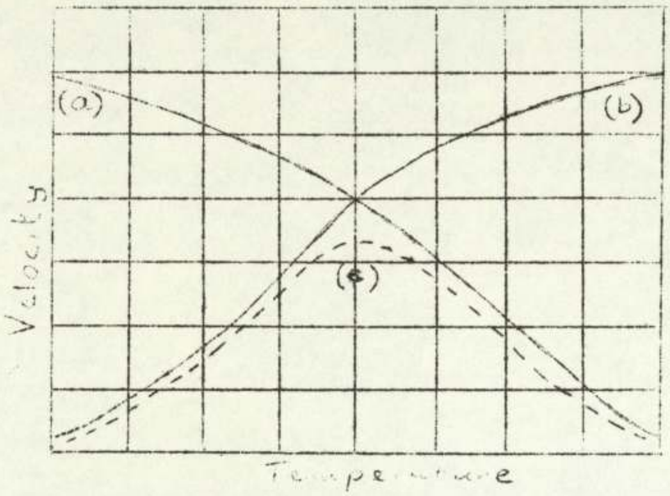
Please complete the answer sheet for this section with all the information required.

SECTION 3.

The effect of Temperature and pH on the rate of Enzyme Reactions.

Before you begin on this section please fill in the answer sheet with all the information required.

3-1 Inthis section we are going to examine separately the effect of temperature and pH on the effect of enzyme reactions. The graph below shows a typical curve which is obtained when the velocity of an enzyme reaction is plotted against the temperature.



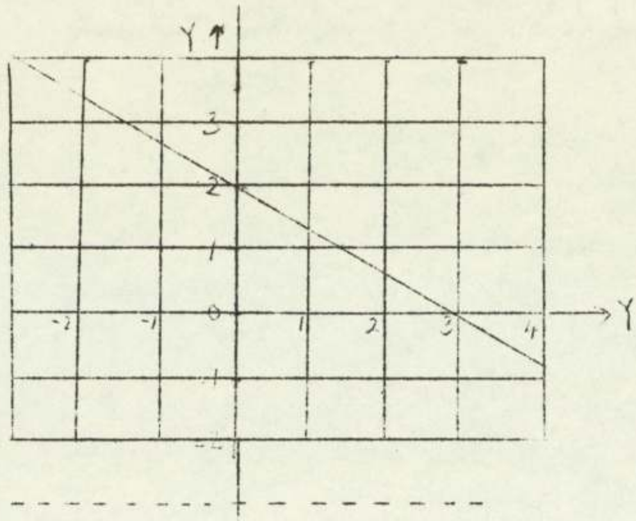
As you can see two processes seem to be influencing the reaction rate; one speeding up the reaction (b) and one slowing down the rate(a). The optimum temperature occurring where there is a balance between these two processes, shown on the resultant dotted curve by(c). No response is needed here go to 3-2.

3-2 Before trying to establish a law which relates increase in the rate with the temperature, let us revise some elementary mathematics.

The equation for a straight line is $y = mx + c$, Where m is the slope of the line and c is a constant equal to the intercept on the y axis when $x = 0$. If x increases as y increases then the slope of the line is positive, whereas if y decreases while x increases then the slope of the line is negative.

What is the slope and value of c in the following graph?

3-2(cont.)

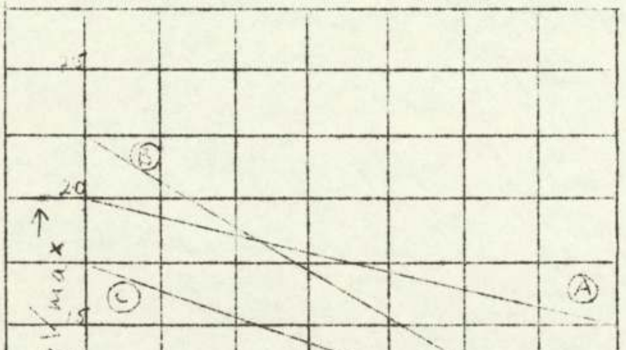


-2/3 and +2.

3-3. We are now going to look more closely at the relationship beween maximum velocity and temperature.

Log V_{max} = A - E/T where A and E are constants determined by experiment and T is the temperature in degrees absolute.

For the next few frames you will need to refer back to the graph shown below. Line (A) shows how the enzyme fumaric hydratase which acts on fumaric acid is influenced by temperature. How does Log V_{max} vary with the temperature?



log V_{max} varies inversely with 1/T

3-4 What is the slope of the line showing how log V_{max} for fumarate hydratase varies with temperature?

- - - - - - - - - - - - - -

-0.5/0.035

3-5 Line (B) shows how $\log V_{max}$ for malic acid dehydrogenase acting on malic acid varies with temperature. What do you notice about this variation?

- - - - - - - - - - - - - -

Log V_{max} varies inversely with 1/T

3-6 What is the slope of this line which shows how log V_{max} for malic acid dehydrogenase varies with temperature?

- - - - - - - - - - - - - -

- 1.25/0.035.

3-7 Line (C) shows how log V_{max} for the action of choline esterase on acetyl choline varies with the temperature. How is $\log V_{max}$ related to the temperature and the slope?

- - - - - - - - - - - - - -

$\log V_{max}$ varies as -0.75/0.035 x 1/T

3-8 What other empirical constant do you notice in the graph on frame 3-3, besides the slope of each line?

- - - - - - - - - - - - - -

The intersection of each line with the y axis. (K)

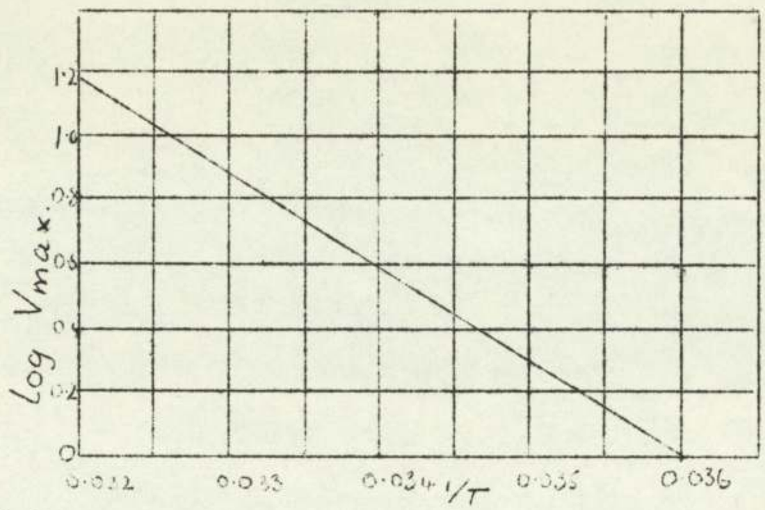
3-9 What empirical relationship appears to hold between $\log V_{max}$ and the absolute temperature?

- - - - - - - - - - - - - -

$\log V_{max} = K - E/T$

3-10 The following graph shows how the hydrolysis of adenosine triphosphate by myosin varies with the temperature.

3-10(cont).



(a) What happens to $\log V_{max}$ as the temperature increases?
(b) What happens to the slope E as the temperature increases?

- - - - - - - - - - - - - - - -

(a) $\log V_{max}$ increases (b) E remains constant.

Ex2·3 R(Where E is the slope obtained when $\log V_{max}$ is plotted against 1/T and R is the universal gas constant) equals the Activation Energy. This activation energy is the minimum energy reacting molecules must have in order to form the products.

3-11 Having considered the process which is responsible for speeding up enzyme reactions when heat is applied, we now examine the opposite process which is serving to slow a reaction down when heat is applied.

The thermal inactivation of enzymes has been shown to be due to their protein nature. Enzyme inactivation by heat has been shown to be due to protein denaturation.

Let us briefly go on to consider the various thermodynamic parameters governing protein denaturation.

No response is needed here go on to frame 3-12.

3-12 A specified chemical system has a fixed heat content(H). When one system(reactants) is converted into another(products), the change in heat content(ΔH), is given by H(products)-H(reactants).

3-11(cont.)

Ifthe heat content of the products is less than that of the reactants i.e. ΔH is negative, the surplus energy is transferred from the system to the surroundings and the reaction is exothermic; conversely if the reaction is endothermic ΔH is positive.

The change from ordered to disordered energy in a system is represented by the change in free energy (ΔG). This is made up of two terms, ΔH which measures change from ordered energy inside the system to disordered heat energy given to the surroundings and $T\Delta S$ which measures change in disordered energy inside the system, where T is temperature in °K and ΔS is the increase in entropy or disorder inside the system resulting from changes in molecular structure.

The terms are cnnected by the equation

$$\Delta G = \Delta H - T\Delta S$$

and a negative value for ΔG indicates that the reaction can theoretically take place spontaneously.

In the case of heat inactivation of enzymes the reaction is endothermic(ie. ΔH is positive) but there is a large accompanying increase in entropy (i.e. ΔS is positive). This means that even at relatively low temperatures ΔG is negative and hence the reaction is spontaneous.

Which of the following reactions is spontaneous :

ReactionA ΔH= +ve. and ΔS = -ve.
ReactionB ΔH= -ve. and ΔS = +ve.

- - - - - - - - - - - - - -

Reaction B.

3-13 $\Delta G = \Delta H - T\Delta S$

For the action of pepsin on carbobenzoxy-l-glutamyl-l-tyrosyl methyl ester at 37°C(310°K) ΔH= +2400 cals/mole and ΔS = + 20·6 cals/deg/mole. What is the value of ΔG?

- - - - - - - - - - - - - - - - -

-3986 cals.

3-14 $\Delta G = \Delta H - T\Delta S$

In the reaction between the enzyme chymotrypsin and the substrate benzoyl-1-tyrosinamide at 40°C (313°K) ΔH = +14400 cal/mole and ΔS = + 438 cals/deg/mole. What is the value of ΔG?

- - - - - - - - - - - - - -

-122694 cals

3-15 $\Delta G = \Delta H - T\Delta S$

When urease acts on urea at a temperature of 25°C (298°K) ΔH is found to be + 3300cals /mole and ΔS is+13.3 cals/deg/mole. What is the value of ΔG?

- - - - - - - - - - - - - -

-663.4 cals

3-16 For the reaction between ribonuclease and ribonucleic acid at 25°C(298°K) ΔH = + 3710 cals/mole and ΔS =+110 cals/deg /mole. Find ΔG.

- - - - - - - - - - - - - -

-29070 cals

3-17 $\Delta G = \Delta H - T\Delta S$

In the reaction between trypsin and benzoyl-1-arginimide ΔH = +6800 cals/mole and ΔS =+213cals/deg/mole at a temperature of 25°C (298°K). What is the value of ΔG?

- - - - - - - - - - - - - -

-56674cals

3-18 $\Delta G = \Delta H - T\Delta S$

In the reaction where lactic dehydrogenase acts on lactic acid ΔH = + 800cals/mole and ΔS =+20 cals/deg/mole at a temperature of 37°C (310°K) Find ΔG

- - - - - - - - - - - - - -

-5400cals

3-19 What relationship appears to hold between the thermodynamic parameters ΔG, ΔH, and ΔS for the reaction in which enzymes are inactivated by heat?

- - - - - - - - - - - - - -

3-19(cont.)

In the case of heat inactivation of enzymes the reaction is endothermic(ie. Δ H Is positive) but there is a large accompanying increase in entropy (ie. Δ S is positive). This means that even at relatively low temperatures ΔG is negative and hence the reaction is spontaneous.

3-20 Whichof the following reactions do you think represents heat inactivation of an enzyme;

Reaction	ΔHcals	T°K	ΔScals/dg/mole
A	-1000	300	+ 24
B	+1000	300	+ 24
C	-1000	300	- 24
D	+1000	300	-24

- - - - - - - - - - - - - -

B

3-21 In this subsection we are going to examine the effect of varying the pH upon the velocity of enzyme reactions. Before doing this it will be necessary toreview a few basic concepts about pH. Acidity can be measured interms of hydrogen ion concentration H^+, in a solution. The concentration of H^+ is usually very small, thus to avoid the inconvenience of working with negative indices the pH scale has been devised, which defines pH as -log$[H^+]$ What would the pH of a solution be whose $[H^+] = 10^{-4}$gramions/litre?

- - - - - - - - - - - -

4

3-22 According to the Bronsted Lowery definition an acid is a substance which yields $H^+$and a base is a substance which accepts H^+.
Consider the system,

Conjugate acid $\rightleftharpoons$ Conjugate base + hydrogen ions

$$HA \rightleftharpoons A^- + H^+$$

3-22(cont.)

The equilibrium constant (K) for the reaction =

$$\frac{[\text{Conjugate base}^-][\text{H}^+]}{[\text{Conjugate acid}]}$$

like the hydrogen ion concentration K is usually very small so again the negative logarithm of K, referred to as pK , is taken

When the concentration of conjugate acid = concentration of conjugate base, pH = -logK

What is the pK expression for the following reaction

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

- - - - - - - - - - - - -

$$\frac{-\log[H^+][CH_3COO^-]}{[CH_3COOH]}$$

3-23 Here is the data from three separate experiments to determine the relationship beween pH and pK value. In the first experiment the pK value is given,can you predict what it will be for the second and third experiment?

Expt. 1

pH	[Conjugate acid] / [Conjugate base]
2	7
4	4
6	1
8	0·3
10	0·02

pK = 6

Expt. 2.

pH	[Conjugate acid] / [conjugate base]
3	5
5	2
7	1
9	0·5
11	0·1

Expt. 3.

pH	[Conjugate acid] / [conjugate base]
2·5	6
4·5	2
6·5	1
7·5	0·5
8·5	0·01

- - - - - - - - - - - - - - - - -

Expt. 2 pK = 7; Expt. 3 pk = 6·5.

3-24 What is the relationship between pH and pK value?

- - - - - - - - - - - - - - -

When the concentration of conjugate acid = concentration of conjugate base, pH = -logK

3-25 The concentration of the conjugate acid H_2PO_4 eqals the concentration of its conjugate base HPO_4 when the pH = 6. What is the pK value of the system

$$H_2PO_4^- \rightleftharpoons HPO_4^{-2} + H^+ \quad ?$$

- - - - - - - - - - - - - - -

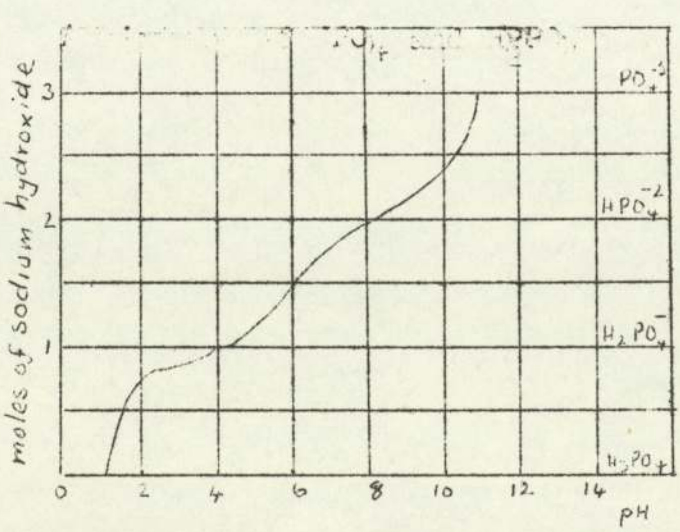
pK = 6

3-26 The curve below is called a titration curve. This particular curve shows the change in pH which is observed when 0·1 molar sodium hydroxide is titrated against 0·1 molar phosphoric acid at 25°C

When the first titration is complete H_3PO_4 has split completely into H^+ and $H_2PO_4^-$. When the second dissociation is complete $H_2PO_4^-$ has split completely into H^+ and HPO_4^{-2}. When the third dissociation is complete, HPO_4^{-2} has split completely into H^+ and PO_4^{-3}.

At a point half way between the pK values only one ionic form of a polyprotic weak acid exists in solution.

In the graph below what conjugate acid and base would you expect to find at pH 6, which is also the pK value?

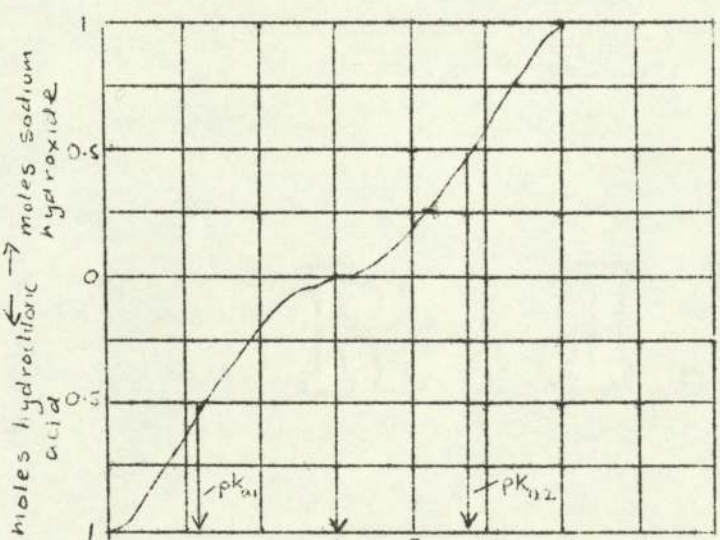


3-26(cont.)
A mixture of HPO_4^{-2} and $H_2PO_4^-$

3-27 The titration curve below shows the results obtained when 0·1 molar glycine is titrated against 0·1 molar hydrochloric acid and 0·1molar sodium hydroxide.

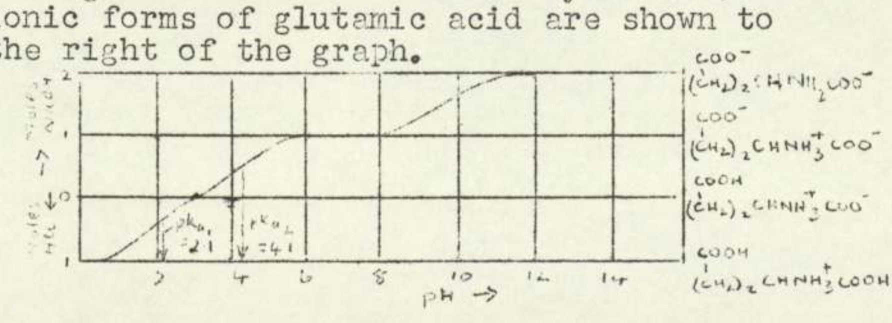
At pH = 2·4 ie. pK_{a_1} equimolar proportions of $CH_2NH_3^+$ (COOH) and $CH_2NH_3^+$ (COO$^-$) are present.

At pH = 9·8 ie. pK_{a_2} equimolar proportions of $CH_2NH_3^+$ (COO$^-$) and CH_2NH_2 (COO$^-$) are present. What would expect to find present at pH = 6 ?



$CH_2NH_3^+$
|
COO$^-$

3-28 The graph following shows the titration curve obtaied when 0·1 molar glutamic acid is titrated against 0·1 molar hydrochloric acid and against 0·1 molar sodium hydroxide. The ionic forms of glutamic acid are shown to the right of the graph.

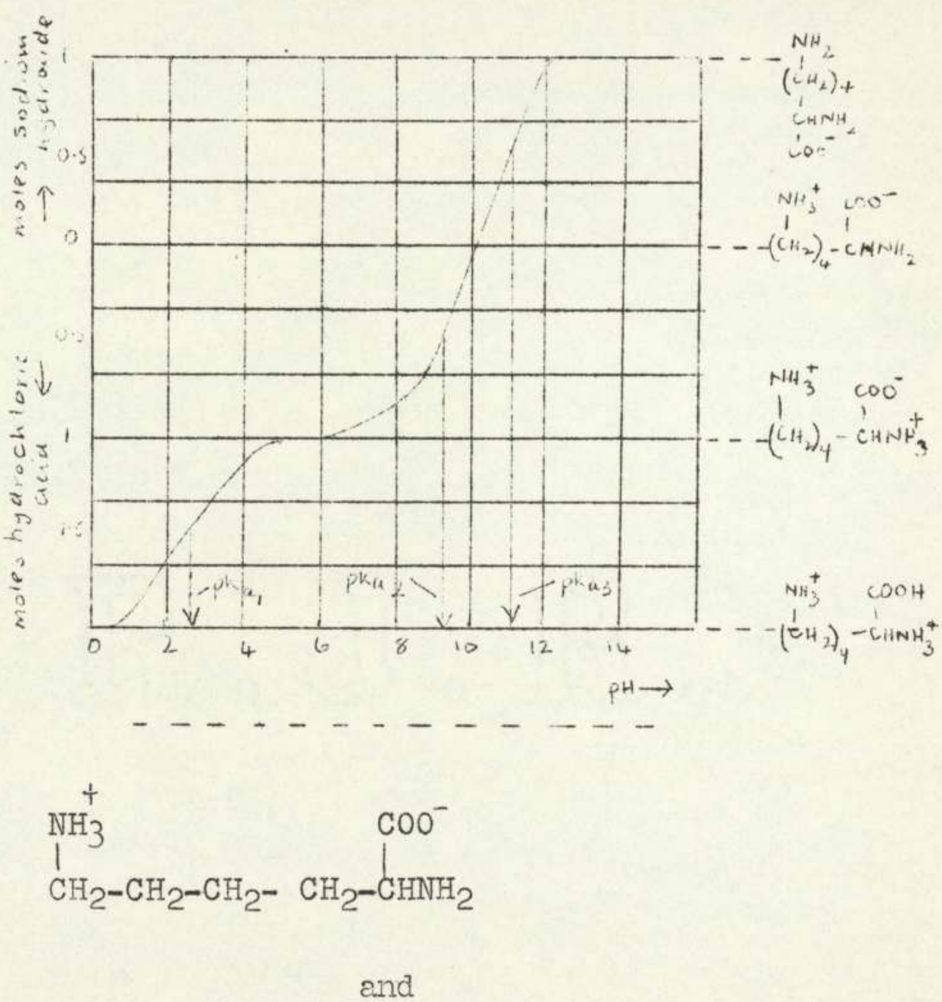


3-28(cont.)
What form would you expect to find present at pH = 3·1?

- - - - - - - - - - - - -

COOH
|
CH_2-CH_2- $CHNH_3^+COO^-$

3-29 Here is the titration curve obtained when 0·1 molar lysine is titrated against 0·1 molar hydrochloric acid and 0·1 molar sodium hydroxide. What forms are present at pK_{a_2}?



- - - - - - - - - - - - -

$\overset{+}{NH_3}$ ... COO^-
CH_2-CH_2-CH_2- CH_2-$CHNH_2$

and

$\overset{+}{NH_3}$ ... COO^-
CH_2-CH_2-CH_2-CH_2-$CHNH_3^+$

3-30 What is the principle that seems to govern the breakdown of a polyprotic weak acid?

- - - - - - - - - - -

At a point halfway between the pK values only one ionic form of a polyprotic weak acid exists in solution.

3-31 At pK = 4 $R - CHNH_3^+COOH$ and

$R - CHNH_3^+COO^-$ exist in solution and at pK = 8

$R - CHNH_3^+COO^-$ and

$R - CHNH_2COO^-$ exist in solution. What form(s) of the amino acid would you expect to find in solution at pH = 6?

(Assume that at each pK there are equal molar quantities of the appropriate ionic forms.)

- - - - - - - - - - - - -

$R - CHNH_3^+COO^-$ only.

3-32 In the following group of frames we are not going to concern ourselves with the irreversible effects of extremes of pH on protein structure of enzymes, or with effects of pH on ionization of substrate. We are only going to consider effects on binding of enzyme to substrate.

The effect of pH on the affinity of enzyme for substrate is readily eliminated by the use of substrate concentrations high enough to saturate the enzyme at all pH's being investigated. One major source of error in this work has been the assumption, usually without experimental verification, that a substrate concentration adequate to saturate an enzyme at one particular pH also does so at all other pH's.

By ensuring that the substrate concentration used is high enough to saturate the enzyme at all pH values listed, then the effect of pH on maximum velocity will be established.

3-32(cont.)
In the following frames these conditions are assumed to be operating, thus ensuring that all the enzyme will be in the form of enzyme substrate complex. Thus we shall be exam ining solely the effect of pH on the enzyme substrate complex.

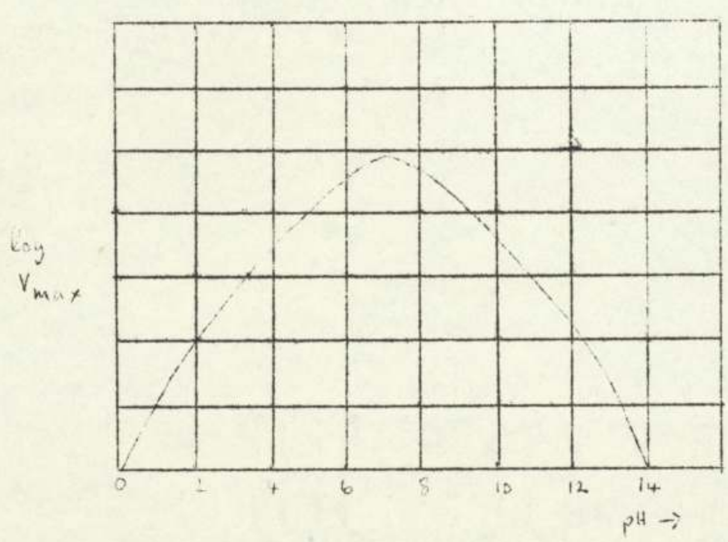
No response is required here, go to frame 3-33.

3-33 The bell-shaped curve shown below is a typical curve which is obtained by plotting the pH of an enzyme reaction against log V_{max}

The optimumpH is that which gives the greatest maximum velocity.

An enzyme has an potimum pH because only one ionic form of enzyme substrate complex breaks down into products, and this is mainly present at the optimum pH.

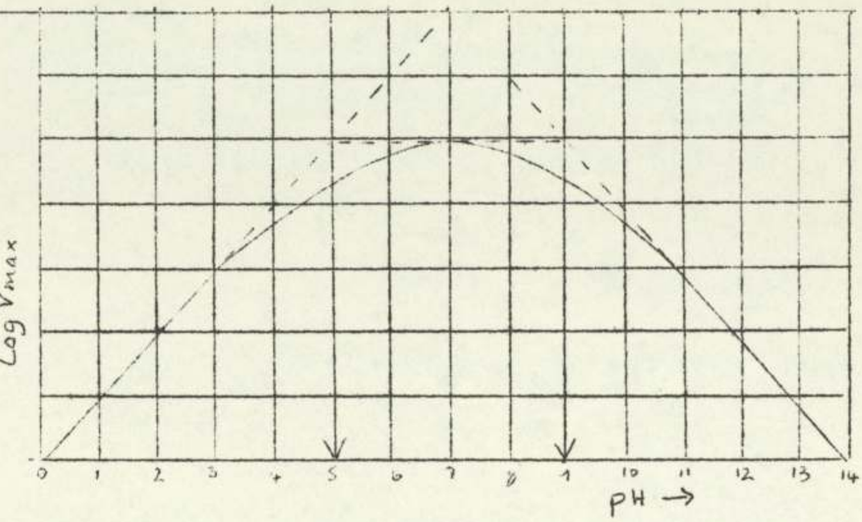
What is the optimum pH in the reaction given below which shows results obtained from the enzyme peroxidase on hydrogen peroxide.



- - - - - - - - - - -

pH = 7 optimum.

3-34 Dixon has shown that by extrapolation of linear portions of the curves to the point of intersection the two pK values can be ascertained. What are the two pK values inthe graph below?



- - - - - - - - - - - - -

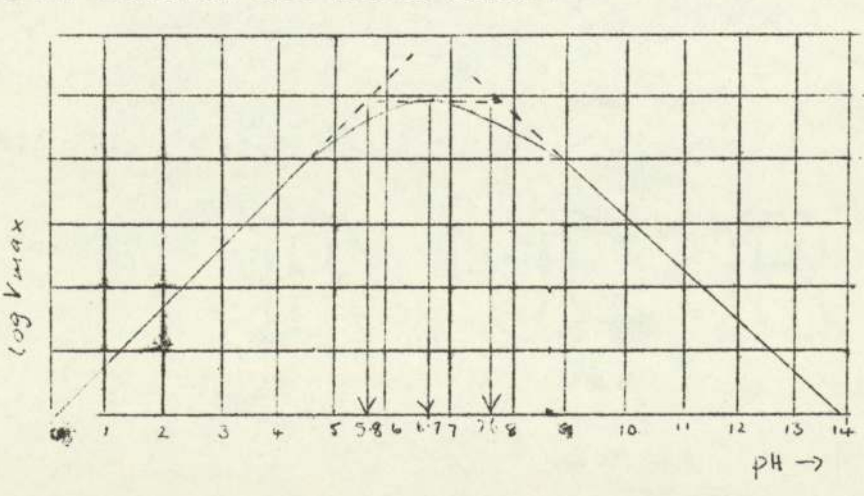
5 and 9

3-35 The optimum pH in frame 3-34 = 6·7 ie. $\frac{pk_1 + pk_2}{2}$. How many ionic forms ofthe enzyme substrate complex will be present at pH = 6·7 which gives the maximum velocity?

- - - - - - - - - - - - - - - -

1 ionic form.

3-36 Massey and Alberty have investigated the action of the enzyme fumarate hydratase on the substrate fumarate at a number of different pHs Their results are shown below.



3-36(cont.)

At what pH is the maximum velocity greatest? How does this relate to the pK values of the of the enzyme substrate complex?

- - - - - - - - - - -

V_{max} is greatest at pH 6·7. This is half way between the two pK values of the enzyme substrate complex.

3-37 Referringback to frame 3-36 determine how many forms of the enzyme substrate complex are present at pH 5·8, pH 6·7 and pH 7·6?

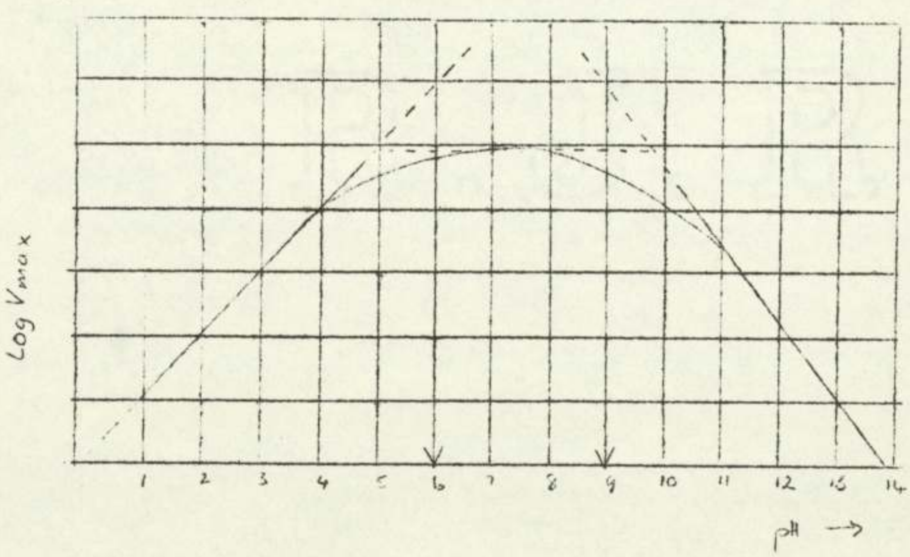
- - - - - - - - - - -

At pH 5·8 2forms of the enzyme substrate complex.

At pH 6·7 1 form of the enzyme substrate complex.

At pH 7·6 2 forms of the enzyme substrate complex.

3-38 The graph below was obtained by Laidler for the action of cholinesterase on acetyl choline. What is the optimum pH and how many forms of the enzyme substrate complex are present at this point?



3-38(cont.)

7.5 is the optimum pH, and only one form of enzyme-substrate complex is present at this point.

3-39 What principle do you think is responsible for causing an enzyme to exhibit an optimum velocity of reaction at a particular pH?

\- - - - - - - - - - - -

An enzyme has an optimum pH because only one ionic form of enzyme substrate complex breaks down into products, and this is mainly present at the optimum pH.

3-40 Alberty and Massey have suggested the following mechanism to explain the effects of pH on enzyme.

(1) Substrate + Enzyme + $2\overset{+}{H}$ ⇌ Enzyme Substrate ⇢ Products

⇅

(2) Substrate + Enzyme-H + $\overset{+}{H}$ ⇌ Enzyme-hydrogen-substrate ⇢ Products

⇅

(3) Substrate + Enzyme-H_2 ⇌ Enzyme 2hydrogen substrate ⇢ Products

Which of these enzyme substrate complexes would you expect to break down into products? 1,2,or 3?

\- - - - - - - - - -

2 Enzyme-hydrogen substrate.

Please complete the answer sheet for this section with all the information required.

PROGRAMME ANSWER SHEET

NAME ________________ Sex __________ College ____________
(Blokc Capitals)
Year ____________ Main Subject ____________

Notes 1. Use this answer sheet as a mask to cover up the answers to each frame.

2. Put a cross in each space corresponding to each response that you make incorrectly.

SECTION NUMBER 1

Starting time to nearest minute ________

1. ____
2. a. ___ b. ___ c. ____
3. ____
4. ____
5. a. ___ b. ____
6. no response
7. ____
8. ____
9. ____
10. a. __ b. ___ c. __
11. ____
12. i. ___ ii. ___ iii. __
13. ____
14. no response
15. ____
16. ____
17. a. _ b. __ c. __
18. ____
19. ____
20. a. ___ b. ___
21. ____
22. ____
23. ____
24. ____
25. a. __ b. ___
26. ____
27. ____
28. a. __ b. ___
29. ____
30. a. __ b. ___
31. a. ___ b. ____
32. a. ___ b. ___ c. __ d. ____
33. a. ___ b. ___ c. ___ d. ____
34. a. __ b. ___ c. ___ d. ____
35. ____
36. a. ___ b. ___ c. ____
37. ____
38. a. ___ b. ___ c. ____
39. ____
40. ____

P.T.O.

Number of minutes required to complete this section

Total number of incorrect responses in this section.

DO NOT BEGIN THE NEXT SECTION UNTIL YOU ARE ASKED TO DO SO.

SECTION NUMBER 2.

Starting time to nearest minute ________

1. ____

2. no response

3. ____

4. ____

5. ____

6. ____

7. ____

8. ____

9. ____

10. a. ____ b. ____ c. ____

11. ____

12. a ____ b. ____ c. ____

13. ____

14. ____

15. a. ____ b. ____ ____

16a. ____ b. ____ c. ____

17. a. ____ b. ____ . ____

18. ____

19. ____

20. a. ____ b. ____ c. ____

21. no response

22. a. ____ b. ____ c. ____

23. ____

24. ____

25. ____

26. ____

27. a ____ b. ____

28. a. ____ b. ____

29. ____

30. ____ (graph paper) provided.

31. ____

32. no response.

33. ____

34. ____

35. ____

36. ____

37. ____

38. ____

39. ____

40. a ____ b. ____ c. ____ (graph paper provided)

Number of minutes required to copmlete this section to the nearest minute. ____________

Total number of incorrect responses in this section. ____________

DO NOT BEGIN THE NEXT SECTION UNTIL YOU ARE ASKED TO DO SO

SECTION NUMBER 3.

Starting time to the nearest minute. ____________

1. no response

2. a.____ b.____

3. ____

4. ____

5. ____

6. ____

7. ____

8. ____

9. ____

10. a.____ b.____

11. no response

12. ____

13. ____

14. ____

15. ____

16. ____

17. ____

18. ____

19. ____

20. ____

21. ____

22. ____

23. a.____ b.____

24. ____

25. ____

26. ____

27. ____

28. ____

29. ____

30. ____

31. ____

32. no response

33. ____

34. ____

35. ____

36. a.____ b.____

37. a.____ b.____ c.____

38. ____

39. ____

40. ____

Number of minutes required to complete this section. (to the nearest minute)____________________

Total number of incorrect responses in this section. ________

Total number of minutes spent on the entire programme (to the nearest minute). ____________________

Total numberof incorrect responses made on the entire programme. ______________________

Appendix D

Pre and Post Tests

Marking Scheme

TEST ON ENZYME

KINETICS

Name ______________________ Time allowed:- 50 minutes.
(Block Capitals).

The test questions in this booklet are about Enzyme Kinetics. They are designed to test your knowledge of the principles of Enzyme Kinetics as taught in the programme and your ability to apply these principles to solve problems.

Please pay particular attention to the following points:-

1. Record all your answers on this answer booklet.

2. Do rough working on the plain paper provided.

3. Use pencil and rub out any answer you may subsequently wish to alter.

YOUR AIM SHOULD BE TO DO AS WELL AS YOU CAN.

PART 1.

Each of the sets of lettered subjects below is followed by a numbered list of phrases and statements. For each numbered phrase or statement insert the letter :-

A. if the phrase or statement is associated with A only.

B. if the phrase or statement is associated with B only.

C. if the phrase or statement is associated with A. and B.

D. if the phrase or statement is associated with neither A nor B

Example.

In an enzymatic reaction which follows the Michaelis Menten Model.

A = Competitive inhibition.

B = Non competitive inhibition.

C = Both.

D = Neither.

( ) 1. Requires that the inhibitor form a complex with the enzyme
(C goes here because both competitive and non competitive inhibitors form a complex with the enzyme).

( ) 2. The presence of an inhibitor decreases K_m.
(D goes here because neither competitive nor non competitive inhibitors decrease K_m)

( ) 3. The presence of an inhibitor decreases V_{max}.
(B goes here because only a non competitive inhibitor decreases V_{max}.)

( ) 4. In the presence of an inhibitor the Lineweaver - Burke plot will have the same intercept on the ordinate as that obtained in the absence of an inhibitor.
(A goes here because only a non competitive inhibitor alters the position of the intercept on the ordinate)

The following set of questions deal with an example reaction corresponding to the Michaelis Menten Model.

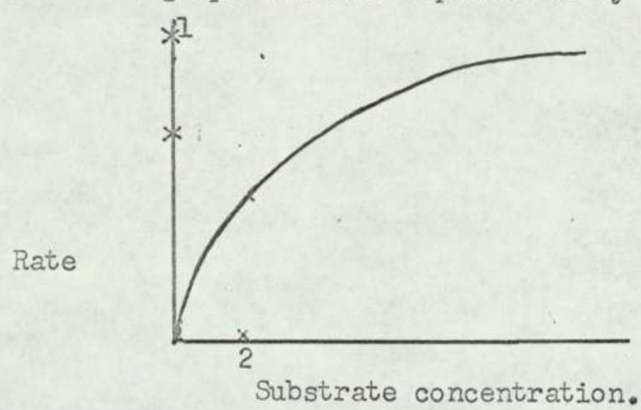
Enzyme + Substrate ⇌ Enzyme Substrate complex. ⇌ Enzyme + Product.

$$E + S \underset{K_{-1}}{\overset{K_{+1}}{\rightleftharpoons}} ES \xrightarrow{K_{+2}} E + P$$

A = K_m ; B = V_{max} ; C = Both ; D = Neither.

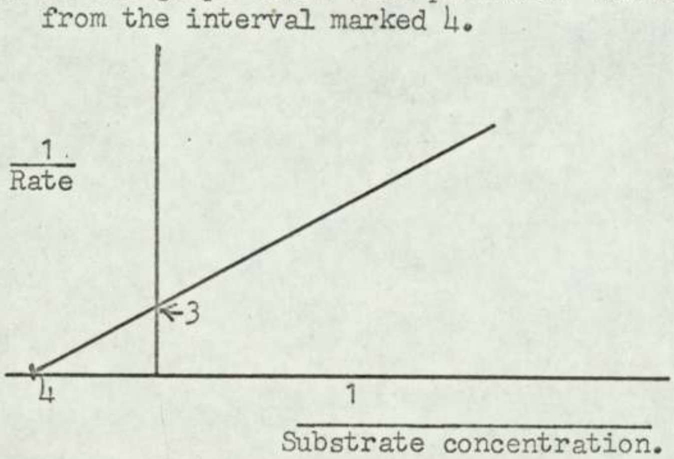
( ) 1. Measures the affinity of the substrate for the enzyme.

( ) 2. In the graph below is represented by point 1.



( ) 3. Is represented approximately by point 2, in the graph above.

( ) 4. In the graph below this parameter can be found from the interval marked 4.



( ) 5. This parameter can be found from the interval marked 3 in the graph above.

( ) 6. Equals k_{+2} $[ES]$

( ) 7. This parameter is $\frac{k_{-1}}{k_{+1}}$.

( ) 8. If the rate of an enzyme reaction is as tabulated below the value of the parameter is very near the value given by line a.

	Substrate Concentration	Rate
(a)	1 m.mole.	405 m.moles/min.
(b)	2 " "	533 " " "
(c)	5 " "	800 " " "

The following set of questions deal with the enzyme substrate system below.

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES \xrightarrow{k_{+2}} E + P$$

A. Will be true when the equilibrium assumption of Michaelis Menten applies.

B. Will be true when the steady state approximation of Briggs Haldane applies.

C. Will be true if either applies

D. Will not be true if either applies.

( ) 9. Velocity $= k_{+2} \ [ES]$

( ) 10. $K_m = \frac{k_{-1}}{k_{+1}}$

( ) 11. $\frac{d\,[ES]}{dt.} = 0$

( ) 12. $k_{+1} \ [ES] = k_{-1} \ [ES]$

( ) 13. Velocity $= \frac{V_{max} + [S]}{K_m \quad [S]}$

The next set of four questions deal with the effect of temperature on a enzymatic reaction.

A = V_{max} ; B = Denaturation ; C = Both ; D = Neither

( ) 14. Reaches a minimum at the optimum temperature.

( ) 15. Increases over the temperature range 15°C - 25°C.

( ) 16. Has a positively valued enthalpy (i.e. ΔH is + ve)

( ) 17. When this is plotted on a graph against $\frac{1}{\text{Temperature } (^\circ A)}$ a straight line with negative slope is obtained.

The last set of questions in this part of the test are about the role pH plays in enzymatic reaction.

A = optimum pH; B = pK ; C = Both ; D = neither.

( ) 18. Is altered by a change in hydrogen ion concentration

( ) 19. The maximum amount of one form of the enzyme substrate complex is present at this point

( ) 20. When the pH equals this value two forms of the enzyme are present in equal concentrations.

( ) 21. Only one ionic form of the enzyme is present when the hydrogen ion concentration is halfway between these two values.

( ) 22. It would be possible to find this variable from a graph in which V_{max} is plotted against pH.

PART 11.

Each of the questions in this part of the test consists of a stem and several alternative answers - only ONE of which is correct. Mark your choice on this test paper by underlining the appropriate answer.

Example.

The rate of an enzyme controlled reaction -

(a) increase at high temperatures.

(b) reaches a maximum at high substrate concentration

(c) is unaffected by very high pH.

(d) is not altered by inhibitors

(e) increases at very low pH.

underline (b) which is the correct answer

When working out your answers to this next set of questions assume that the equilibrium assumption of Michaelis Menten applies to the enzymatic model given on page 3 of this booklet.

(23) What is the concentration of the Enzyme Substrate complex ?

(a) $[E][S] \; k_{+1} . k_{-1}$

(b) $\frac{k_{+1}}{k-1} [E][S]$

(c) $k_{+1} [E][S]$

(d) $k_{-1} [E][S]$

(e) $\frac{k_{-1}}{k_{+1}} [E][S]$

(24) What is the velocity of the foward reaction ?

(a) $k_{-1}[ES] + k_{+2}[ES]$

(b) $k_{-1}[ES] - k_{+2}[ES]$

(c) $k_{+2}[ES]$

(d) $k_{+1}[ES] + k_{+2}[ES]$

(e) $k_{+1}[ES] + k_{-1}[ES]$

(25) What is the concentration of enzyme substrate complex in terms of the total amount of enzyme present ?

NB. Enzyme Total = Enzyme Free + Enzyme in complex.

$$[E_T] = [E_F] + [ES]$$

(a) $\frac{k_{-1}}{k_{+1}}\left([E_T] - [ES]\right)[S]$

(b) $K_m \div \left([E_T]\ [S]\right)$

(c) $K_m \div \left([E_T]\ [S]\right)$

(d) $[E_T][S] \div \left(\frac{k_{-1}}{k_{+1}} + [S]\right)$

(e) $K_m \div [E_T - E_F]$

(26) What is the maximum velocity for the forward reaction ?

(a) $k_{-1}[E_T][S] - k_{+1}[ES]$

(b) $k_{+2}[ES]$

(c) $k_{+2}[E_T]$

(d) $k_{+1}[ES] - [E_T][S]$

(e) $k_{-1}[E_T][S] + k_{+1}[ES]$

(27) What is the velocity of the forward reaction at a given substrate concentration in terms of the maximum velocity ?

(a) $k_{+2} \; [E_T][S] \div \left(K_m + [S]\right)$

(b) $[S] + \dfrac{k_{-1} + k_{+2}}{k_{+1}} \div \left(k_{+2}\,[E_T]\,[S]\right)$

(c) $\dfrac{k_{-1} + k_{+2}}{k_{+1}} \div \left(k_{+2}\;[E_T]\;[S]\right)$

(d) $\dfrac{k_{-1}}{k_{+1}} \; [E_T][S] \div [S]$

(e) $k_{+2} \; [E_T][S] \qquad [S] + \dfrac{k_{-1} + k_{+2}}{k_{+1}}$

(28) Which of the following expressions gives the velocity of an enzyme reaction at low substrate concentrations?

(a) $K_m \; [S]$

(b) $\dfrac{K_m + [S]}{V_{max}}$

(c) $\dfrac{K_m + [S]}{V_{max}[S]}$

(d) $V_{max} \; [S]$

(e) $\dfrac{V_{max} \; [S]}{K_m}$

(29) In a Lineweaver-Burke graph $\dfrac{1}{\text{velocity}}$ on the y axis is plotted against $\dfrac{1}{\text{Substrate concentration}}$ on the x axis.

In such a graph which of the following expressions would give k_{-1} for the enzyme reaction ?

(a) Slope x V_{max} x k_{+1}

(b) Slope x V_{max} x $\dfrac{k_{+1}}{k_{+2}}$

(c) $\dfrac{\text{Slope} \times k_{+2}}{V_{max} \times k_{+1}}$

(d) $\dfrac{V_{max} \times k_{+2}}{\text{Slope} \times k_{+1}}$

(e) $\dfrac{1}{\text{Slope}}$ x $\dfrac{\text{Substrate concentration}}{V_{max}}$

In working out your answers to the next 6-questions assume that the steady state assumption of Briggs-Haldane applies to the model given on page (3) of this booklet.

NB. E_T = total enzyme present - see page (8)

(30) What is the concentration of enzyme-substrate complex ?

(a) $k_{+1} [E_T] [S]$

(b) $\frac{k_{+1}}{k_{-1}} [E] [S]$

(c) $\frac{k_{+1} [E_T] [S]}{k_{+1}[S] + k_{-1} + k_{+2}}$

(d) $\frac{k_{-1}}{k_{+1}} [E] [S]$

(e) $\frac{k_{-1}}{k_{+1}} [E_T] [S]$

(31) What is the velocity of the forward reaction ?

(a) $k_{-1} [ES] - k_{+2} [ES]$

(b) $\frac{k_{+1} [E_T] [S]}{[S] + \frac{k_{-1} + k_{+2}}{k_{+1}}}$

(c) $k_{+1} [E] + k_{+2} [ES]$

(d) $\frac{k_{+2} [E_T] [S]}{[S] + \frac{k_{-1} + k_{+2}}{k_{+1}}}$

(e) $k_{+1} [E_T] - [ES] [S] + k_{-1} [ES] + k_{+2} [ES]$

(32) What is the rate of change in the concentration of the enzyme substrate complex ?

(a) 0

(b) $k_{+1} [E] [S]$

(c) $\frac{k_{+1} [E] [S]}{k_{-1} + k_{+2}}$

(d) $k_{+2} [ES]$

(e) $k_{+2} [ES] - k_{-1} [ES]$

(33) What is the maximum velocity of the forward reaction ?

(a) $k_{-1} \left[E_T\right] \left[S\right] - k_{+1} \left[ES\right]$

(b) $k_{+2} \left[ES\right]$

(c) $k_{+2} \left[E_T\right]$

(d) $k_{+1} \left[ES\right] - k_{-1} \left[E_T\right] \left[S\right]$

(e) $k_{-1} \left[E_T\right]\left[S\right] + k_{+1} \left[ES\right]$

(34) What is the velocity of the forward reaction at a given substrate concentration [S] ?

(a) $k_{+2} \left[E_T\right] \left[S\right] \div \left(\frac{k_{-1}}{k_{+1}} + \left[S\right]\right)$

(b) $k_{+2} \left[E_T\right] \left[S\right]$

(c) $\frac{k_{-1}}{k_{+1}} \left[E_T\right] \left[S\right] \div \left[S\right]$

(d) $\frac{k_{+1}}{k_{-1}} \left[E_T\right] \left[S\right]$

(e) $k_{+2} \left[E_T\right] \left[S\right] \div \left(\frac{k_{-1} + k_{+2}}{k_{+1}} + \left[S\right]\right)$

(35) In the Lineweaver - Burke graph $\frac{1}{\text{Velocity}}$ is plotted on the y axis and $\frac{1}{\text{Substrate Concentration}}$ on the x axis

(a) $\frac{\text{Slope}}{V_{max}} \times k_{+1}$

(b) $\text{Slope} \times V_{max} \times \frac{k_{+2}}{k_{+1}}$

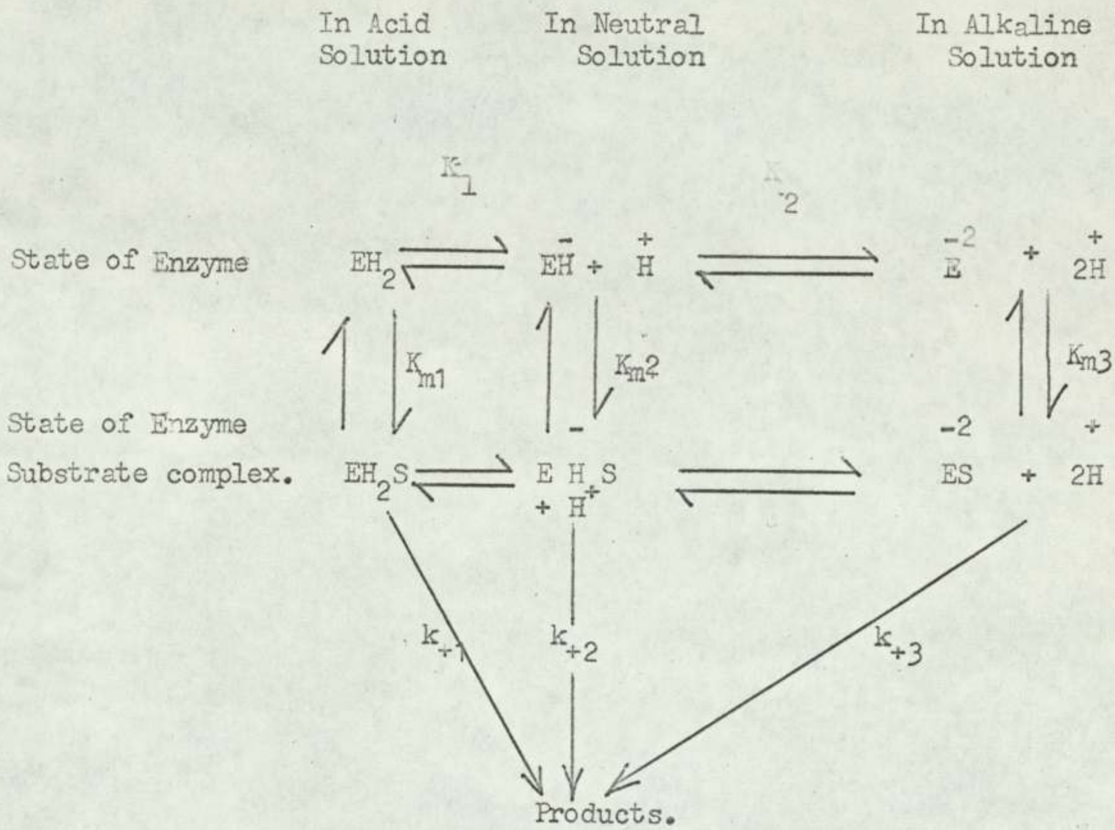
(c) $\frac{\text{Slope}}{V_{max}} \times \frac{k_{+1}}{k_{+2}}$

(d) $\frac{\left[S\right]}{\text{Slope } V_{max}}$

(e) $\text{Slope} \times V_{max} \times k_{+1}$

Which of the above expressions would give k_{-1} for the enzyme reaction?

The next three questions deal with the effect of pH on enzyme reactions. In answering the questions assume that the enzyme ionises as a dibasic acid i.e.



(36) $EH^- \rightleftharpoons E^{-2} + H^+$

The equilibrium constant for the above reaction is k_2 which of the following expressions gives the pH.

(a) $k_2 - \frac{\log [EH^-]}{[E^{-2}]}$

(b) $K_2 - \log \frac{[E^{-2}]}{[EH^-]}$

(c) $-pk + \log \frac{[E^{-2}]}{[EH^-]}$

(d) $k - \log [EH^-] - \log [E^{-2}]$

(e) $pk + \log \frac{[E^{-2}]}{[EH^-]}$

(37) What is the rate of breakdown of theenzyme substrate complex at the optimum pH.

(a) $k_{+2} \left(\left[\overset{-1}{EHS} \right] + \left[\overset{-2}{ES} \right] + \left[EH_2 . S \right] \right)$

(b) $k_{+2} \left[E \bar{H} S \right]$

(c) $k_{+3} \left[\overset{-2}{ES} \right] + k_{+1} \left[E\ H_2\ S \right]$

(d) $K_{m1} \left[EH_2\ S \right]$

(e) $K_{m3} \left[E^{-2} S \right]$

(38) What is the rate of breakdown in terms of the total enzyme present at a point halfway between the two pk values.

(a) $k_{+2} \left[E \bar{H} S \right| - \left(EH_2 + \overset{-2}{ES} \right) \right]$

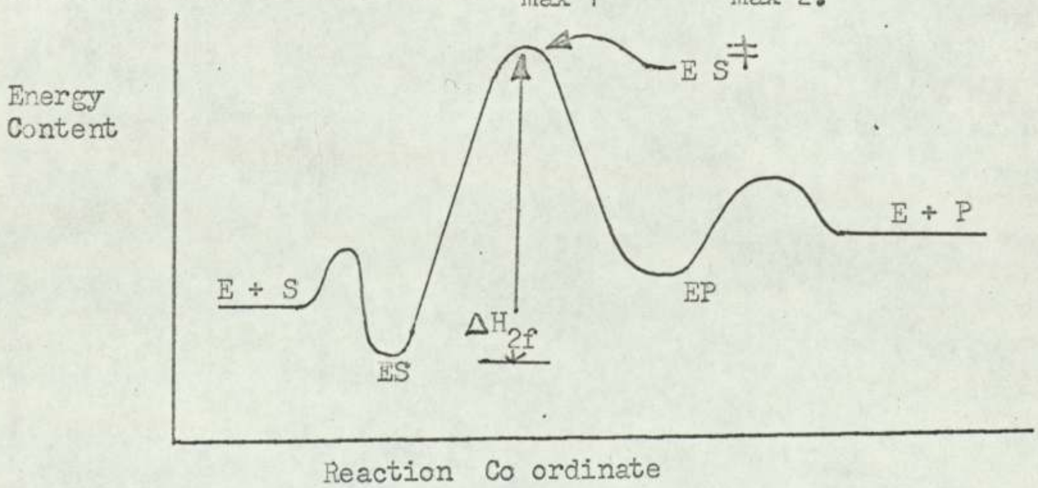
(b) $K_{m1} \left[E\ H_2 S \right] + K_{m3} \left[\overset{-2}{ES} \right]$

(c) $\left(k_{+1} + k_{+2} + k_{+3} \right) \left[\overline{EHS} + EH_2 + \overset{-2}{ES} \right]$

(d) $\frac{1}{2} \left(K_{m1} \left[\bar{E}\ \bar{H}\ S \right] + K_{m3} \left[\overset{-2}{ES} \right] \right)$

(e) $k_{+2} \left[E \bar{H} S \right]$

The last two questions deal with the effect of heat on the rate of enzyme reactions. In the following questions assume that the temperature is raised from T_1 to T_2 and that at these two temperatures the Michaelis Constant equals K_{m1} and K_{m2} respectively, and the maximum velocity equals $V_{max\ 1}$ and $V_{max\ 2}$.



The above energy profile shows the various energy barriers which the enzyme and substrate have to pass through in order to form enzyme and products. Each different energy complex is in equilibrium with the preceeding complex form, i.e.,

$$E + S \rightleftharpoons ES \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES^{\ddagger} \rightleftharpoons EP \rightleftharpoons E + P$$

(39) What is the heat of formation ΔH_{2F} of the activated form of the enzyme substrate complex ES

(a) $2.303 \log \frac{K_{m2}}{K_{m1}} \quad \frac{R\ T_2\ T_1}{(T_2 - T_1)}$

(b) $2.303 \log \frac{V_{max\ 1}}{V_{max\ 2}} \quad \frac{R\ T_1\ T_2}{(T_2 - T_1)}$

(c) $2.303 \log \frac{K_{m1}}{K_{m2}} \quad \frac{R\ T_2\ T_1}{(T_2 - T_1)}$

(d) $2.303 \log \frac{K_{m1}}{K_{m2}} \quad \frac{(T_2 - T_1)}{R\ T_2\ T_1}$

(e) $2.303 \log \frac{V_{max\ 2}}{V_{max\ 1}} \quad \frac{(T_2 - T_1)}{RT_1\ T_2}$

(40) The free energy ΔG for an equilibrium constant K is given by the expression $\Delta G = -2.303\ RT \log K$ What is the entropy for the formation of the activated form of the enzyme $ES^{\ddagger}$

(a) $\dfrac{-2.303\ R\ T \log \frac{k_{-1}}{k_{+1}} - \Delta H_{2f}}{T}$

(b) $\dfrac{-2.303\ R\ T \log \frac{k_{+1}}{k_{-1}} - \Delta H_{2f}}{T}$

(c) $-2.303\ R\ T \log \frac{k_{-1}}{k_{+1}} - \Delta H_{2f}$

(d) $-T\ 2.303\ R\ T \log \frac{k_{-1}}{k_{+1}} - \Delta H_{2f}$

(e) $\Delta H_{2f} - T\ 2.303\ R\ T \log \frac{1}{k_{+1}}$

MARKING SCHEME FOR THE PRE AND POST TESTS.

PART 1.

Question No.	Correct Response.	Question No.	Correct Response.
1	D	12	A
2	B	13	D
3	A	14	D
4	A	15	C
5	B	16	B
6	B	17	A
7	A	18	D
8	A	19	A
9	C	20	B
10	A	21	B
11	B	22	C

1-mark is given for each of the above correct responses making maximum total on this part of the best 22-marks.

PART 2.

Question No.	Alternative corresponding to correct application of 2-principles.	Alternative corresponding to correct application of 1-principle.
23	b	e
24	c	d
25	d	a
26	c	b
27	a	c
28	c	b
29	a	b
30	c	b
31	d	b
32	a	c
33	c	b

Question No.	Alternative corresponding to correct application of 2-principles.	Alternative corresponding to correct application of 1-principle.
34	c	a
35	b	e
36	e	c
37	a	b
38	e	a
39	b	c
40	b	a

2 - marks are given for the correct application of both principles one mark for the application of one principle. The total number of marks possible for this section of the test is 36.

APPENDIX E.

Test Anxiety Questionnaire

T.A.Q.

Name ______________ Sex ________ College ______________
(Block Capitals)

SECTION I

The following questions relate to your attitude towards and experience with group intelligence or aptitude tests. By group intelligence tests we refer to a test which is administered to several individuals at one time. This test contains different types oF items and are usually paper and pencil tests, with answers requiring fill ins or choice of several possible answers. Scores on these tests are given with reference to the standing of the individual within the group tested or within specific age and educational norms. Please try to remember how you usually reacted towards these tests and how you felt while taking them.

IN THE FOLLOWING QUESTIONNAIRE THE MIDPOINT IS ONLY FOR YOUR GUIDANCE. DO NOT HESITATE TO PUT A MARK AT ANY POINT ON THE SCALE AS LONG AS THAT MARK REPRESENTS THE STRENGTH OF YOUR FEELING OR ATTITUDE.

1 How valuable do you think group intelligence tests are in determining a persons ability?

Very valuable	Valuable in some respects valueless in others.	Valuless

2. Do you think that group intelligence tests should be used more widely than at present to classify students?

Should be used less widely	Should be used as at present	should be used more widely

3. Would you be willing to stake your continuance in college on the outcome of a group intelligence test which has previously predicted success in a fairly reliable fashion?

Very willing	Uncertain	not willing

4. If you knew that you are going to take a group intelligence test how do you feel beforehand?

Feel very unconfident	Midpoint	feel very confident

5. After you have taken a group intelligence test how confident do you feel that you have done your best?

Feel very unconfident	Midpoint	Feel very confident

6. When you are taking a group intelligence test to what extent do your emotional feelings interfere with or lower your performance?

Do not interfere at all	Midpoint	Interfere a great deal

7. Before taking a group intelligence test to what extent are you aware of an uneasy feeling ?

Am very much aware of it	Midpoint	Am not aware of it at all

8. While taking a group intelligence test to what extent do you experience accelerated heartbeat?

Heartbeat does not accelerate at all	Midpoint	Heartbeat noticeably accelerated

9. Before taking a group intelligence test to what extent do you experience an accelerated heartbeat?

Heartbeat does not acccelerate at all	Midpoint	Heartbeat noticeably accelerated

10. While taking a group intelligence test to what extent do you worry?

Worry a lot	Midpoint	Worry not at all

11. Before taking a group intelligence test to what extent do you worry?

Worry a lot	Midpoint	Worry not at all

12. While taking a group intelligence test to what extent do you perspire?

Perspire not at all	Midpoint	perspire a lot

13. Before taking a group intelligence test to what extent do you perspire?

Perspire not at all	Midpoint	perspire a lot

14. In comparison with other students how often do you think of avoiding a group intelligence test?

Less than other students	Midpoint	More than other students.

15. To what extent do you feel that your performance on the AH/5 Intelligence test was affected by your emotional feelings at the time?

Affected a great deal	Midpoint	Not affected at all

SECTION 11

The following questions relate to your attitude towards individual intelligence tests and your experience with them. By individual intelligence tests werefer to the tests which are administerednto one individual at a time by an examiner. These tests contain different types of item and thus present a variety of tasks. Those tasks can be both verbal and manipulative i.e. verbal or written answers to questions or manipulation of objects, such as involved in puzzles, form boards etc. Examples of tests of this type of test are the Stanford-Binet test and the WechslerBellevue test. Please try to remember how you have usually reacted to these tests or how you would expect to react to them.

16. Have you ever taken any individual intelligence tests?

YES NO

If the answer to the above question is yes, indicate in the following questions how youdo or did react to the individual intelligence tests. If your answer to the above question is no indicate in the following questions how you think you would react to or feel about individual intelligence tests.

17. When you are taking an individual intelligence test to what extent do (or would) your emotional feelings interfere with your performance?

Would not interfere with it at all	Midpoint	Would interfere a great deal

18. If you know that you are going to take an individual intelligence test, how do you feel (or expect that you would feel) beforehand?

Would feel very unconfident	Midpoint	Would feel very confident

19. While you are taking an indiviual intelligence test, how confident do you feel(or would you expect to feel) that you were doing your best?

Would feel very confident	Midpoint	Would feel very unconfident

20. After you have taken an individual intelligence test how confident do you feel (or expect that you would feel) that you have done your your best?

Would feel very unconfident	Midpoint	would feel very confident

21. Before taking an individual intelligence test to what estent are you (or would you be) aware of an "uneasy feeling"?

Am not aware of it at all	Midpoint	Am very mch aware of it

22. While taking an individual intelligence test to what extent do you(or would you) experience accelerated heart beat?

Heartbeat does not accelerate at all	Midpoint	Heart beat noticeably accelerated

23. Before taking an individual intelligence test to what extent do you (or would you) experience an accelerated heart beat?

Heart beat does not accelerate at all	Midpoint	Heart beat noticeably accelerated

24. While taking an individual intelligence test, to what extent do you(would you) worry?

Worry a lot	Midpoint	Worry not at all

25. Before taking an individual intelligence test to what extent do you (would you) worry?

Worry a lot	Midpoint	Worry not at all

26. While taking an individual intelligence test to what extent do you(would you) perspire?

Would never perspire	Midpoint	Would perspire a lot

27. Before taking an individual intelligence test to what extent do you (would You) perspire?

Would never perspire	Midpoint	Would perspire a lot

28. In comparison to other students, how often do you(would you) think of avoiding taking anindividual intelligence test?

More often than other students	Midpoint	less often than other students

SECTION 111

The following questions relate to your attitude and experience with course examinations. We refer to major examinations like end of the year exams and finals in all courses not specifically in any one course. Try to represent your usual feelings and attitudes towards these examinations in general not towards any specific examination you have taken. We realise that the comparative ease or difficulty ofa particular course and your attitude towards the subject matter of the course may influence yourattitude towards the examinations, however, we would like you to try to express your feelings towards course examinations generally. Remember that your answers to these questions will not be available at any time to any other person but the experimenter carrying out the research.

29. Before taking a course examination to what extent are you aware of an uneasy feeling?

Am not aware of it at all	Midpoint	Am very much aware of it

30. When taking a course examination to what extent do your emotional reactions interfere with or lower your performance?

Do not interfere a with it at all	Midpoint	Interfere a great deal

31. If you know that you are going to take a course examination, how do you feel beforehand?

Feel very unconfident	Midpoint	Feel very confident

32. After you have taken a course examination, how confident do you feel that you have done your best?

Feel very unconfident	Midpoint	Feel very confident

33. While taking a course examination to what extent do you experience accelerated heartbeat?

Heartbeat does not accelerate at all	Midpoint	Heartbeat noticeably accelerated

34. Before taking a course examination to what extent do you experience an accelerated heartbeat?

Heartbeat does not accelerate at all	Midpoint	Heartbeat noticeably accelerated

35. While taking a course examination to what extent do you worry?

Worry a lot	Midpoint	Worry not at all

36. Before taking a course examination to what extent do you worry?

Worry a lot — Midpoint — Worry not at all

37. While taking a course examination to what extent do you perspire?

Never perspire — Midpoint — Perspire a lot

38. Before taking a course examination to what extent do you perspire?

Never perspire — Midpoint — Perspire a lot

39. When in your opinion you feel well prepared for a course examination, hoe do you usually feel just before the examination?

Confident — Midpoint — Anxious

APPENDIX F

Bibliography

BIBLIOGRAPHY.

Atkinson, J.W. — *Motives in Fantasy Action and Society* Van Nostrand. 1958

Atkinson, J.W. and Litwin, G.H. — Achievement motive and test anxiety conceived as a motive to approach success and a motive to avoid failure. *J. Abnorm Soc. Psychol.* 60, 52 - 63 1960

Ausubel, D.P. — *The Psychology of Meaningful verbal Learning.* Grune and Stratton. 1963

Birney, R.C. Burdick, H. and Teevan, R.C. — *Fear of Failure* Van Nostrand- 1969

Bjerstedt, J.L. — Mapping the effect structure of Self instructional materials *Programmed Learning 2,* 99 - 109 1965

Bruner, J.S. Goodnow, J.J. and Austin, G.A. — *A study in Thinking* J. Wiley 1956

Carey, G.L. — Sex differences in problem solving performance as a function of attitude differences *J. Abnorm Soc. Psychol.* 55, 208 - 212 1957

Carrol, J. B. Words meanings and concepts
Harrard Educational Review 34, 178 - 202 1964

Corman, B. R. The effects of varying amounts and kinds of information as guidance in problem solving.
Pyschol. Monogr. 71 No.2. 1957

Craig, R. C. Directed versus independent discovery of established relations
J. Educ. Pyschol. 47 223 - 234 1956

Cronbach, L. J. The logic of Experiments of Discovery.
In Shulman, L. S. and Keislar, E.R. (eds)
Learning by Discovery Rand McNally 1966

Edwards, A.L. Experimental Design in Psychological Research
Holt Rinehart and Winston 1965

Elley, W. B. The role of errors in learning with feedback
British J. of Educ. Psychol. 36 296-300 1966

Evans, J. L., Homme, L. E. and Glaser, R. The ruleg system for the construction of verbal learning sequences
J. of Educ. Res 55 515 - 518 1962

Feather N.T. Persistence at a difficult task with alternative task of intermediate difficulty.
J. Abnorm. Soc. Psychol. 66 604 - 609 1963

Festinger, L.	A theoretical interpretation of shifts in level of aspiration *Psychol. Rev.* 49 235 - 250	1942
Gagne, R. M.	*The conditions of Learning* Holt, Rinehart and Winston	1965
Gagne , R.M.	Varieties of Learning and the Concept of Discovery in Shueman, L.S. and Keislar, E.R. (Eds) *Learning by Discovery*	1966
Gagne, R. M. (Ed)	*Learning and Individual Differences* Merrill Books.	1967
Gagne, R. M. and Brown, L.T.	Some factors in the programming of conceptual learning *J. Exp. Psychol.* 62. 4, 313-321	1961
Gagne, R.M. and Rowher, W. D.	Instructional Psychology *Ann Rev. Psych.* 20. 381 - 418	1969
Gagne, R.M. and Smith, E.C.	A study of the effects of verbalisation on problem solving. *J. Exp. Psychol.* 63 12 - 18	1962
Garai, J.E. and Scheinfeld, A.	Sex differences in mental and behavioural traits. *Genet. Psychol. Monogr.* 77 169 - 299	1968

Glaser, R. | *Teaching Machines and Programmed Learning* Volume 11. Data and Directions Dept. of Androvisual Instruction National Ed. Assoc. of United States. | 1965

Glaser, R. | Variables in Discovery Learning in Shulman, L. S. and Keislar, E.R. (eds) *Learning by Discovery* Rand McNally | 1966

Gronhund, | *Measurement and Evaluation in Teaching* Macmillan | 1967

Guthrie, J. T. | Expository instruction versus a discovery method. *J. Educ. Psychol.* 58, 45 - 49 | 1967

Haselrud, G. M. and Meyers, S. | The transfer value of given and individually derived principles. *J. Educ. Psychol.* 49, 293 - 298 | 1958

Hays, W.L. | *Statistics for Psycologists.* Holt, Rinehart and Winston | 1963

Heckhausen, H. | Achievement Motive Research Current problems and some contributions towards a general Theory of Motivation. *Nebraska Symposium on Motivation.* University of Nebraska Press 103-162 | 1968

Hedlund, J.L. — Construction and evaluation of an objective test of Achievement Imagery. Unpublished Doctoral Dissertation University of Iowa. 1953

Heidbreder, E. and Zimmerman, C. — The attainments of concepts. 1X Semantic efficiency and concept attainment J. Psychol. 40, 325 - 335 1955

Hendrix, G. — A new clue to transfer of training. Elem. Sch. J. 48. 197 - 208 1947

Hendrix, G. — Learning bu discovery. Math. Teacher 54 290 - 299 1961

Hilgard, E.R. Irvine, R.P., and Whipple, J. E. — Rotememorisation understanding and transfer. An extension of Katona's, card trick experiments. J. Exp. Psychol. 46, 288 -292 1953

Holland, J. G. — Research on programming veriables in Glaser (ed) Teaching Machines and Programmed Learning vol. 11. Data and Directions 1965

House, N.J. and Zeaman, D. — The relation of I.Q. and Learning in Gagne R.M. (ed) Learning and Individual Differences 1967

Hurley, J.R. Performance in verbal learning as a function of instructions and achievement imagery score. Unpublished Doctoral Dissertation State University of Iowa. 1953

Hurley, J.R. Achievement imagery and motivational instructions as determinants of verbal learning. J. Pers. 25. 274 - 282 1957

Johnson, R.A. The effect of Achievement imagery on maze learning performance. J. Pers. 24. 145 - 152 1955

Keislar, E.R. and Shurman, L.S. Learning by Discovery Rand McNally 1966

Kersh, B.Y. and Wittrock, M.C. Learning by discovery an interpretation of recent research. J. Teacher Educ. 13 461 - 468 1962

Kostick, M. M. A. A study of transfer. Sex Differences in the reasoning process. J. Educ. Psychol. 45 449 - 458 1954

Lewin, K. Dembo, Tamara, Festinger, L., and Sears, P.S. Level of aspiration in J.McV. Hunt (Ed) Personality and Behaviour Disorders vol. 1. Ronald. 1944

Lewis, D. G. _Experimental design in Education._ London University Press 1968

Maltzman, I. Eisman, E. and Brooks, L.O. Some relationships between methods of instruction, personality variables and problem solving behaviour. _J. Educ. Psycol._ 47, 71 - 78 1950

Mandler, G. and Sarason, S.B. A study of Anxiety and Learning. _J. Abnorm. Soc. Psychol._ 47, 166 - 173 1952

McClelland, D.C., Atkinson, J.W. Clark, R.A. and Lowell, E.L. _The Achievement Motive_ Appleton Century Crofts 1953

McClelland, D.C. Risk Taking in Children with high and low need for achievement In Atkinson, J.W. (Ed) _Motives in Fantasy Action and Society_ Van Nostrand 1958

Milton. T. Effect of Sex role identification on problem solving skill J. Abnorm. Soc. Psychol 55, 208 - 212 1957

Moulton, R. W. Notes for a projective measure for fear of failure In Atkinson, J.W. (Ed) *Motives in Fantasy Action and Society* Van Nostrand 1958

Murray, H.A. *Explorations in personality* Oxford University Press 1938

Russell, D.G. and Sarason, E.G. Test Anxiety, sex and experimental conditions in relation to anagram solution. *J. Pers Soc. Psycol.* 493 - 496 1965

Shadbott, D.R. Interaction of personality and other learner variables with strategies of teaching M. Ed. Thesis (Unpublished) University of Birmingham 1969

Sherriffs, A.C. and Boomers, D.S. Who is penalised by the penalty for guessing? *J. Educ. Psycol.* 45 81 - 90 1954

Spence, J.T. and Spence, K.W. The motivational components of Manifest Anxiety Drive, and Drive Stimuli in Spielberger, C.D.(Ed) *Anxiety and Behaviour* Academic Press 1966

Spielberger, C.D. (Ed) Anxiety and Behaviour
Academic Press 1966

Taylor, P.H. A study of the effects of instructions in a multiple choice mathematics test.
Brit. J. Educ. Psychol. 36 1 - 6. 1966

Williams, J.E. Effect on speed of performance of interference tendencies Achievement imagery and mode of inducing failure.
Unpublished Doctorial Dissertation
State University of Iowa 1954

Wittrock, M.C. Verbal stimuli in concept formation: learning by discovery
J. Educ. Psychol. 54 4 183 - 190 1963

Wittrock, M.C. The learning by discovery Hypotheses.
In Shulman, L.S. and Keislar, E.R. (Ed)
Learning By Discovery Rand McNally 1966