GROWTH RATE

OF

BARIUM CHROMATE CRYSTALS

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SUMMARY

The crystallisation of barium chromate was investigated with the objective of producing crystals of 10^{-4}m in size instead of the commercially available size of 2×10^{-6}m. This was achieved by the method of controlled homogeneous precipitation from solutions of low pH. However, this was not an optimum operation. Two basic requirements were established for the quantitative study of the kinetics of barium chromate crystallisation.

The first requirement was a knowledge of the overall solubility of barium chromate in acid solutions at different temperatures. The experimental results showed that it is possible to increase the overall solubility by ∿3 orders of magnitude to ∿20g/dm^3 of solution.

The second requirement was a knowledge of the concentration of (CrO_4^{2-}) ions in solution. A mathematical model was developed to predict this concentration. The results show that, although the overall solubility increased with a decrease in pH, the chromate ion concentration decreased by over an order of magnitude.

As part of the study the equilibrium constants for the reactions:

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

and

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} ,$$

were evaluated independently at different temperatures by spectrophotometry and applying a different mathematical approach from that published in the literature.

The work ended at this stage and although no quantitative crystallisation kinetics were carried out the feasibility of a method to produce the required size of barium chromate crystals was qualitatively demonstrated.

Key Words

Barium chromate.
Crystallisation.
Equilibrium.
Solubility.

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A	Concentration of $[H_2CrO_4^{2-}]$	M/dm^3
A_λ	Absorption of Light	
B	Concentration of $[HCrO_4^-]$	M/dm^3
C	Concentration of $[Cr_2O_7^{2-}]$	M/dm^3
C_i	Concentration of Species i	M/dm^3
C_T	Total concentration of $BaCrO_4$	M/dm^3
c	Concentration	M/dm^3
D	Concentration of $[CrO_4^{2-}]$	M/dm^3
d	Crystal size	m
E	Concentration of $[CrO_3Cl^-]$	M/dm^3
e_{11}	Coefficient of molar absorptivity of $[HCrO_4^-]$	dm^3/Mmm
e_{20}	Coefficient of molar absorptivity of $[Cr_2O_7^{2-}]$	dm^3/Mmm
$e_{\lambda x}$	Coefficient of molar absorptivity	dm^3/Mmm
F	Concentration of $[H_2Cr_2O_7]$	M/dm^3
f_i	Activity coefficient of species i	
f(d)	Frequency of (d)	
H	Hydrogen ion concentration	M/dm^3
I	Transmitted light intensity	
I_o	Incident light intensity	
K_i	Equilibrium constant for reaction i	
K_i^o	Thermodynamic equilibrium constants	
K_{sp}	Solubility product	$(M/dm^3)^2$
k	Crystallisation rate constant	
l	Path length of absorption cells	mm
M	Mass of materials weighed	g
N	Number of crystals/unit volume	dm^{-3}
n	Population density	dm^{-3}

Q	Rate of removal of crystal magma	$dm^3 s^{-1}$
R	Universal gas constant	
r	Crystal size	m
$\dot{r}$	Crystal growth rate	ms^{-1}
S	Solubility	M/dm^3
T	Absolute temperature	K
V	Volume	dm^3
Z_i	Charge an ionic species i	coulombs
$\alpha/2$	Mole fraction $[Cr_2O_7^{2-}]$	
β	Mole fraction of $BaCrO_4$ not ionised	
$\Delta\varepsilon_i$	Error in $e_{\lambda x}$	
ΔF^o	Free energy change	J
ΔH^o	Heat of reaction	J/ mole
λ	Wavelength	nm
λ_e	Equivalent conductance	mho
μ	ionic strength	M/dm^3
σ_{n-1}	Standard deviation	

CHAPTER 1

Introduction

Materials which have a reasonable solubility in a solvent (typically of the order of 0.1 mass fraction)are comparatively easy to convert into crystals of the order of 10^{-3}m in size. This is done principally either by cooling the solution or evaporating the solvent. However, materials having a very low solubility (typically of the order of 10^{-6} mass fraction), while they may be easily precipitated, often have a crystal size only of the order of 10^{-6}m. If these low solubility materials are to be produced with a crystal size of the order of 10^{-4}m or more, then specialised techniques must be used. Several such techniques are qualitatively recorded in the literature from as far back as the early 1930's. They are usually developed for the primary purpose of "coarsening" precipitates to aid quantitative analysis but as yet there seems to have been no large scale industrial application of them.

The particular system investigated in this work is that of barium chromate / water and the objective is to produce crystals of 10^{-4}m in size instead of the commercially available size of 2×10^{-6}m.

In order to study quantitiatively the kinetics of the crystal growth process the first requirement is a knowledge of the solubility of the substance under various conditions so that, together with the actual solution concentration, the driving force may be computed.

The second requirement is that the concentration of the crystallising species in the solution must be known. In order to calculate this for the barium chromate system it is necessary to know the equilibrium constants of the various complex equilibria in which the chromate ion takes part in solution.

The work reported here ended at this stage and although no quantitative crystallisation kinetics were carried out the feasibility of a method to produce the required size of barium chromate crystals was qualitatively demonstrated.

CHAPTER (2)

Literature Review on Barium Chromate ($BaCrO_4$)

2.0 Introduction

The literature concerning Barium chromate is reviewed from the point of view of its aqueous solubility and aspects related to the control of supersaturation, and the effects of temperature, pH and additives on the solubility. Also considered is the generation of CrO_4^{2-} and barium chromate crystal growth in aqueous solution.

2.1 Physical and Thermal Properties of Barium Chromate

Barium chromate is usually obtained as a pale yellow precipitate when a soluble barium salt is added to a solution of an alkali chromate (1).

At ambient temperature it has an orthorombic crystal structure of lattice dimensions (2, 3) $a_o = 9.103$, $b_o = 5.526$, and $c_o = 7.337$ (Å). The molecular weight is 253.33 (4). The crystal density at 15°C is 4.498 (g/cm^3)(4), and the Heat of Formation is -341.3 (kcal/mol)(5).

Barium chromate is reported to lose oxygen at 1000°C (6, 7) and the surface energy is reported to be 120 erg/cm^2 (8). The coefficient of thermal expansion of the lattice co-ordinates have been measured from ambient to 813°C as (9)

$$\alpha_a = 1.65 \times 10^{-5}$$

$$\alpha_b = 3.38 \times 10^{-5} \; (^\circ C^{-1})$$

$$\alpha_c = 2.04 \times 10^{-5}$$

The lattice dimensions at 20°C given by these authors are slightly larger than those given in (2) being

$$\left.\begin{array}{l} a = 9.105\ \text{Å} \\ b = 5.541\ \text{Å} \\ c = 7.343\ \text{Å} \end{array}\right\} \quad \pm\ 0.004\text{A}$$

No polymorphism or decomposition was found up to 813°C. When prepared from melts, the chromate has been found to be isomorphous with barium sulphate over the whole composition range. The lattice dimensions of the sulphate are some 2% smaller than for the chromate (10)

The heat of crystallisation of barium chromate has been experimentally determined (11) by isothermal calorimetry as - 6.4 ± 0.1 kcal/mole (exothermic) at 25°C and pH = 7 (assumed). This figure may not be reliable as the paper also gives data for strontium chromate which appears to be inconsistent in the use of the sign convention for heats of reaction. The figure has, however, been quoted in NTIS Catch Tables. (12) Assuming that the figure is correct and that the dissolution is endothermic then the solubility would be expected to increase with temperature by c a. 4% / K.

Barium dichromate does not crystallise out from solutions of barium and dichromate ions and is prepared either by heating moist barium with chromium trioxide,(1) or boiling barium chromate solution with a mixture of nitric and chromic acids. (16) The crystals are slender needles, and are decomposed by water to the chromate and chromic acid. (13) The dihydrate $BaCrO_4.2H_2O$ is obtained by evaporation of the acid solutions: it forms yellowish-brown rhombic crystals (1).

2.2 Solubility of Barium Chromate in Water

The published data on solubility of barium chromate in water are few and in poor agreement (see table 2.2). Most of those reported p.7 in the literature have been determined by direct or indirect conductivity methods. Waddle(14)studied the solubility of barium chromate in distilled water and various salt solutions at room temperature (assumed). He used a volumetric titration method to determine the chromate by the iodine released when adding potassium iodide to the saturated chromate solution. There is a query concerning the method of preparing the solutions in that they were prepared by washing freshly made $BaCrO_4$ with a constant volume of water and therefore there is the possibility that equilibrium was not reached. This gives rise to the conclusion that although the solubility he gives is approximately twice as great as that given by most other workers it is probably lower than the true solubility. The results of his work are given in table 2.1.

As seen from table 2.2 the solubility data are conflicting. Mellor (6) reports values 10^3 times larger than those given in table 2.2. for ambient temperatures. A clue to a possible cause of this conflicting data may be found in the book by Vogal (16) where it is indicated that the solubility of barium chromate increases considerably as the pH falls. The only data found showing the change of solubility of barium chromate with pH is in the work done by Osawa, (21) who gives the effect of acetic acid addition on the solubility as shown in table 2.3. The pH values for acetic acid have been interpolated from published data. (24) Also reported in the literature are data available in the International critical tables (22) which gives us the solubility of barium chromate in high acid concentration at 18°C and 37°C and these are shown in table 2.4. Although Gorden and Firshing (23) give no data, they indicate that there is a minimum value for solubility at about pH 5.7. Therefore, without indicating the pH at which the above values in table 2.2 were determined, it is difficult to consider them very reliable.

2.3 Chemistry of Cr^{+6} in Solution

In order to understand the solubility of barium chromate in

Table 2.1: Effect of various additives on the solubility on barium chromate in water at 20°C (14).

Solvent	Solubility (M/dm^3) x 10^6
Water	30.8
1% aqueous ammonium acetate	110.7
10% aqueous ammonium acetate	141.5
20% aqueous ammonium acetate	200.0
10% ammonium acetate + 10% acetic acid	346.6
10% aqueous ammonium nitrate	193.2
10% aqueous potassium nitrate	70.4
10% aqueous sodium chloride	94.5
1% aqueous acetic acid	436.4

pH

?

Table 2.1 Solubility of Barium Chromate in Water

Temperature °c	Solubility M/dm^3 x 10^6	References
0	7.9	15
0.88	8.1	26
10	11.05	15
16	13.4	3
20	14.6,30.8,39.8	15,14,18
25	11.5,15.0,12.6	17,16,1
	16.2	15
28	17.4	3
28.08	17.2	26
30	18.2	15
40	14.9	17
100	170.0	19

Table 2.3: Effect of Acetic Acid on the solubility of Barium Chromate (21).

Acetic Acid conc. $(M)/dm^3$	pH	Calculated $BaCrO_4$ Sol. (M/dm^3)	Experimental Solubility (M/dm^3)
0.0	7	1.42×10^{-5} 10^{-6}	- or 10^{-4}
0.06	3.02	1.27×10^{-4}	52.5×10^{-6}
0.12	2.88	1.87×10^{-4}	144×10^{-6}
0.18	2.78	-	160×10^{-6}
0.30	2.67	2.78×10^{-4}	220×10^{-6}
0.36	2.62	-	309×10^{-6}
0.48	2.55	-	288×10^{-6}
0.60	2.51	-	357×10^{-6}
2.40	2.20	8.01×10^{-4}	428×10^{-6}

Table 2.4: Effect of HCl concentration on the solubility of Barium Chromate (22).

18°C		37.1°C	
pH	[Cr] M/dm^3	pH	[Cr] M/dm^3
0.69	0.0251	1.0	0.0202
0.52	0.0355	0.69	0.0367
0.40	0.0443	0.52	0.0535
0.30	0.0548	0.40	0.0702
0.22	0.0662	0.30	0.0875

acid solutions it is necessary to know more about Cr^{+6} in solution.

Chromium (VI) does not give rise to the extensive and complex series of poly acids and anions characteristic of the somewhat less acidic oxides of V(V), Mo(VI) and W(VI). The reason for this is perhaps the greater extent of multiple bonding Cr = O for the smaller chromium ion. (25) The most common oxyacids(or anions) of major importance are those of the chromate and dichromate although trichromate ($Cr_3O_{10}^{2-}$) and tetrachromate ($Cr_4O_{13}^{2-}$) have been reported (25). The equilibria prevailing in acid aqueous chromium (VI) solutions have been investigated by various workers. As far back as 1888 Walden (26) and Oswald (27) using conductivity and freezing point measurements indicated that solutions of chromium trioxide contain mainly dichromate ions. Sherrill, (28) using freezing point depressions claimed the existence of the equilibrium:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad 2.1$$

Neuss and Rieman (29) postulated in addition to the above equilibrium the existence of the following equilibrium in the pH range 6.0 - 6.5:-

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad 2.2$$

Tong and King (30) stated that both undissociated chromic acid molecules and hydrogen dichromate ions are present at high $[H^+]$ values (from 0.277 - 1.0M)and hence the following equilibria prevail simultaneously with equilibrium. 2.2

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad 2.3$$

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^{2-} + H^+ \qquad 2.4$$

Sasaki (31) confirmed the possible existence of the above equilibria, but he found no conclusive evidence to confirm the existence of the undissociated dichromic acid ($H_2Cr_2O_7$) in the very highly acid media. Nevertheless, data on the dissociation constant of the dichromic acid molecule are quoted by Freiser and Fernando.(32)

Davies and Prue (33) and others (31, 34, 35, 36) stated that over the pH range 11 - 13 only the chromate ions exists, while Moore et al.(37) claim the value is as low as pH = 8.

It is believed that a number of acids form complexes with Cr^{+6} such as sulphuric acid to form $CrSO_7^{2-}$ (30, 38) and HCl to form CrO_3Cl^- (30, 38, 39, 40). Lee and Stewart (41) proposed that ions of the type CrO_3A^- do not exist in large amounts in concentrated acid solutions when the predominant Cr^{+6} species are the monomer but that the molecule $HCrO_3A$ does. The equilibrium being:

$$HCrO_4^- + H^+ + HA \rightleftharpoons HCrO_3A + H_2O \qquad 2.5$$

where $A = H_2PO_4^-,\ Cl^-,\ HSO_4^-,\ ClO_4^-,\ NO_3^-$ or OAc^-.

However, many investigaters (30, 31, 34, 38, 42) believe that perchloric acid ($HClO_4$) does not form any complexes with Cr^{+6}: Haight et al.(38) found no evidence of reaction of the nitrate or acetate ions with Cr^{+6} species.

Haight et al.(38) reported that Cr^{+6} is slowly changed to Cr^{+3} if the solutions contained more than 1.0 M perchloric acid. Lukkari (39) found this reduction both in the presence of hydrochloric acid and perchloric acid - sodium chloride solutions. He claimed that both hydrogen and chloride ions and light were found to promote the reduction.

It can be concluded that Cr^{+6} in acid aqueous solutions forms the following equilibria to a greater or lesser extent.

$$H_2CrO_4 \overset{K_1}{\rightleftharpoons} HCrO_4^- + H^+ \qquad 2.3$$

$$HCrO_4^- \overset{K_2}{\rightleftharpoons} CrO_4^{2-} + H^+ \qquad 2.2$$

$$2HCrO_4^- \overset{K_d}{\rightleftharpoons} Cr_2O_7^{2-} + H_2O \qquad 2.1$$

$$HCr_2O_7^- \quad \xrightleftharpoons{K_{d2}} \quad Cr_2O_7^{2-} + H^+ \qquad 2.4$$

$$H_2Cr_2O_7 \quad \xrightleftharpoons{K_{d1}} \quad HCr_2O_7^- + H^+ \qquad 2.6$$

In the presence of hydrochloric acid the following equilibrium can be considered in addition to the above.

$$HCrO_4^- + H^+ + Cl^- + \quad \xrightleftharpoons{K_c} \quad CrO_3Cl^- + H_2O \qquad 2.7$$

The published equilibrium constants for these reactions have been tabulated in table 6.1. The original data have been extrapolated to zero ionic strength for comparison purposes. The extrapolation was done on the basis of the equations given in appendix 2. p.55

The equilibrium constants from the above equilibria can be presented mathematically as follows:-

$$K_1^o = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]} \quad \frac{f_1 \; f_2}{f_3} \qquad 2.8$$

$$K_2^o = \frac{[CrO_4^{2-}][H^+]}{[HCrO_4^-]} \quad \frac{f_4 \; f_2}{f_1} \qquad 2.9$$

$$K_d^o = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} \quad \frac{f_5}{f_1^2} \qquad 2.10$$

$$K_{d1}^o = \frac{[HCr_2O_7^-][H^+]}{[H_2Cr_2O_7]} \quad \frac{f_6 \; f_2}{f_7} \qquad 2.11$$

$$K_{d2}^o = \frac{[Cr_2O_7^{2-}][H^+]}{[HCr_2O_7^{2-}]} \quad \frac{f_5 \; f_2}{f_7} \qquad 2.12$$

$$K_c^o = \frac{[CrO_3Cl]}{[HCrO_4^-][H^+][Cl^-]} \quad \frac{f_3}{f_1 f_2 f_9} \qquad 2.13$$

Where f_i is the activity coefficient of the species i.

2.4 Crystal Growth Rate of Barium Chromate

The literature on the growth of barium chromate crystals from aqueous solutions is sparce and somewhat inconsistent. Bindra (43) has used the precipitation and growth method of Nielson (98) to investigate the growth kinetics of $BaCrO_4$ in neutral solutions at 20 and 25°C. The final crystal size was c a. $5\mu m$ and during the course of a test, growth rates changed by an order of magnitude from c a. 0 . 01 $\mu m/s$ at $\Delta c = 0.2\ mM/dm^3$ to 0.001 $\mu m/s$ at $\Delta c = 0.06\ mM/dm^3$. The most reproducible tests at 20°C could be corredted by an equation of the form

$$dr/dt = k(\Delta c)^n \qquad 2.14$$

where $k = 0.080 \pm 0.018$ m/s and $n = 1.15 \pm 0.09$. At 25°C the results were less reproducible and it was found that $100<k<1500$ and $2<n<3$. Induction periods were found to be c a. 100s at 25°C and 50s at 20°C.

Packter (20) studied the crystallisation rates of barium chromate and other sparingly soluble salts at 20°C. The approach was from the point of view of analytical chemistry and the methods of presenting the results did not readily permit extraction of linear growth rate data. However, based on some assumptions the growth rate varied from $dr/dt = 0.002$ m/s at $\Delta c = 0.00077\ mole/dm^3$ to 0.0054 m/s at $\Delta c = 0.00184\ mole/dm^3$ when the rate of development of the solution concentration $R = 0.33 \times 10^{-6}\ mole/dm^3\ s$ and $n \approx 2.0$ (Eqn 2.14).

Using a similar technique to Bindra the work of Rychly (73) has shown that the growth rate of barium chromate crystals falls as they increase in size, other things being equal, which is contrary to expectations for a process controlled by surface kinetics. Crystals up to 10 μ m were obtained, $k \approx 0.02$ and $n \approx 1.4$ (eqn. 2.14).

Benez (102) found that the kinetics of precipitation of barium chromate are considerably affected by temperature when precipitating using EDTA as a complexing agents.

Rychly (73) claims that it is not advantageous to work in acidic solutions while Lewin et al (103) found that in solutions of high acid concentration crystals of strontium sulphate were about 200 times larger than those grown in neutral solutions. Bindra found that an increase in ionic strength increased the growth rate.

CHAPTER 3

Literature Review of Solubility Measurements

3.1 The Phenomena of Solution

The solubility of a solid in liquid depends on the difference between the energy used in separating the ions or molecules from the crystal lattice and the energy used in the solvation of these ions or molecules.

In an ionic solid this energy is due to the interionic forces which favour the retention of ions in the crystal lattice. The solvation energy (hydration energy in aqueous solutions) is due to the attraction between the ions or molecules and the solvent molecules, whose job is to aid the separation of the ions or molecules of the solid from the solid. The power of a solvent is dependent on the dielectric constant of the liquid. Water which has a high dielectric constant is a very suitable solvent for most ionic salts. Figure 3.1 shows a schematic diagram of the dissolution of an ionic crystal.

With many electrolytes, the lattice energy is greater than the hydration energy so that the dissociation of the electrolytes is generally an endothermic process. Hence, the solubility of most solids in water increases with increase of temperature of the system. Other factors, such as the nature of the bonding between adjacent particles in the crystals, the characteristic of particular lattice geometries and the cation-anion ratios involved, also affect the solubility of ionic substances in water in ways that are difficult to estimate. In the absence of simple principles to predict the solubility, experimental determinations must be employed.

3.2 Experimental Determination of Solubility

Before carrying out any study of the solubility of any compound it is necessary to determine the technique by which the solubility is to be measured and the time taken for an equilibrium to be reached.

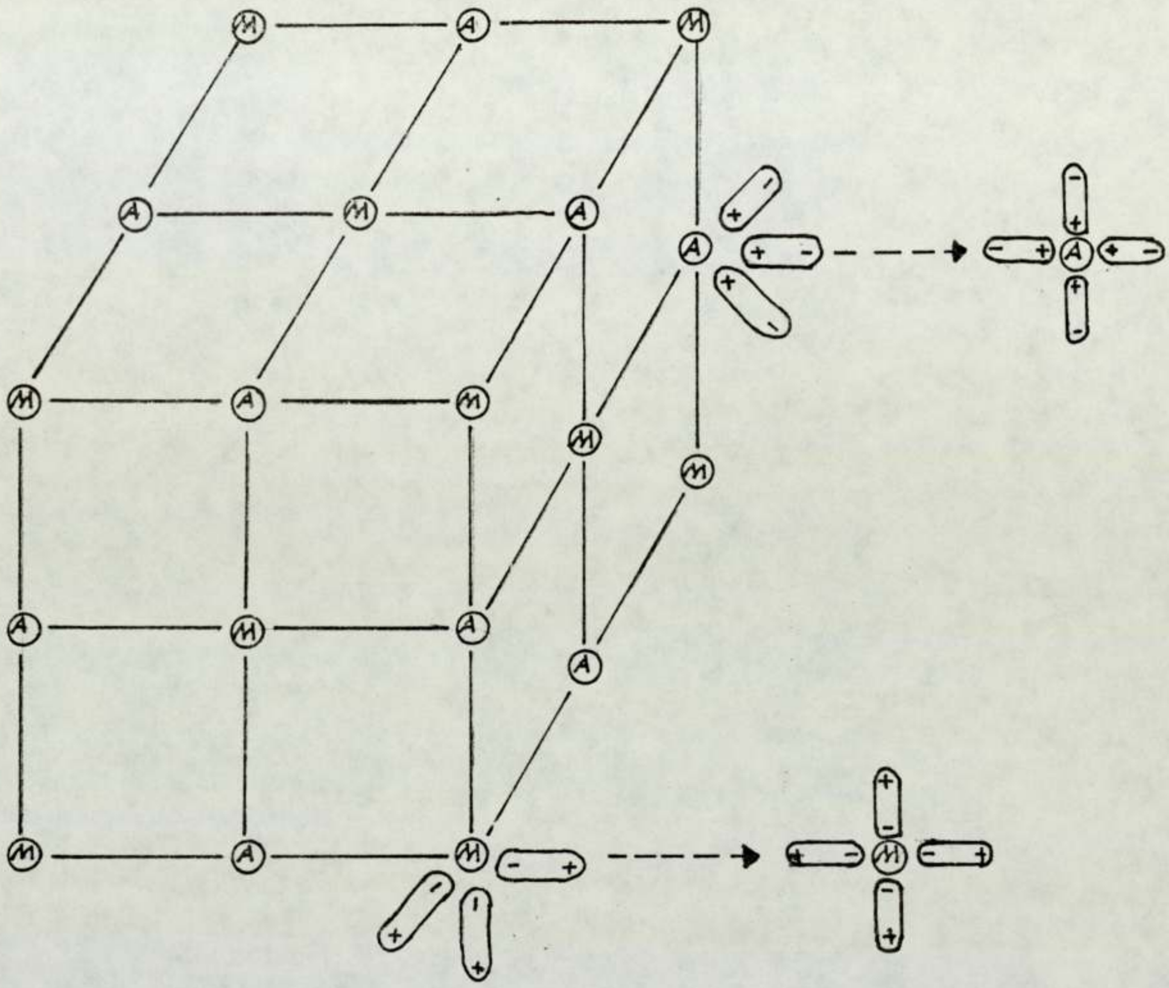

FIGURE 3.1: solubilisation of an ionic salt

Owing to the low concentrations involved, in the study of the solubility of barium chromate a very sensitive analytical method is required and many factors have to be considered. Zimmerman (48) in a general review states that among the foremost of these factors is the purity of the materials used. Kolthoff (49) attributes the variation in published values of the solubility data of metallic sulphides, (which covers 10 orders of magnitude) to be due to the presence of CO_2 and O_2 impurities when using the conductivity method. Morimoto (50) found that the electrokinetic potential of low solubility salts is affected by the method of precipitating these salts. He found for barium chromate in excess of $BaCl_2$ the electrokinetic potential is + 10.2 mV, while when an excess of K_2CrO_4 was used the electrokinetic potential is - 7.75 mV. He attributes this to the absorption of the excess CrO_4^{2-} ions into the surface lattice of the crystals.

Secondly, another important factor is whether the system studied has reached equilibrium. Anderson et al. (51) found that the published data on the solubility of arsenic trioxide were conflicting, and attributed this to the fact that the equilibrium is reached very slowly. In fact, they found that it took some 48 hours for equilibrium to be established at a temperature of 100°C and up to 2 weeks at a temperature of 0°C. Friend (52) found that when studying the solubility of Neodynium sulphate he could not get reproducible results. He overcame this by checking the samples until the system reached equilibrium. This took some 24 hours of vigorous stirring. Zimmerman also states that to avoid problems of supersaturation it is important to have the system kept seeded with traces of the solute. In studying the solubility of silver nitrite Creighton and Ward (56) found it necessary to keep the system well agitated with excess solid for up to 14 hours when the temperature was below 40°C and for several hours when the temperature was above this value.

A third consideration is the precise control of temperature. Zimmerman (48) states that it is frequently not sufficient to know the temperature at any one instant but that precise control and measurement must be carried out throughout the entire period of equilibration.

Fourthly, in the presence of more than one solid phase, Herriot (57) showed that there is a possibility that the solubility may not be constant (such as is in the case of the study of the solubility of proteins). However, as barium chromate has only one component in the solid phase this effect is not relevant.

Finally, the inertness of the vessel and equipment used must be considered. In the study of the solubility of sodium carbonate at high temperatures, Waldeck et al.(58) found that their system was being contaminated by a yellow colouring which they showed to be due to the formation of sodium chromate from the stainless steel vessel. Also, Harkins (59) found that when studying the solubility of silver sulphate a slight darkening occurred on exposure to light and the solubility increased. Therefore, he had to ensure that the solutions were kept in the dark.

3.3 Methods of Measuring Solubility

These can be split into two categories: Those methods which involve the removal of a sample for analysis and can be called "analytic" methods and those where no samples are removed and can be called "isosystic". (48)

3.3.1 Sampling

The primary consideration in these methods is to obtain a sample which reflects the true equilibrium composition. There are three methods of obtaining samples of a saturated solution free of solid phase:-

a) filtration of a hetrogeneous saturated suspension, or

b) settling and decantation, or

c) percolation of solvent through a confined portion of solute. all describ

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3.3.1.1 Filtration

This is the most widely used method for the separation of phases in solubility studies. There are many types of filter materials used depending on the fineness of the solids and chemical inertness towards the system under study.

Cloth fabrics (60) cotton wool and asbestos (62, 63, 64, 65) have been used in various forms of sampling apparatus. Harkins (64) found that he needed to reject the first 50cc of his filtrate to avoid errors of absorption when using cotton wool while Noyes et al.(61) and Robinson (60) found it necessary to soak their filters in saturated solutions first.

This precaution was not found necessary with the commonly used packed glass wool. (56, 66, 67, 68, 53). Parks and Campanella found that glass wool was more suitable than chamois leather or Jena glass crucibles, because it was more rapid. Sintered glass filters (69, 54) have also been used successfully.

3.3.1.2 Decantation

Separation of the phases by decantation is useful when the saturated solution is sufficiently fluid and the solid phase is sufficiently granular to allow it to settle readily and various suitable equipment is described in the literature (48, 70, 71). The basic problem with decantation is that there is always a possibility of very fine particles not settling out or even being disturbed when sampling begins. The improvement of decantation by centrifuging has been suggested, (57, 72) but King (72) found that even 15 minutes at a speed of 3500 r.p.m. did not completely settle particles below 10 μm. This suggests that this procedure is not suitable for the work with barium chromate which has an average particle size of 2 μm.

3.4 Analysis of Samples

Once a sample is obtained there are various methods for analysing the concentration of solute in the sample. These are:-

3.4.1. Residue Weight

This is the simplest and most straight forward method. It consists of evaporating a sample to dryness to find the amount of solute in solution. (74, 75, 76) However, this method is not very useful when the solubility to be measured is low such as in the case of barium chromate where the amount of solute is too small to be measured accurately unless very large quantities of solution are used. There is also the risk that a residue other than barium chromate may be obtained at low pH values.

3.4.2 Chemical Analysis

In this case the amount of solute in a known volume (or mass) of sample solution is estimated by some means.

The actual technique used will depend on the chemical nature of the solute and the analytical equipment available. A number of methods have been used for the study of solubility of slightly soluble salts. [e.g titration with alkali (78, 79) iodometry for the study of the solubility of iodine (80), and precipitation (77)].

Seward and Schumb (77) determined the solubility of barium nitrate by weighing as barium sulphate. However, they found that due to the very low solubility of the nitrate (40 g/dm^3) and consequent small weight of barium sulphate, the results contained a considerable error.

Purdum and Rutherford (81) studied the solubility of lead sulphate by mixing excess lead sulphate in 5 gallon pyrex bottles and then removing 6 litres of samples. These were evaporated in the acid media and the lead precipitated as lead chromate by titrating with potassium dichromate. However, no account of the solubility of the lead chromate had been considered and it would be interesting to see if these authors obtained a different answer had they neutralised the system (since a potassium dichromate solution is also slightly acidic).

It is therefore concluded that although chemical analysis can be used to determine the solubility of slightly soluble compounds it gives rise to inaccuracies.

3.4.3 Electrical Methods

The two most common electrical methods for measuring concentration of electrolytes involve the measurement of the electromotive force and the conductivity. Both these methods depend on the presence of ions of the dissolved substances and are very useful in the study of the solubility of slightly soluble salts where analytical procedures are of doubtful accuracy. (83, 84) These methods also have the advantage that the equipment is very simple.

Kolthoff (49) discussed the work done on the solubility of a number of metallic sulphides with solubilities in the range 10^{-5} to 10^{-20} M/dm^3. He found that great inaccuracies arose with the use of conductivity methods as in many cases the conductivity of impurities swamped that due to the salt in question. Zimmerman (48) states that this method is extremely sensitive to conducting impurities and that their contribution must be known as accurately as possible. Glasstone and Lewis (82) stated that if a sparingly soluble electrolyte ionises in a simple manner, it is possible to calculate the solubility from conductance measurements. However, no mention is made of the case when the ionisation is as complex as in the case of barium chromate.

Zimmerman (48) states that the maximum errors encountered in the use of electromotive methods are only 3.7% for bivalent metallic salts, while the errors of the conductivity method depend on the order of magnitude of the solubility. If the solubility is 10^{-5} mole/dm^3 or less the error could be about 10%. The use of the electromotive method is limited to the availability of suitable electrochemical couples for a particular investigation. With non isosystic analysis these errors could be compounded with sampling errors. It is considered that with the great number of different ions involved in the acid barium chromate system that the above electrical methods are perhaps not the most suitable.

3.4.4 Optical Methods

Spectrophotometry is a very quick and convenient method for measuring concentrations, so long as the solutions under study obey Beer's Law in the range of concentration concerned (48, 85, 86, 89). This method relies on the plot of a calibration curve, which in dilute solutions gives a straight line, according to Beer's Law, which states ~~that~~ "the light absorbed by a solution is directly proportional to the concentration of the solution". Mathematically it can be written as:

$$A = ecl$$

where A = the light absorbed
e = coefficient of molar absorptivity
c = concentration of the material studied
l = path length.

This method has the advantage that it is very sensitive to the solution being studied and can also be applied over a wide range of concentrations using a single calibration curve (87). It also has the advantage that even if there are more than one species their concentrations can be determined separately provided a wavelength is found at which only one substance absorbs light (88).

This method has been used in the study of the solubility of silica by converting the silica to silica-molybdic acid and measuring the intensity of the absorbance (72). Gayer and Garrett (54) studied the effect of the pH and pOH on the solubility of $Co(OH)_2$, which has a solubility of about 10^{-5} M/dm^3. Using spectrophotometry to analyse the Co^{2+} concentration they found that the analysis was reproducible to ± 2%. However, they found that with water as solvent the results were not reproducible due to the collodial nature of highly purified samples of cobalt hyroxide. Richardson et al.(55) used colour comparison to determine the concentrations of CrO_4^{2-} in solutions and achieved an accuracy of 4% with the eye in daylight. However, Horn (101) in studying the sensitivity of chromate solutions in colorimetric analysis using K_2CrO_4 found that a change 0.02 mg/dm^3 Cr^{+6} gave a detectable change in colour depth, and that the minimum detectable chromium concentration, in comparison with distilled water was 0.26 mg/dm^3 Cr^{+6}.

3.4.5 Other Methods

Although the above methods are perhaps the most commonly used in analysing the solubility of any salt in solution. There are a number of other special methods reported in the literature.

3.4.5.1 Cloud Method (90, 91, 92)

The principle of this method is to prepare a solute - solvent system of known composition and confine it in such a way as to prevent loss of the components. Then change the temperature in order to determine the temperature above which only the one phase exists and below which both exist. This method has been used in a large variety of systems (48). However, it has the disadvantage that it is not very applicable to very low solubility salts since they usually have metastable regions of up to 2 - 3 orders of magnitude of the solubility.

3.4.5.2 Dilatometer Method (48, 93)

This method is based on the change in volume when one phase dissolves in another. Besides the fact that is is not suitable for low solubility salts it gives rise to a number of other errors (48, 94).

3.4.5.3 Radio Active Tracer Methods

The principle of this method requires the inclusion of a known proportion of a radio active form of one of the elements of the substance whose solubility is to be determined. This has been used in the study of slightly soluble salts such as strontium sulphate (95) by taking a sample of the solution evaporating to dryness and counting the β emissions of S^{35} using a Geiger-Muller counter. Also the change in solubility of zinc oxalate with pH was studied by measuring the emission of gamma rays from Zn^{65} (96, 97).

3.4.5.4 Chromatography

There have been a number of methods developed for the study of solubility of slightly soluble materials. Krishnamurti and Dhareshwar (99) used filter paper dipped in Agar gel as a chromatographic technique for determining the concentrations of various silver salts and chromates. They found that if the solubility of the silver salts is plotted against the distance diffused, a straight line plot is obtained and they claim that this is applicable to any group of metallic salts.

Krishnamurti and Miraz (100) found that there is a shift in the peak of the absorption curves of a sparingly soluble silver salt from that of the potassium or sodium salt By plotting the peak shift versus the solubility of these silver salts they obtained a straight line and claimed that by using this method they could determine the solubility of the sparingly soluble salts. No mention was made in these two methods of the effect of additives, nor whether they could be used at higher temperatures and acidities. The suitability is therefore doubtful for the present problem.

diffusivity
~~solubil~~ity needs to be known first ?

CHAPTER 4

Measuring the Solubility

4.0 Introduction

Of the methods reviewed in the last chapter the most commonly used with low solubility compounds such as barium chromate are the electrical methods (49, 77, 81, 83, 84) and the spectrophotometric (colorimetric) methods (55, 75, 72).

The electrical methods have the advantage that they do not need a sampling procedure, removing all sampling errors or errors due to disturbing the equilibrium. The disadvantage of this method is that large errors could arise due to the swamping of the system by impurities (48, 87), also errors could arise due to the neglect of some of the reactions that occur in the solution (49). With the spectrophotometric method a wavelength could be chosen where only the Cr^{+6} absorbed light. This was considered to give the spectrophotometric method a greater advantage over the electrical method in spite of the risk of sampling errors and hence was chosen to measure the concentration of Cr^{+6} in saturated solutions.

4.1 Solubility Apparatus and Material

4.1.1 Materials

a) De-ionised water; this was freshly prepared and used in all the solubility experiments and preliminary growth rate experiments.

b) Barium chromate; G.P.R. grade from Hopkin and Williams with an assay of 99% with a maximum limit of Na and K of 0.02%.

c) Hydrochloric acid; concentrated Analar grade acid from Hopkin and Williams. Density 1.16 g/cm^3 (31-32% assay) was used and diluted to 1M according to the method outlined in Vogel. (141) The actual strength was then determined by titrating against freshly prepared Borax using methyl orange as an indicator.

d) Sodium Hydroxide; G.P.R. grade pellets from Hopkin and Williams was used.

e) Borax; (sodium tetraborate) crystalline Analar grade (≮ 99%) from Hopkin and Williams was used.

4.1.2 Equipment

Four insulated water jacketed glass vessels of capacity 0.5 dm^3 were connected up in parallel to a Townson and Mercer Thermo-circulator as shown in fig. 4.1. The vessels were continuously stirred by magnetic followers coated with PTFE. The temperature control was to ± 0.03 K.

The pH was measured with an EIL pH meter model 7010, range 0-14 pH with a discrimination of ± 0.04 pH and indicator accuracy ± 0.14 pH. Drift was found to be typically less than 0.002 pH/ K. It has a normal temperature compensation. An EIL combination pH electrode (No. 1160-200) was used with the instrument. Samples were made up in grade A, 25 cm^3 glass stoppered volumetric flasks, having an accuracy of ± 0.03 cm^3 at 20°C.

The graduated pipettes used were grade A and subdivided into 0.01 and 0.02 cm^3 respectively. The 1 cm^3 pipettes have an accuracy of ± 0.006 cm^3.

Samples were withdrawn through "Sinta Glass" immersion filters, of 10 mm dia and porosity 4, the sintered plates (maximum pore dia 5 - 10 μm : pattern to BS 1428 part F1).

Analysis of solutions was carried out on a standard Pye-Unicam SP1800 UV Spectrophotometer. This is a manually operated double

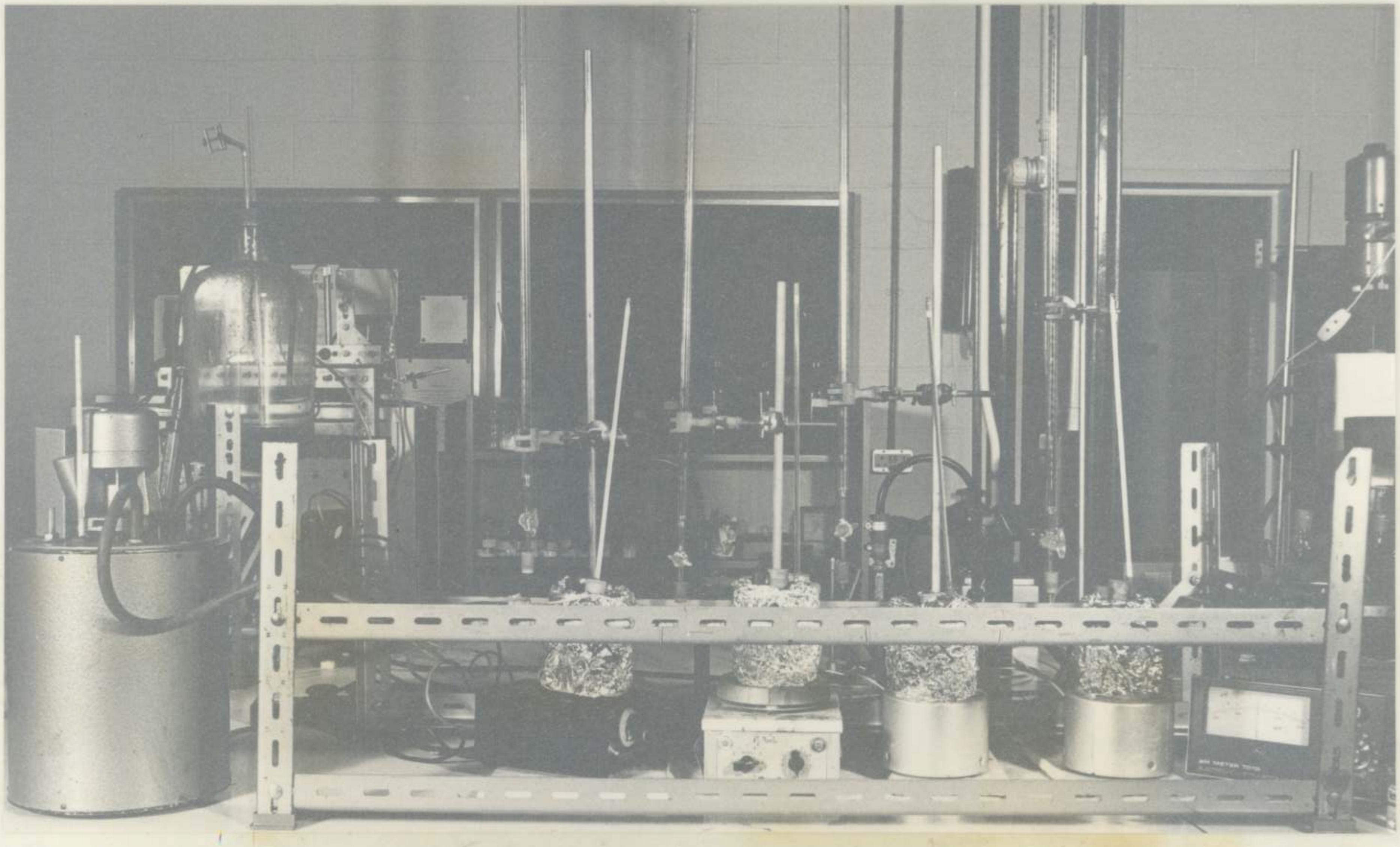

FIGURE 4.1: apparatus used to prepare supernatent solutions of barium chromate.

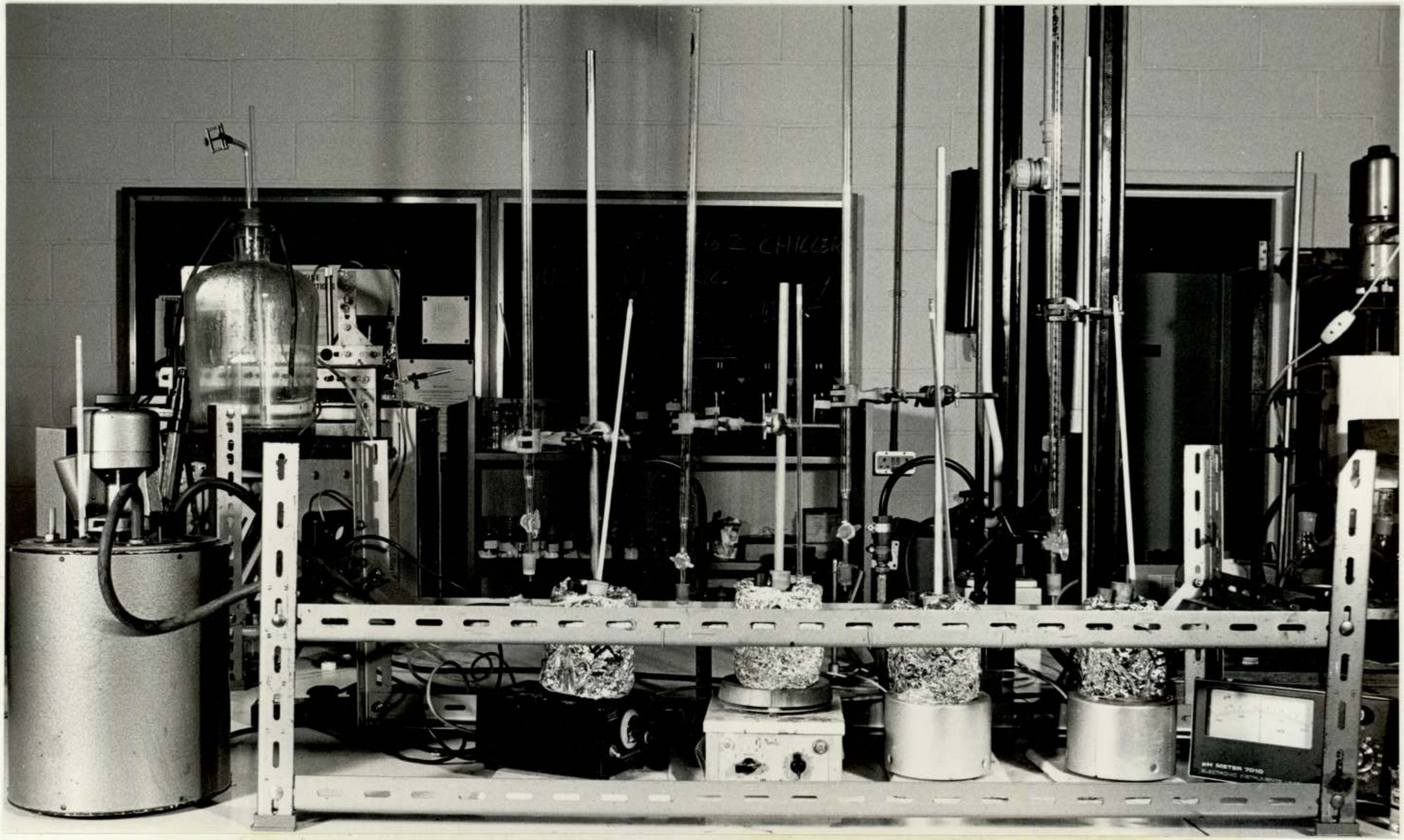

FIGURE 4.1: apparatus used to prepare supernatent solutions of barium chromate.

beam grating instrument with a solid state circuit measuring the logarithmic ratio of references and sample beam light intensities. As source it uses air cooled deuterium arc and tungsten filament lamps. The output has four absorbance ranges, 0-2, 0-1, 0-.5 and 0-0.2 and could be read from a meter and also recorded directly on a chart recorder.

The instrument specification is given as follows:-

Photometric Accuracy = ± 1% of full scale on all ranges.
Photometric reproducibility = ± 1% of full scale on all ranges.
Wavelength accuracy = ± 0.5 nm.
Wavelength reproducibility = ± 0.5 nm.

Beam balance constant to within ± 0.01 absorbance units over wavelength range.

Stray light less than 1% at 200 nm.

Precision optical cells (BS 3875) made from U.V. grade silica ("spectrosil") with path lengths ranging from 0.5 nm to 40 nm.

4.2 Procedure (Analytical)

Before any samples were analysed the two cells were rinsed thoroughly with deionised water and placed in their holder in the SP1800. The zero on the meter was then set for the wavelength region required.

The sample cell was then rinsed 3 times with the sample before finally filling and replacing in the holder. The same was done with the reference cell. The absorbtion was then read directly off the meter after adjusting to the appropriate scale, or a wavelength region was scanned and a print-out obtained on the chart plotter.

The measurements on solubility samples were carried out with the cells kept at a temperature of 22°C.

As the optical faces of the cells are very sensitive they were handled with extreme care and were carefully wiped on the outside with absorbent tissue paper. After use the cells were immediately placed in a weak cleansing solution specified for silica glass ware. During the use of the cells it was noticed that a slight build up of deposit occurred on the inner surface of the cells (especially the smaller ones). This was removed by periodically soaking them for a couple of hours in concentrated nitric acid.

4.3 Procedure (Experimental)

Before any solubility tests were carried out three preliminary experiments were done;

(i) to determine the wavelength at which to measure the absorption;

(ii) to determine the calibration curve and;

(iii) to determine the equilibrium time required.

4.3.1 Determination of Suitable Wavelength

This experiment was to determine a peak at which only Cr^{+6} had any absorbence. Samples of barium chromate, hydrochloric acid, urea and sodium hydroxide were prepared and their absorption was scanned and recorded as shown in figure 4.2.

a. Barium Chromate

A solution of barium chromate (0.592×10^{-3}M) was prepared in a 0.1 dm^3 volumetric flask. The sample was then analysed using 2mm path length cells and the procedure described in section 4.2.1. The results showed that barium chromate had absorption peaks at wavelengths 198nm, 258nm, and 360nm. The most sensitive was the 198nm wavelength having an absorption of 84.2% or A = 4.21. The next sensitive at 258nm having an

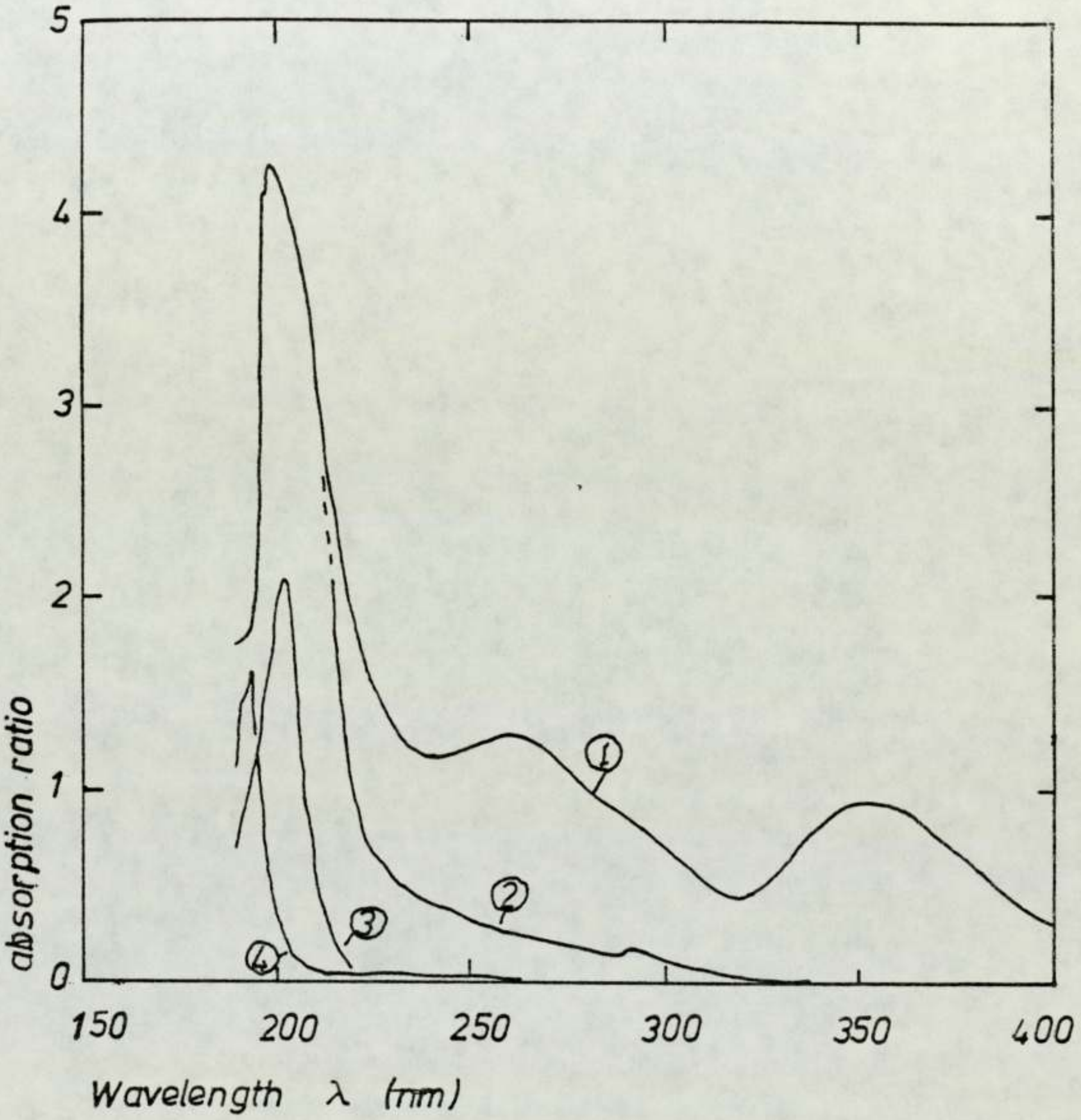

FIGURE 4·2: absorption spectra of likely solution components

1) $BaCrO_4$	$0{\cdot}592 \times 10^{-3}$	M/dm^3
2) NaOH	0·5	M/dm^3
3) Urea	1·998	M/dm^3
4) HCl	0·196	M/dm^3

absorption of 26.6% (A = 1.22) and at 360 the absorption was 19.3% (A = 0.965).

b. Urea:- A urea solution 1.998 M was prepared in a 0.1 dm^3 volumetric flask and analysed in the same way. It was found that urea absorbed strongly at 205nm in the region of 190 - 230 nm, and had another very slight peak at 270 nm A = 0.03.

c. Hydrochloric acid

A HCl solution of 0.196M was prepared in a 0.1 dm^3 volumetric flask and analysed by the above method. It was found to give a peak at 194 nm A = 1.6 but then dropped rapidly at longer wavelengths to vary between A = 0.02 and A = 0.004.

d. Sodium hydroxide

A NaOH solution 0.5M was prepared and analysed as above. The absorption of sodium hydroxide varied from A = 4.0 at 210 nm to A = 0.4 at 250 nm with a small peak of A = 0.25 at 290 nm.

It is concluded from the above that the wavelength to be used for measuring the absorption should be 360nm.

4.3.2 Determination of Calibration Curve

Barium chromate 0.5069g was accurately weighed and added to a 0.5 dm^3 volumetric flask containing 0.05 dm^3 of 0.995 M HCl. The solution was then made up to the mark. From this solution various concentrations of barium chromate were prepared in 0.1 dm^3 volumetric flasks, by pipetting various volumes from the original solutions. HCl 0.995M was added to the samples in varying amounts (as shown in table 4.1) in order to keep the solution pH 1.24. The amount of acid added was based on mass balance calculations given in Appendix A1. The final pH of all the samples was checked on the EIL meter to be 1.24 ± 0.01.

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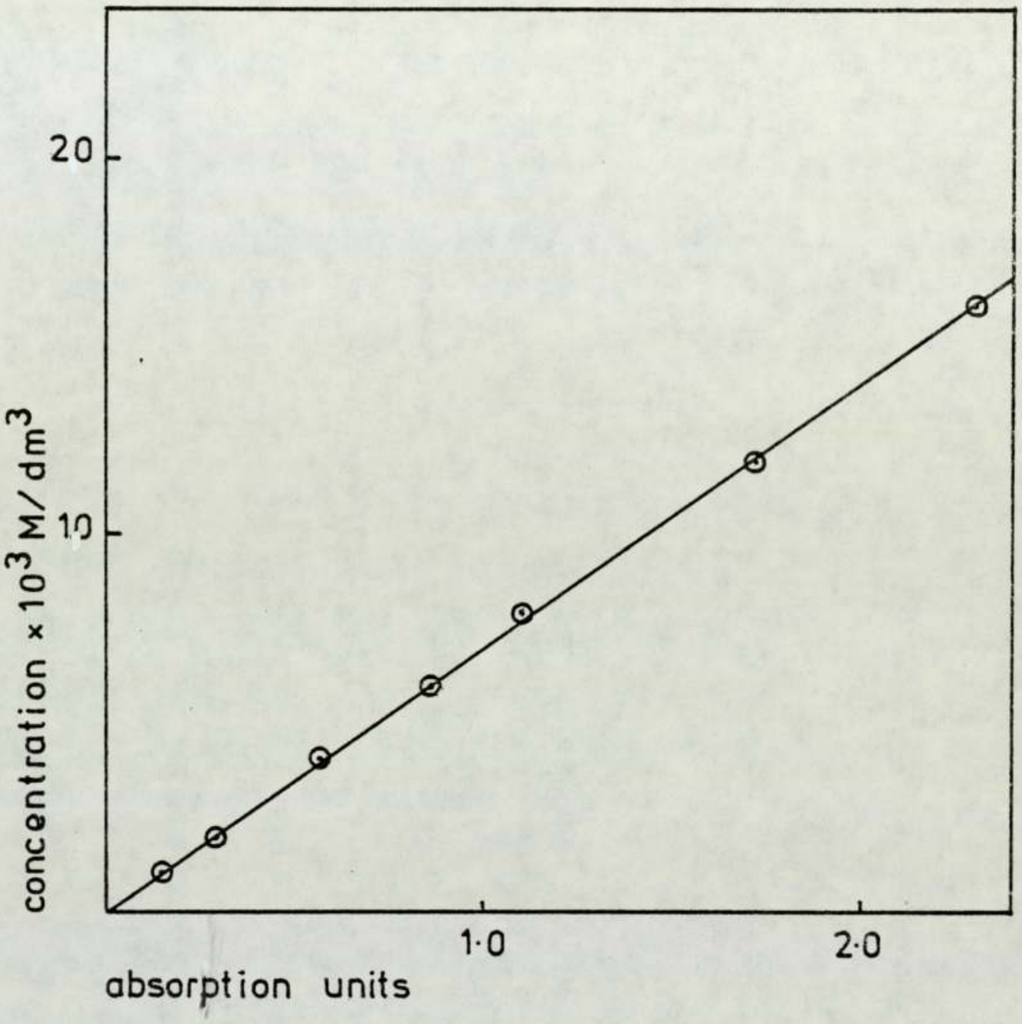


FIGURE 4·3 calibration curve for the measurement of the concentration of Cr^{+6} solutions on the SP1800 spectrophotometer

pH of solutions = 1·24
temperature = 20°C
wavelength = 360 nm
band width = 1 nm
slit width = 0·3 nm

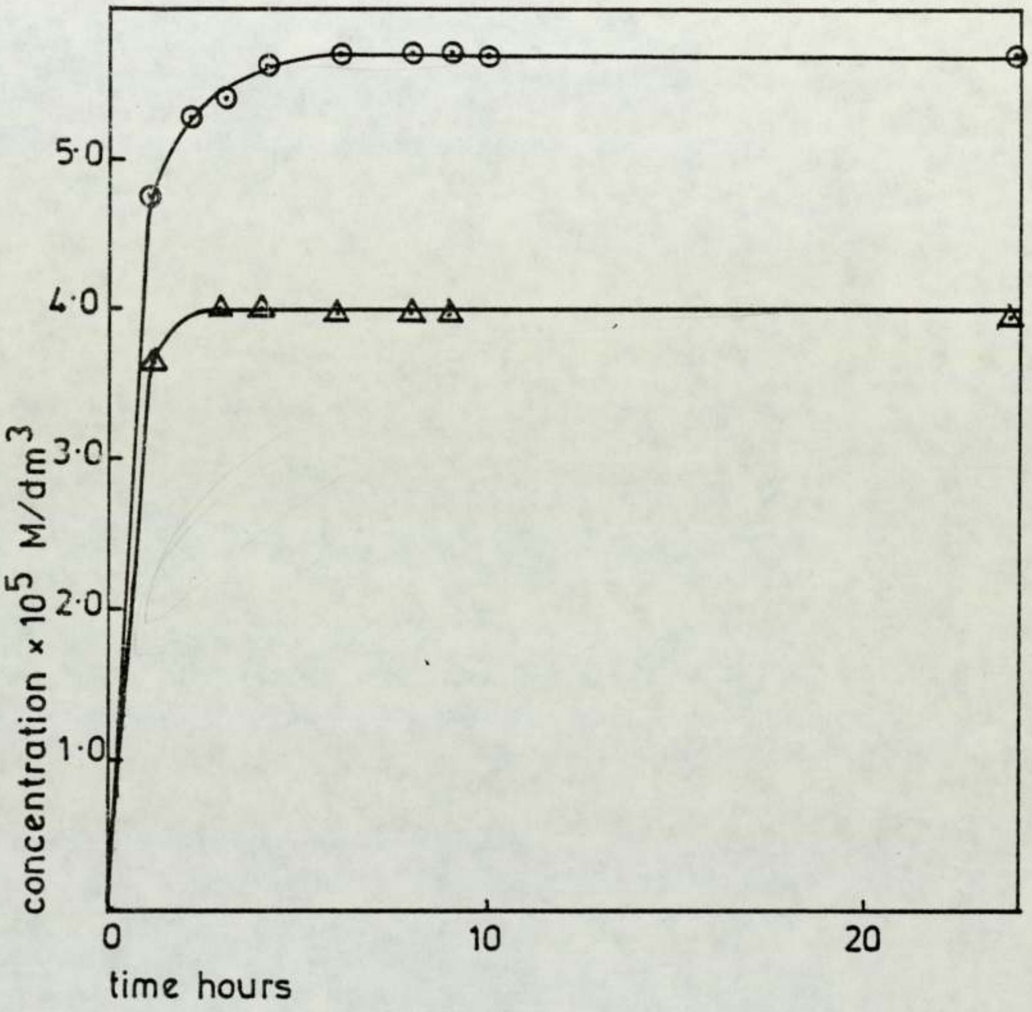


FIGURE 4:4 graph to show a solution of barium chromate reaching equilibrum at 30·4°C and at

△ pH = 6·4
⊙ pH = 7·6

Table 4.1: Variation of absorbance with concentration of Barium Chromate as pH = 1.0 and 22°C.

Conc. of $BaCrO_4$ (M/dm^3) ($\times 10^3$)	HCl required to bring pH to 1.0	Path Length l (mm)	Absorbance
0.040	9.94	10	0.0542
0.100	9.8	10	0.1365
0.200	9.55	10	0.288
0.400	9.05	10	0.561
0.600	8.54	10	0.858
6.9×10^{-4} 0.800	8.04	10	1.0 1.1135
1.200	7.04	2	0.341
1.600	6.03	2	0.458
2.00	5.03	2	0.585 – used in Fig 4.3

From the above results a calibration curve was plotted by converting all values to path lengths 10 mm giving a slope s = 6.94×10^{-4} M/ absorption unit.

4.3.3 Determination of equilibrium time

Barium chromate (ca. 2g) was added to de-ionised water (ca. 0.40 dm^3) in two of the jacketed vessels. The pH of the first was left at 7.6 while the pH of the second was adjusted to 6.4 by the addition of 0.2M HCl from a burette. Both samples were stirred continuously and maintained at 30.4°C.

Samples of supernatant solution (1 cm^3) were withdrawn using a pipette with a filter attached to it, at hourly intervals for the first 4 hours, then bi-hourly for the next 4 hours. Two more samples were taken after 24 hours and 48 hours. These samples were introduced into 25 cm^3 volumetric flasks containing the appropriate amount of 0.995 M HCl to bring the total acid concentration to 0.1 M. (Appendix A1). They were then made up to the mark and analysed on the SP1800

Table 4.2: Results of Equilibrium Experiments (30.4°C)

pH 7.6		pH 6.4	
Time (h)	Conc. 10^3 x M/dm^3	Time (h)	Conc. 10^3 x M/dm^3
1	0.0472	1	0.036
2	0.0523	2	0.0405
3	0.0546	3	0.0393
4	0.0563	4	0.0394
6	0.0568	6	0.0391
8	0.0568	8	0.0392
9	0.0570	9	0.0394
10	0.0570		
24	0.0570	24	0.0401
48	0.0580	48	0.0405

It was concluded that the time needed to reach equilibrium in the neutral solution (pH = 7.6) is greater than that when there was acid in the system (pH = 6.4).

a) <u>pH 7.6</u>: The change in concentration between 6 hours and 24 hours was about 2% which is within the estimated experimental error due to sampling and measurements. Therefore all further experiments carried out in the neutral solution were allowed 6 hours to reach equilibrium before the samples were withdrawn.

b) <u>pH 6.4</u>: As there was no significant change in the concentration within experimental error after 2 hours all experiments with acid were allowed at least 2 hours to reach equilibrium.

4.3.4. Comparison of absorption through cells with different path length

As a number of cells with different path lengths were used a subsidiary experiment was carried out to compare the absorption through the cells.

A barium chromate solution of concentration 8.36×10^{-2} mM/dm^3 was prepared and the absorption was measured through cells of path lengths 40, 20, 10, 2 and 1 mm. The absorption was recorded in table 4.3. The 10 mm cell was then taken as standard and the absorption of the solution through the other cells was then compared to it by calculating the absorption had the measurement been done through a 10 mm path length cell. This then produced the equivalent absorption given in table 4.3. This ratio was then used to correct for the solubilities given in the next chapter.

4.4. Determination of Solubility of Barium Chromate in water at different temperatures

Barium Chromate (c.a. 2g) was added to 3 jacketed vessels containing de-ionised water (c.a. 0.40 dm^3) and continuously stirred at approximately 30°C with the pH and temperature monitored. After 6 hours a sample (1 cm^3) was withdrawn by pipette through the sintered glass filter tip from each vessel. The sample was then placed in a 2.5 cm^3 volumetric flask and the pH adjusted by adding 2.52 cm^3 (appendix A1) of 0.995 M HCl and made up to the mark. They were analysed using 40 mm path length cells and the test was repeated at temperature of 40, 50, 60, 70, 80 and 90°C.

4.5 Determination of Change of Solubility with pH and Temperature

Barium chromate (c.a. 2 - 4g, depending on the acid content) was added to de-ionised water (c.a. 0.4 dm^3) in the 4 jacketed vessels, the pH of the solutions were adjusted to the desired pH by the drop-wise addition 0.2 M HCl while the system was being continuously stirred at 30°C. After 2 hours samples were withdrawn and analysed as described in the previous section, using 10 mm and 2 mm path length cells, This was repeated at temperatures 40, 50, 70 and 90°C.

Table 4.3: Ratio of absorption through cells to absorption through standard 10 mm cell.

Path length (mm)	Absorbance	Ratio
40	0.480	0.996
20	0.242	1.006
10	0.1205	1.000
2	0.0240	0.995
1	0.0120	0.996

CHAPTER 5

Results and Discussion

In the first few solubility tests no great attention was given to the final pH of the sample analysed by the SP1800. This lead to a great scatter of the results and also to the solubility at temperatures 50 and 70 °C overlapping. The reason for this was attributed to the fact that as the samples had varying amounts of acid, the equilibrium composition varied. By the nature of these equilibria (section 2.3), if the $[H^+]$ is kept constant the proportion of the concentration of the species is kept constant (provided not too much of the dimer is formed). For this reason the pH of all the samples measured was adjusted to 1.25 ± 0.02 pH units.

5.1 Solubility of $BaCrO_4$ in Water

The solubility of barium chromate in water is plotted in figure 5.1, which is obtained from table 5.1
This shows that the dissolution is endothermic and the solubility increases with temperature by about 3-4% /K. This agrees with the value calculated from the literature (11,12).

However, it is also noticed that the solubility values obtained here are higher than most of those given in the literature (table 2.2) by a factor of ≈2, except for the values obtained by Waddel (table 2.1) which are much more in agreement with present results, dispite the fact that with his method results were obtained from solutions that might not have reached equilibrium.

The difference between the present results and those published could therefore be attributed to the fact that the solubility of barium chromate is very sensitive to the pH value of the solution.

5.2 Effect of pH and Temperature on the Solubility of $BaCrO_4$

The solubility data obtained are plotted in figure 5.2. It is evident

Table 5.1: Solubility of $BaCrO_4$ in deionised water.

Temp.	pH	mls HCl added	Pipette Factor	A	Cell Path length mm	Cell Factor	Dill Factor	Conc. 10^5 x M/dm^3	Final pH	$\frac{1}{T}$ x 10^3
29.9	7.67	2.52	1.0019	0.011	40	0.9959	25/4	4.78	1.24	3.30
29.9	7.70	2.52	1.0019	0.012	40	0.9959	25/4	5.22	1.23	3.30
29.9	7.73	2.52	1.0019	0.012	40	0.9959	25/4	5.22	1.24	3.30
39.7	7.70	2.52	1.0051	0.016	40	0.9959	25/4	6.94	1.24	3.20
39.7	7.82	2.52	1.0051	0.0175	40	0.9959	25/4	7.58	1.24	3.20
39.7	7.83	2.52	1.0051	0.018	40	0.9959	25/4	7.74	1.23	3.20
49.6	7.38	2.52	1.0092	0.0195	40	0.9959	25/4	8.42	1.23	3.10
49.6	7.97	2.52	1.0092	0.0200	40	0.9959	25/4	8.63	1.24	3.10
49.6	7.85	2.52	1.0092	0.025	40	0.9959	25/4	10.79	1.24	3.10
59.2	7.39	2.52	1.0104	0.027	40	0.9959	25/4	11.64	1.25	3.01
59.2	8.04	2.52	1.0104	0.0275	40	0.9959	25/4	11.85	1.23	3.01
59.2	7.96	2.52	1.0104	0.030	40	0.9959	25/4	12.83	1.23	3.01
69.4	7.12	2.52	1.0126	0.0215	20	1.0062	25/2	18.31	1.25	2.92
69.4	7.91	2.52	1.0126	0.022	20	1.0062	25/2	18.73	1.24	2.92

Table 5.1: Continued

Temp.	pH	mls HCl added	Pipette Factor	A	Cell Path length mm	Cell Factor	Dill Factor	Conc. 10^5 x M/dm^3	Final pH	$\frac{1}{T} \times 10^3$
69.4	7.69	2.52	1.026	0.0225	20	1.0062	25/2	19.16	1.24	2.92
80.1	6.91	2.52	0.9981	0.028	20	1.0062	25/2	23.84	1.23	2.83
80.1	7.87	2.52	0.9981	0.026	20	1.0062	12.5	22.46	1.24	2.83
80.1	7.57	2.52	0.9981	0.030	20	1.0062	12.5	25.91	1.25	2.83
89.6	6.91	2.52	0.9781	0.0325	20	1.0062	12.5	28.65	1.25	2.76
89.6	7.85	2.52	0.9781	0.0325	20	1.0062	12.5	28.65	1.25	2.76
89.6	7.46	2.52	0.9781	0.0320	20	1.0062	12.5	28.21	1.23	2.76

Table 5.2: Of the variation of the solubility of Cr^{+6} with pH at a temperature of 30°C.

Temp. °C	pH	mls HCL added	A	Pipette factor	Cell Length mm	Cell factor	Dill factor	Conc. 10^3 x M/1	Final pH	$\frac{a}{1}$
31.1	4.18	2.52	0.0068	1.0019	10	1.000	25	0.118	1.25	0.0299
31.1	3.80	2.52	0.0095	1.0019	10	1.000	25	0.165	1.25	0.0418
31.1	3.50	2.52	0.0190	1.0019	10	1.000	25	0.329	1.25	0.0834
31.1	3.05	2.52	0.0335	1.0019	10	1.000	25	0.580	1.25	0.147
31.1	2.80	2.52	0.049	1.0019	10	1.000	25	0.849	1.25	0.215
31.1	2.40	2.51	0.097	1.0019	10	1.000	25	1.680	1.25	0.426
31.1	2.10	2.50	0.162	1.0019	10	1.000	25	2.805	1.25	0.711
31.1	1.75	2.49	0.264	1.0019	10	1.000	25	4.572	1.25	1.158
31.1	1.55	2.48	0.335	1.0019	10	1.000	25	5.801	1.25	1.470
31.1	1.40	2.46	0.465	1.0019	10	1.000	25	8.052	1.25	2.037
31.1	1.30	2.45	0.500	1.0019	10	1.000	25	8.659	1.25	2.194
31.1	1.00	2.41	0.801	1.0019	10	1.000	25	13.87	1.25	3.514
31.1	0.75	2.36	1.050	1.0019	10	1.000	25	18.18	1.25	4.608
31.1	0.60	2.26	0.458	1.0019	2	0.9958	125	39.82	1.25	10.08

Table 5.3: The Solubility of Cr^{+6} with pH at temperature 50°C.

Temp. °C.	pH	mls of acid added	A	Pipette Factor	Cell Length mm	Cell Factor	Conc. x 10^3 m/1	Final pH	Dilution Factor
49.80	4.25	2.52	0.0144	1.0092	10	1.000	0.247	1.27	25
49.80	3.15	2.52	0.0760	1.0092	10	1.000	1.314	1.27	25
49.85	2.90	2.51	0.0880	1.0092	10	1.000	1.513	1.27	25
49.80	2.70	2.51	0.1220	1.0092	10	1.000	2.097	1.27	25
49.80	2.55	2.51	0.1470	1.0092	10	1.000	2.527	1.27	25
49.75	2.35	2.51	0.220	1.0092	10	1.000	3.782	1.28	25
49.80	1.95	2.49	0.432	1.0092	10	1.000	7.427	1.27	25
49.85	1.65	2.48	0.695	1.0092	10	1.000	11.948	1.27	25
49.70	1.40	2.46	0.215	1.0092	2	0.9958	18.56	1.27	125
49.70	1.20	2.44	1.240	1.0092	10	1.000	21.32	1.27	25
49.70	0.95	2.41	0.378	1.0092	2	0.9958	32.63	1.27	125
49.70	0.85	2.39	0.572	1.0092	2	0.9958	49.62	1.27	125
49.75	0.60	2.26	0.835	1.0092	2	0.9958	72.08	1.27	125
49.70	0.35	2.08	1.05	1.0092	2	0.9958	90.64	1.28	125

Table 5.4: Of the variation of the solubility of Cr^{+6} with pH at a temperature of 40.5°C.

Temp.	pH	mls of HCl added	*A*	Pipette Factor	Cell Length mm	Cell Factor	Dill Factor	Conc. 10^3 x M/l	Final pH
40.5	5.5	2.52	0.004	1.0051	10	1.000	25	0.069	1.25
40.5	4.75	2.52	0.005	1.0051	10	1.000	25	0.086	1.25
40.5	4.40	2.52	0.007	1.0051	10	1.000	25	0.121	1.25
40.5	3.90	2.52	0.015	1.0051	10	1.000	25	0.259	1.25
40.5	3.50	2.52	0.028	1.0051	10	1.000	25	0.483	1.25
40.5	3.25	2.52	0.042	1.0051	10	1.000	25	0.725	1.25
40.5	3.05	2.52	0.055	1.0051	10	1.000	25	0.949	1.25
40.5	2.55	2.51	0.118	1.0051	10	1.000	25	2.037	1.25
40.5	2.40	2.51	0.135	1.0051	10	1.000	25	2.342	1.25
40.5	2.20	2.50	0.175	1.0051	10	1.000	25	3.021	1.24
40.5	1.90	2.49	0.310	1.0051	10	1.000	25	5.351	1.24
40.5	1.45	2.47	0.670	1.0051	10	1.000	25	11.57	1.24
40.5	1.05	2.42	1.24	1.0051	10	1.000	25	21.40	1.24
40.5	0.8	2.37	0.357	1.0051	2	0.9958	125	30.94	1.24
40.5	0.65	2.29	0.455	1.0051	2	0.9958	125	39.44	1.24

Table 5.5: Solubility of Cr^{+6} with pH at a temperature of 70°C.

Temp. °C	pH	mls added	A	Pipette Factor	Cell Length mm	Cell Factor	Dill Factor	Conc. 10^3 x M/1	Final pH
69.5	4.25	2.52	0.024	1.0126	10	1.000	25	0.411	1.25
69.5	3.80	2.52	0.040	1.0126	10	1.000	25	0.685	1.25
69.5	3.45	2.52	0.069	1.0126	10	1.000	25	1.182	1.25
69.5	3.15	2.52	0.105	1.0126	10	1.000	25	1.799	1.25
69.5	2.95	2.51	0.144	1.0126	10	1.000	25	2.467	1.25
69.5	2.75	2.51	0.218	1.0126	10	1.000	25	3.735	1.25
69.5	2.55	2.51	0.260	1.0126	10	1.000	25	4.455	1.25
69.5	2.25	2.50	0.134	1.0126	2	0.9958	125	11.528	1.25
69.5	1.59	2.47	0.280	1.0126	2	0.9958	125	24.089	1.25
69.5	1.15	2.44	0.435	1.0126	2	0.9958	125	37.424	1.26
69.5	1.15	2.44	0.438	1.0126	2	0.9958	125	37.682	1.25
69.5	1.05	2.42	0.485	1.0126	2	0.9958	125	41.725	1.25
69.5	0.90	2.39	0.645	1.0126	2	0.9958	125	55.491	1.25

Table 5.5: Continued

Temp. ^{o}C	pH	mls added	A	Pipette Factor	Cell Length mm	Cell Factor	Dill Factor	Conc. 10^3 x M/1	Final pH
69.5	0.80	2.36	0.770	1.0126	2	0.9958	125	66.244	1.25
69.5	0.70	2.31	0.900	1.0126	2	0.9958	125	77.428	1.25
69.5	0.60	2.26	1.070	1.0126	2	0.9958	125	92.064	1.25

Table 5.6: The Solubility of Cr^{+6} with pH at temperature 90°C.

Temp °C	pH	mls of acid added	*A*	Pipette Factor	Cell Length mm	Dill. Factor	Final pH	Conc. 10^3 x M/1
89.6	4.50	2.52	0.026	0.9781	10	25	1.25	0.461
89.5	4.15	2.52	0.041	0.9781	10	25	1.25	0.727
89.6	3.85	2.52	0.063	0.9781	10	25	1.25	1.118
89.5	3.60	2.52	0.095	0.9781	10	25	1.24	1.685
89.6	3.25	2.52	0.1395	0.9781	10	25	1.24	2.475
89.5	2.95	2.51	0.200	0.9781	10	25	1.24	3.550
89.4	2.85	2.51	0.259	0.9781	10	25	1.24	4.594
89.5	2.10	2.50	0.775	0.9781	10	25	1.24	13.75
89.5	2.00	2.50	0.1835	0.9781	2	125	1.23	16.344
89.5	1.85	2.49	0.220	0.9781	2	125	1.23	19.595
89.5	1.60	2.48	0.285	0.9781	2	125	1.23	25.384
89.5	1.20	2.44	0.495	0.9781	2	125	1.23	44.088
89.5	1.10	2.43	0.685	0.9781	2	125	1.24	61.011

Table 5.6: Continued.

Temp. ^{o}C	pH	mls of acid added	A	Pipette Factor	Cell Length	Dill Factor	Final pH	Conc. 10^3 x M/1
89.5	1.00	2.45	0.785	0.9781	2	125	1.24	70.808
89.5	0.80	2.38	1.15	0.9781	2	125	1.24	102.42
89.5	0.75	2.35	1.20	0.9781	2	125	1.24	106.88

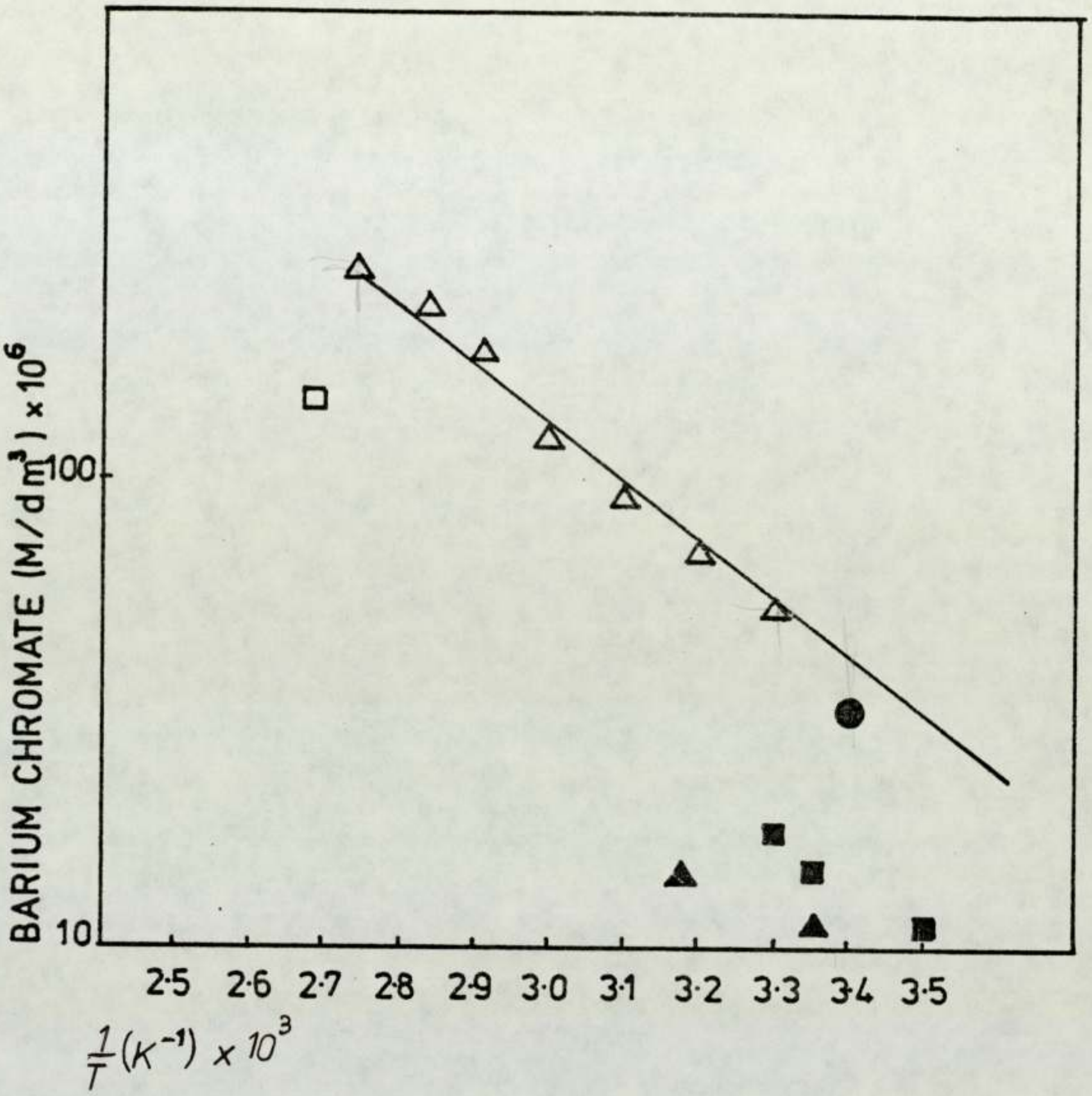


FIGURE 5·1 CHANGE OF SOLUBILITY OF BARIUM CHROMATE IN DE-IONISED WATER WITH TEMPERATURE

pH = ?

(7 < pH < 7.3)

- △ PRESENT WORK
- ● WADDEL (14)
- ■ KOHLRUSCH (15)
- ▲ BOYER AND RIEMAN (17)
- □ MESCHERZKI (19)

that the solubility increased with temperature and with the hydrogen ion concentration. These results (figure 5.2) are similar to Osawa's results (21) given in table 2.3. However, though his results are apparently slightly lower than these results, the pH values given in table 2.3 are based on pure acetic acid and do not take into consideration the equilibria existing due to the formation of $HCrO_4^-$. This will give a higher pH value and thus give higher concentration values for a given pH, bringing his data nearer to the present values.

5.3 Effect of pH

The reason for the solubility increase with the hydrogen ion concentration is due to the formation of the protonated chromate ions, dichromate ions, protonated dichromate ions and chlorochromate ions, as the acid concentration increases. This causes the basic stabilisation reaction,

$$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-} \qquad \text{....5.1}$$

to shift to the right, increasing the overall amount of $BaCrO_4$ going into solution. Defining this amount as S and the hydrogen ion concentration as H. The solubility S can be related to the equilibrium constants (equations 2.8 to 2.13) by the following equation (appendix 4)

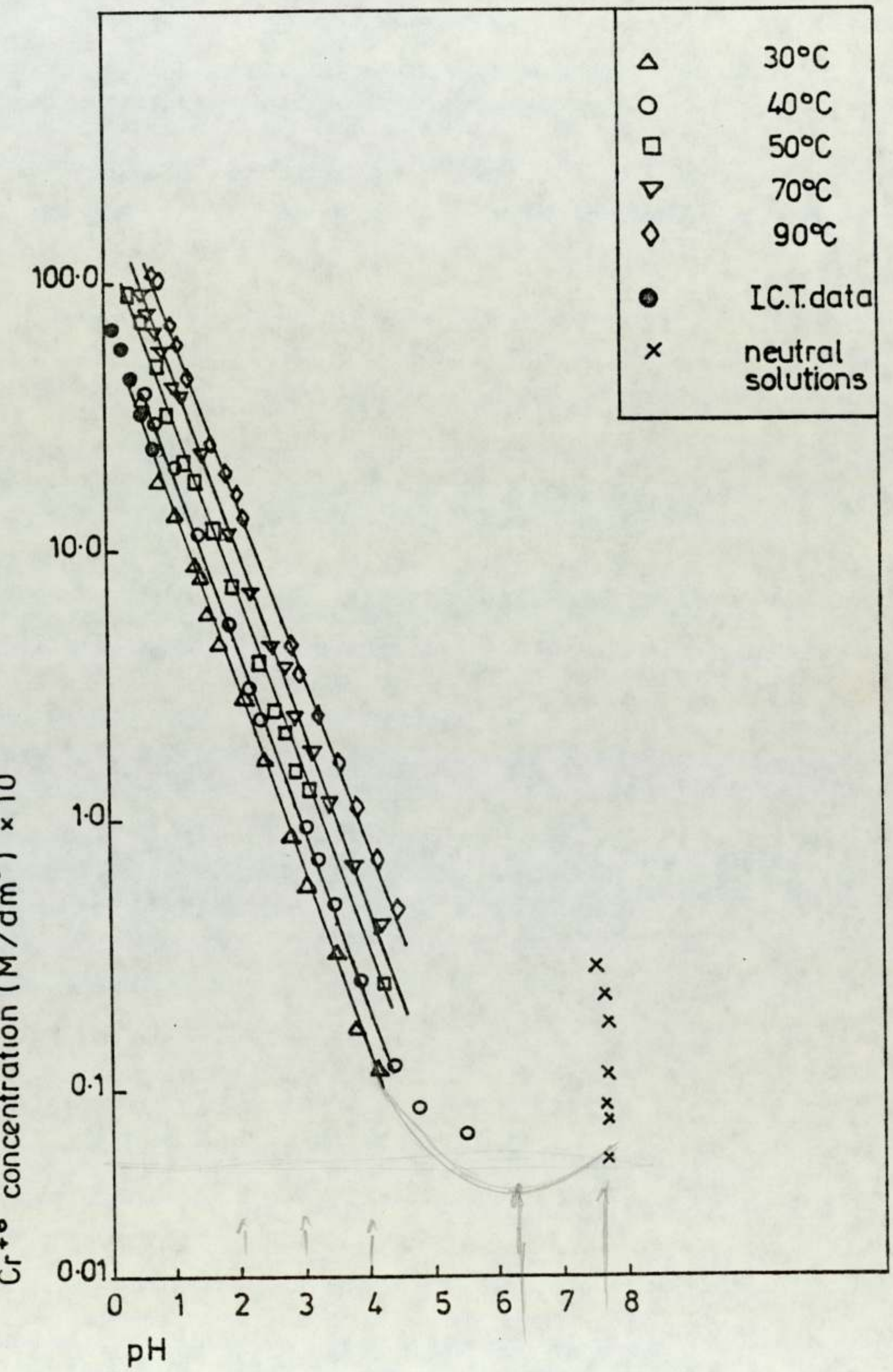
$$S^3 - SA - B = 0 \qquad \text{...5.2}$$

where $$A = K_{sp}\left[1 + \frac{H}{K_2} + H^2 \times \frac{1}{K_1K_2} + \frac{\overset{3}{H}K_c}{K_2}\right]$$

and $$B = \frac{2K_{sp}{}^2 K_d}{K_2^2}\left[H^2 + \frac{H^3}{K_{d2}} + \frac{H^4}{K_{d1}K_{d2}}\right]$$

where the K's are the equilibrium constants and K_{sp} the solubility product.

FIGURE 5:2 CHANGE OF SOLUBILITY OF BARIUM CHROMATE WITH TEMPERATURE AND pH



A Nelder and Mead algorithm optimisation program attempted to estimate the equilibrium constants from the experimental data using an optimisation of the function:-

$$Y_i = \Sigma (S_i - YVAL_i)^2 \qquad ...5.3$$

where $YVAL_i$ is the calculated solubility (based on equation 5.2) at any pH_i and S_i is the experimental value of the solubility at any pH_i.

The Nelder and Mead program is a package program and the YVAL subroutine is given in Appendix 4.

However the optimisation was not successful. It was found that starting from different initial guesses gave different values for the equilibrium constant as shown in table 5.8. It was also noticed that only K_2 kept optimising to the same value. The reason for this is the possible insignificance of some of the equilibria (postulated by equation 4.2) in the range of pH examined. A hurestic approach was then tried to see the effect of each of the K values on the solubility.

A function

$$F = \frac{AS + B}{S^3}$$

was evaluated by choosing different combinations of the orders of magnitude of the equilibrium constants. The correct values of the equilibrium constants should give a value of F = 1.

The following combinations (table 5.7) were taken on the basis of values reported in the literature.

Table 5.7: Equilibrium Constants used in H$\overset{e}{\hat{u}}$ristic approach

K_1	K_2	K_c	K_D	K_D	K_D
10^{-2}	10^{-7}	10^{0}	10^{-2}	10^{-2}	10^{-2}
10^{-1}	10^{-6}	10^{1}	10^{-1}	10^{-1}	10^{-1}

Table 5.8: Results of optimisation search for the equilibrium constants, from the solubility data of barium chromate at 70°C, using the Nelder and Mead alogorithm with different initial points.

Equilibrium Constant	K_1	$K_2 \times 10^6$	K_d	K_c	K_{d1}	K_{d2}
Initial value	0.10	3.05	10.0	2.3	0.36	0.10
Optimum value	471.2	5.89	37.5	0.010	0.001	473.0
Initial value	0.10	3.05	10.0	36.5	0.10	0.10
Optimum value	9116.0	5.80	37.5	0.014	0.08	7.42
Initial value	0.11	3.05	20.0	4.5	0.3	0.12
Optimum value	0.367	5.89	34.6	14.5	0.003	5.5×10^{-4}
Initial values	497.0	3.05	37.7	0.011	0.0012	0.0022
Optimum value	492.0	5.89	37.5	0.012	0.0012	0.0022

Table 5.7: Continued.

K_1	K_2	K_c	K_D	K_D	K_D
10^0	10^{-5}	10^2	10^0	-	-
-	-	-	10^1	-	-
-	-	-	10^2	-	-

The hydrogen ion concentration $[H^+]$ was taken at two values (10^{-1} and 10^{-4}) to cover the range of the experimental data. Defining the terms in A and B as follows;

$$A = K_{sp}\left[\underset{[A1]}{1} + \underset{[A2]}{\frac{H}{K_2}} + \underset{[A3]}{\frac{H^2}{K_2K_1}} + \underset{[A4]}{\frac{K_cH^3}{K_2}}\right] \qquad \ldots.5.4$$

$$B = \frac{2K_{sp}{}^2K_D}{K_2^2}\left[\underset{[B2]}{H^2} + \underset{[B3]}{\frac{H^3}{K_{D2}}} + \underset{[B4]}{\frac{H^4}{K_{d1}K_{d2}}}\right] \qquad \ldots.5.5$$

The calculations were carried out using computer programme SK22 (Appendix 4). All combinations that gave $0.8 > F > 2$ were discarded as being of too great an error. The results of this estimation are given in appendix 5 and summarised below.

5.3.1. Components of the B Term

When the hydrogen ion concentration was set at 10^{-4} (table A5.2) the value of $\frac{AS}{B}$ varied from 10^6 to 10^2; this meant that at the best the value of the B term was 1% or less than the (AS) term. Whenever the hydrogen ion concentration was set at 10^{-1} the ratio (table A5.1) $\frac{AS}{B}$ varied from 10^6 to 10^1. It was found that even with the best significant value of B, the term B_4 ($H_2Cr_2O_7$) only contributed 0.1%

of the value of B. Furthermore, varying K_{d1} from 10^2 to 10^7 only changed F by 0.1%.

This indicated that in the region of study, the data is not sensitive to the values of K_{d1} and as B4 is of very small significance anyway of the terms in B only the B2 term need be considered in equation 4.2 without significantly affecting the accuracy.

5.3.2 Components of the A term

When setting the hydrogen ion concentration to 10^{-4} A4 (CrO_3Cl^-) had at best a value 5 orders of magnitude smaller than the major term in A. While A3 (H_2CrO_4) at best contributed 1% or less to A.

When setting the hydrogen ion concentration to 10^{-1}, A2 ($HCrO_4$) and A3 are of equal standing and A4 showed a contribution of about 10%.

From the above analysis equation 5.2 may be simplified to

$$S^3 = K_{sp} \left[1 + \frac{H}{K_2} + \frac{H^2}{K_2K_1} + \frac{H^3}{K_2} K_c \right] S + \frac{2K_{sp}{}^2 K_d H^2}{K_2^2} \qquad .....5.6$$

CHAPTER 6

Literature Review on Equilibria in Cr^{+6} Solutions

6.1 Introduction:

The composition of chromate species in aqueous acidic solutions has been the subject of a number of investigations over the past 70 years as referred to in Section 2.3. However, as seen in Table 6.1 a variation in the reported values of the equilibrium constants is noted in some cases the variation is as much as an order of magnitude as in the case of K_{d2} while in the cases of K_1 and K_d the variation is only by a factor of 2. As these equilibrium constants are of great importance in the determination of the CrO_4^{2-} ion, the literature is reviewed here from the point of view of the experimental work carried out by these researchers. To follow their work an introduction into equilibria in solutions and the factors that affect it are outlined first.

6.2 Equilibrium in Solutions (32, 82, 104, 105)

The concept of dynamic equilibrium provides a simple means for determining the relationship between the quantities of reacting substances and products that are present at equilibrium.

For one mole of a substance in a solution its free energy can be defined as,

$$F = F^{o} + RT \ln a \qquad .....6.1$$

where R is the universal gas constant

T the absolute temperature

a the active mass

By applying the free energy functions to the general reaction system in solution:

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots \qquad .....6.2$$

Table 6.1: Equilibrium constants for equations 2.1 to 2.6 corrected to ion strength ($\mu = 0$)

Temperature °C	5	10	15	20	25	30	35	40	45	50	55	60	65	Reference	
K_2	5.4				5.5				4.1				3.3	Galea	44
					3.2									Neuss	29
					3.2									Moore et al	37
					3.6									Galea	45
			3.3		3.1		2.9		2.6					Linge & Jones	36[a]
	3.6		3.3		3.2		3.0		2.7				7.3	Linge & Jones	36[b]
					2.0									Sasaki	31
					3.0										32
					2.8									Arnek	46
K_1			4.1		2.5		1.6							Tong & Johnson	40
					0.73									Tong & King	30
					3.0									Haight et al	38

Table 6.1: Continued

Temperature °C	5	10	15	20	25	30	35	40	45	50	55	60	65	Reference	
K_1					3.0									Haight et al	39
					5.6										32
K_{d1}					25.1										32
K_{d2}					0.18									Tong & King	30
					0.023										32
K_c					9.6									Haight et al	38
			6.1		6.2		7.0							Tong & Johnson	40
					6.0									Lukkari	39
K_d			43.5		3.4		2.5		20.1					Linge & Jones	116
					35.2									Sasaki	31
				3.5										Lukkari	39
			40.8		30.9		26.5							Pladziewicz et al	43

Table 6.1: Continued

Temperature °C	5	10	15	20	25	30	35	40	45	50	55	60	65	Reference	
					39.8									Moore et al	37
				37.7	33.0									Davies & Prue	33
					44.9									Neuss & Rieman	29
	42.3				35.1				18.5				11.6	Galea et al	44
					35.5									Tong & King	30
					58.7									Arnek & Johnson	46
					40.2									Jain and Jain	47

the change in free energy of this system is:

$$\Delta F = (pF_P + qF_Q + \ldots) - (aF_A + bF_B + \ldots) \quad \ldots\ldots 6.3$$

substituting from equation 6.1 and separating the concentration dependent terms from the others,

$$\Delta F = pF_P^o + qF_Q^{\ o} + \ldots - aF_A^o - 6F_B^o \ldots$$

$$+ \ RT\ln \frac{a_P^p \cdot a_Q^q \ldots}{a_A^a \cdot a_B^b \ldots} \quad \ldots\ldots 6.5$$

defining $\Delta F^o = pF_P^o + qF_Q^o + \ldots - aF_A^o - bF_B^o \ldots$ 6.6

$$\therefore \quad \Delta F = \Delta F^o + RT\ln \frac{a_P^p \cdot a_Q^q \ldots.}{a_A^a \cdot a_B^b \ldots.} \ . \quad \ldots\ldots 6.7$$

since at equilibrium $\Delta F = 0$,

$$\therefore \ -\Delta F^o = RT\ln \frac{a_P^p \cdot a_Q^q \cdot \ldots}{a_A^a \cdot a_B^b \ \ldots}$$

or

$$e^{-\frac{\Delta F^o}{RT}} = K^o = \frac{a_P^p \cdot a_Q^q \ldots.}{a_A^a \cdot a_B^b \ldots.} \ . \quad \ldots\ldots 6.8$$

The term K^o is a constant at constant temperature and is known as the thermodynamic equilibrium constant.

6.3 Factors that affect equilibrium

One of the most well known principles that describe equilibrium chemistry is the Le Chatelier principle which states that: "If a change occurs in one of the factors under which a system is in equilibrium, the system will adjust itself so as to tend to annul, as far as possible, the effect of the change". The factors which affect complex formation in solution are the active concentrations in the solution, the temperature of the solution and the solvent used.

6.3.1 Effect of active concentrations

The departure of a solution from ideal behaviour is usually represented in terms of a property known as the activity as seen in equation 6.1. This activity is related to the actual concentration in solution by a quantity known as the activity coefficient. If the concentration of a solution is C_1 moles, it is possible to express its activity a_1 by the relationship:

$$a_1 = f_1 c_1$$

where f_1 is the activity coefficient.
The value of the activity coefficient is dependent on the total concentration of ions in solutions or, the "ionic strength" (32) which is given by the relationship:

$$\mu = \Sigma c_i z_i^2$$

where z_i is the valency of the ions.

In a solution of ionic strength μ, Debye and Huckel showed that the activity coefficient f_i can be given the relation:(32)

$$\log f_i = \frac{A_{zi}^2 \sqrt{\mu}}{1 + Ba \sqrt{\mu}} \quad ..$$

The definition of the terms in this equation are given in appendix 2. Although the above equation predicts a decrease in the activity coefficient with increase in ionic strength, in practice it is found that this only holds for ionic strength up to about 0.1 . Beyond this value the activity coefficient decreases more slowly, passes through a minimum and then increases with ionic strength. Allowance for this can be made by adding a term proportioned to μ : thus,

$$\log f_i = \frac{A_{zi}^2 \sqrt{\mu}}{1 + Ba\sqrt{\mu}} + C'\mu$$

where C' is an empirical constant and can only be evaluated from experimental values.

The value of C' is entirely dependent on the type of ions in solution. As seen in appendix 2 the equilibrium constant for any reaction can be related to the ionic strength. e.g. for the dimerisation of the chromate ion at low ionic strengths (up to about 0.1 M):

$$\log K_d = \log K_d^o + \frac{A' \sqrt{\mu}}{1 + B'\sqrt{\mu}} .$$

At higher ionic strengths Lukkari (39) showed experimentaly (at 25^{0}C) that,

$$\log K_d = \log K_d^o + \frac{A'\sqrt{\mu}}{1 + B'\sqrt{\mu}} + C''\mu$$

where $C'' = 0.06$.

If the last term is neglected, upto ionic strengths of 0.5 M , only a 5% error is introduced in the value of K_d. At ion strengths of 1.0 M an error of about 10% is introduced. This is probably within the experimental error of the measurement of K_d.

6.3.2 Effect of Temperature

The effect of temperature on the equilibrium constant is dependent on whether the reaction is endothermic or exothermic as seen from the following mathematical relationships, from equation 6.8.

$$\Delta F^{\circ} = -RT \ln K_{o} \qquad .....6.9$$

Differentiating equation 6.9 at constant pressure and substituting the Gibbs - Helmholtz equation (106)

$$\Delta F^{\circ} = \Delta H^{\circ} + T\left(\frac{\partial \Delta F^{\circ}}{\partial T}\right)_{P}$$

into 6.9 gives:-

$$\frac{d \ln K_{o}}{dT} = \frac{\Delta H^{\circ}}{RT^{2}}$$

This is known as the Van't Hoff equation and ΔH° is the heat of reaction at constant pressure.

6.3.3 Effect of Solvents

Interionic forces in solids are of great magnitudes however in solutions a number of factors reduce these forces to enable the existence of ions.

A major factor is the "dielectric constant" which is a result of an electric field being set up by the polarity of the solvent molecules. Water is distinctive from other solvents in having a very high dielectric constant ~ 79 at 25°C compared with 24 for ethyl alcohol and 4.2 for diethyl ether. The higher the dielectric constant of a solvent the easier it is for ions to be separated.

A second factor can be seen from the fact that although, a number of solvents have a higher polarity than water their dielectric constants are not as high as that for water. This can be attributed to random thermal vibrations which tend to disrupt the orderly alignment of polar molecules between ions in most solvents, thus reducing the observed value of the dielectric constant. Where as, in the case of water hydrogen ion banding between the slightly positive hydrogen of one molecule and the lone electron pairs of the oxygen of a neighbouring water molecule, aids the alignment of the water molecules thus, counteracting the effect of the random thermal vibrations.

Another factor which accounts for the existence of ions in solution is the solvation energy which results from the net attractive force between the ions and the dipole of the solvent molecules.

6.4 Measurement of Equilibrium Constants

The most obvious method of measuring an equilibrium constant is to allow the system to come to equilibrium and to analyse the resulting solution for each of the chemical species present without disturbing the equilibrium. Unfortunately, most analytical methods involve reacting the species to be analysed with some other compound, and hence disturbing the equilibrium. However, there are a number of methods by which the concentrations of some (or all) the species may be measured without disturbing the equilibrium.

6.4.1 Rapid Analysis

It may be possible to use conventional analytical methods to determine the equilibrium composition of a system if the system departs very slowly from equilibrium, and the analysis can be performed quickly. Bjerrum (107) in 1914 used direct chemical analysis to determine the equilibrium constants for the complexes of trivalent chromium with thiocyanate ion. He used a series of precipitations and extractions to separate the various complexes. However, most systems reach equilibrium very quickly and seperations such as Bjerrums cannot be used.

6.4.2 Spectrophotometric Methods

Beer and Lambert have proposed laws of light absorption well known in their combined form as the Beer-Lambert Law of light absorption. This states that the fraction of incident light absorbed is proportional to the number of molecules in its path. That is, if a substance is dissolved in a solvent, the absorption by the solution will be proportional to its molecular concentrations, provided the solvent itself does not absorb light in that region. This law is expressed as:

$$\text{Absorbance (or optical density)} = \log_{10}\frac{I_o}{I} = eCl$$

where I_o is the incident light intensity

I the transmitted light intensity.

e is the absorption coefficient.

C concentration.

l path length.

Light absorption or spectroscopy is a powerful method for analysis of solutions in terms of the simplicity of the basic calculations of the Beer-Lambert Law. In single component solutions as long as no reactions take place (such as dissociation, ionisation or association) the light absorbed is directly proportional to the concentration. In multicomponent solutions with no reactions occurring, the total absorption is equal to the sum of the absorbtion of the individual species (88, 108, 109). Mixtures of substances can therefore be analysed providing one of the two following conditions apply:-

a) If the mixture of substances have absorption maxima at widely separated wavelengths they may be readily analysed using the Beer's Law for each component independently,

or

b) if the mixture of substances absorbed in the same wavelength region they may still be analysed from observations of the absorption of the mixture at a number of suitable wavelengths. For this second condition it is necessary that the components absorb independently and that the extinction coefficients of each pure component is known. The measured optical density at any wavelength in this case can therefore be given by the equation:

$$D = \log I_o/I = (e_{\lambda 1} c_1 + e_{\lambda 2} c_2 + \ldots.) \, l. \qquad \ldots..6.10$$

In the literature there are a number of papers dealing with the general analysis of multicomponent systems by spectrophotometry (88, 110, 111, 112). However, they all depend on the knowledge of the coefficient of molar absorptivity of the individual components.

This, as seen from equation 6.10, is a straight forward solution of a series of equations depending on the number of components. However, in many equilibria in solutions it becomes very difficult to separate out individual species for separate measurements of $e_{\lambda x}$, as in the case of Cr^{+6} complex's in solution (104), without making assumptions and pushing the equilibria to the limits. Even then it is not possible to isolate all the species that could arise in any one set of conditions.

6.4.3 Electrical Methods

The two most commonly used electrical methods for measuring concentrations of electrolytes are the potentiometric method and the conductivity method. Both these methods depend on the presence of ions in solution.

a) Potentiometric method: This method is dependent on the fact that the potential of a reversible electrochemical cell is directly related to the activity of the ions involved in the cell reaction. Harned (113) et al. give a good example in the study of weak acids. Using the following electrochemical cell:

$$Pt / H_{2(g)} / HA, A^-, H^+, Cl^- / A_gCl_{(s)} / A_g,$$

with an overall cell reaction:

$$AgCl\ (s) + \frac{1}{2}\ H,\ (g) \rightleftharpoons Ag + H^+ + Cl^-\ (E^o = +\ 0.222\ \text{volts})$$

and according to the Nernest equation:

$$E = E^o - 0.0592 \log [H^+][Cl^-].$$

By holding the activity of the chloride ion constant with potassium chloride and changing the concentrate of the weak acid the concentration $[H^+]$ will vary according to:

$$K_a = [A^-][H^+] / [HA]. \qquad .....6.11$$

Hence, measurement of the potential difference across the cell yeilds the value of K_a.

6.4.4 Conductivity Methods:

Ions in solution conduct electricity, therefore, the conductance of a solution can be used as a measure of the number of ions in solution. When the concentration in the solution approaches zero the activity approaches 1, and hence the conductance can be considered as a measure of the total number of ions in the system. The equivalent conductance of a system can be defined as:

$$\lambda_e = 1000\ x / cz, \qquad .....6.12$$

where x = is the specific conductance of the system, and z = the total number of +ve ions in the system from one formula unit of salt.

The advantages and disadvantages of these two methods were discussed in section 3.4.3.

6.5 The study of Cr^{+6} equilibria in solutions

Sherrill et al, used the fact that the freezing point of a solution of Cr^{+6} will fall due to the presence of dichromate ion and hydrochromic acid to study the equilibrium:

$$2HCrO_4^- \rightleftharpoons H_2O + Cr_2O_7^{=}.$$

They did this by studying the freezing point of various solutions of dichromate. By calculating the Van't Hoff factor (i), which is the lowering in freezing point divided by the calculated freezing point had there been no dissociation of the dichromate salt, and solving a series of simultaneous equations they obtained values of $70 > K_d > 25$ at 25°C. However, they found that their calculations were very sensitive to error and varation of < 3% in the value of i changed the value of K_d by as much as factor of the value of the dimerization constant.

Neuss and Rieman (29) studied the equilibria between mixtures of potassium chromate and potassium dichromate to determine the equilibria constants:

$$K_2 = \frac{[H^+]\,[CrO_4^{2-}]}{[HCrO_4^-]} \qquad .....6.13$$

and

$$K_d = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} \qquad .....6.14$$

They assumed that all the potassium chromate formed only chromate ions and that only potassium dichromate gave rise to the $HCrO_4^-$ and $Cr_2O_7^{=}$ ions

Substituting these two assumptions into equations 6.13 and 14 they obtained:

$$[H^+]^2 \ D = \frac{1}{n} \ (K_2^2 \, K_d \ - \ K_d K_2 \, [H^+]) \qquad ....6.15$$

where D is the concentration of $CrO_4^{=}$ ion, n the ratio of the chromate to dichromate salt, and $[H^+]$ the hydrogen ion concentration obtained from pH measurements. By plotting $[H^+]^2 D$ vs. $[H^+]$ values of K_2 and K_d were obtained as 3.2×10^{-7} and 43.5 respectively (25°C, $\mu = 0$). However, their basic assumption that no $HCrO_4^-$ ions are formed from the potassium chromate salt is questionable as all their pH measurements were in the region of pH = 6. In this region (as Ramette(114) showed in a paper published in 1972) the $CrO_4^{=}$ ions and $HCrO_4^-$ are at least in equimolar proportions and it is probable that $HCrO_4$ may even be in greater proportion.

Tong and King (30) used spectrophotometry to study a number of equilibria:

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad ....2.3$$

$$2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{=} + H_2O \qquad ....2.1$$

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^- + H^+ \qquad ....2.4$$

They took their measurements at the wavelengths 370, 380, 390 and 400 nm as the variation in absorption with concentration was

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significant at these wavelengths. Their method of experiment was based on assuming dimer monomer relations. Using concentrations varying from 3.6×10^{-5} - 2.7×10^{-3} M Cr^{+6} the first part of their experiment was to analyse the following relations:

$$\bar{e} = e_{11}(1 - \alpha) + \frac{1}{2} e_{20}\alpha \qquad .....6.16$$

and

$$2K_dC_T = \alpha / (1 - \alpha)^2$$

where $\bar{e}$ is the overall coefficient of molar absorptivity and e_{11} and e_{20} the coefficients of absorptivity of $HCrO_4^-$ and $Cr_2O_7^=$ respectively. By an optimisation technique a value of $K_d = 35.5$ was obtained (25°C, $\mu = 0$).

It was noticed that this value of K_d and e_{11} varied with pH and it was therefore found necessary to consider H_2CrO_4 and $HCr_2O_7^-$. From the calculations K_1 was found to be 1.22 and $K_{d2} = 0.85$.

Davies and Prue (33) used a similar method to that of Tong and King and they obtained values of $K_d = 37.7$ at 20°C and 33.0 at 25°C at ionic strength zero.

Sasaki (115) studied the equilibria of the ions CrO_4^{2-} and $Cr_2O_7^=$ by both EMF and spectrophotometric methods at 25°C and ionic strength $\mu = 3$. His work was by measuring the hydrogen ion concentration resulting in changing the concentrations of the acid and the chromate salt, in a cell of the following structure:

Ag	AgCl	0.01M $AgClO_4$	2.99M $NaClO_4$	3M $NaClO_4$ Cr^{+6}solution	glass or silver chromate electrode.

His results gave values of $K_d = 35.9$ at ionic strength $\mu = 0$ which is slightly lower than the values obtained by Davies and Prue. A value for $K_2 = 2 \times 10^{-7}$ was also obtained which as seen from table 6.1 is lower than those for most other workers. In these results errors could have arisen due to ions used to keep the ionic strength constant. These errors he believes were overcome when using the spectrophotometric method of analysis. In the spectrophotometric method he measured the absorption of solutions when varying the $[H^+]$ and the chromate salt concentrations. He found for every concentration of chromate salt and at pH < 3 the overall coefficient of absorption $\bar{e}$ did not vary and he took this to be the coefficient of molar absorptivity of $HCrO_4^-$ even though the coefficients of absorptivity did change with the change in the concentration of the chromate salt. This indicated the presence of the dichromate (or another) ion. Therefore, although his spectrophotometric results agree with the EMF results they could be questionable.

Haight et al.(38) studied the following equilibria spectrophotometrically:

$$H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4 \qquad .....2.3$$

$$H^+ + Cl^- + HCrO_4^- \rightleftharpoons CrO_3Cl^- + H_2O. \qquad .....2.7$$

They assumed that at certain pH ranges they could isolate the ion $HCrO_4^-$ and by using comparison techniques were able to determine the equilibrium for the above two reactions constants. Their value for $K_1 = 0.11$ at ionic strength $\mu = 0$ is very much lower than that of Tong and King. This is possibly accounted for by their assumptions that only $HCrO_4^-$ ion existed in the reference solution, and by the fact that they used values of the coefficient of molar absorptivity of H_2CrO_4 obtained from data at ionic strength $\mu = 3.0$ to obtain their values at

μ = 1.0.

Tong & Johnson (40) determined the equilibrium constant for CrO_3Cl^- in solutions of Cr^{6+} with HCl acid. They kept a constant hydrogen ion concentration and varied the chlorine ion concentration. They then related the chlorine complexed ions to the uncomplexed ions by a constant K_G = (uncomplexed Cr^{+6}) (Cl^-) (complexed Cr^{+6})....6.17 They obtained values of K_G which varied with the $[H^+]$ and by plotting K_G vs 1 / $[H^+]$ they deduced values for interpolated K_c and K_2 at temperatures of 15, 25 and 35°C. (see table 6.1). Although their value of K_c at 25°C is lower than that given by Haight et al.(28) (6.2 compared with 9.6) their method seems to be a more rigorous one.

Jain et al.(47) studied the protonation equilibrium of CrO_4^{2-} and the dimerisation equilibrium by looking at the effect of the sodium chromate salt, at various conditions, on the transition temperature of Glauber's salt (sodium sulphate decahydrate). Although their results were similar to results by other workers (K_d = 231 and $K_2 = 1.1 \times 10^{-6}$ at 32 °C) they were not directly comparable as the ionic strengths were very high (ca. μ = 10) and the simple Debye Hückel relationship tends not to hold at such high ionic strengths, thus making it rather difficult to reduce the values to zero ionic strength.

Linge and Jones (116), using a method similar to that of Tong and King (30) and Davies and Prue (33), studied the dimerisation equilibrium constant in the temperature range 15 - 45°C. Their results are given in table 6.1 and show a definate decrease in the value of K_d with increase in temperature. Their value for K_d (25°C, μ = 0) is consistent with that given by Tong and King (30). In a further paper Linge and Jones (36) carried out spectrophotometric measurements on solutions of chromate salts around 6 < pH < 7 to determine the first protonation equilibrium constant K_2 in the temperature range 15 - 45°C. Their method of calculation depended on the coefficients of molar absorbtivity which they had previously (116) determined. Their results for the values of K_2 are given in table 6.1 and show a decrease in K_2 with increase in temperature. Their value (at 25°C) was consistent with that of Howard et al.(35), and were also consistent with their earlier results obtained by the potentiometric technique (see table 6.1).

Galia et al.(44) used a potentiometric technique to determine the dimerisation constant at $\mu = 3$ and the temperature range 5 - 65°C. Their results were consistent with those obtained spectrophotometrically by Linge and Jones (36). However, they found difficulties with their measurements at $[Cr^{+6}] < 10^{-3}$ M which they attribute to impurities formed from the dissolution of their glass apparatus.

Lukkari (39) used spectrophotometry to study the effect of ionic strength on the dimerisation equilibrium constant. He used the same method as Tong and King (30) for the evaluation of K_d (at 25°C, μ = 1.0, 0.5 and 0.25). He fitted these values to the equation (similar to that used by Davies et al.(117) in their work on the dissociation of H_2SO_4):

$$\log K_d = \log K_d^o + \frac{1.01\sqrt{\mu}}{1 + 1.6\sqrt{\mu}} + C\mu \qquad .....6.18$$

where $\log K_d^o = 1.54$ (K_d^o = 35, 25°C) and the empirical constant C = 0.06 (25°C). Using the same mathematical and experimental technique as in the evaluation of K_d, Lukkari went on to evaluate K_1 by evaluating another constant,

$$K^1 = \frac{[\text{Total Dimers}]}{[\text{Total Monomers}]^2}$$

in solutions of acid concentrations > 1.0 M. K_1 was then evaluated from:

$$K_1 = \frac{[H^+]}{\sqrt{K_d/K^1 - 1}} \qquad \text{.....6.19}$$

In evaluating K_c Lukkari treated measurements from solutions containing chlorine ions in the same way as above and then calculated the value of K_c from the equation:

$$K_c = \frac{\sqrt{(K_d / K')} - 1}{[H^+]\,[Cl^-]} - \frac{1}{K_1\,[Cl^-]}$$

His value for K_c was consistent with that obtained by Tong. and Johnson (40).

CHAPTER 7

Determination of Equilbrium Constants

7.0 Introduction

As seen in chapter 6, although a number of researchers have measured the equilibrium constants in aqueous solutions of Cr^{+6}, there is a considerable variation in the reported values of these constants. An attempt has been made here to estimate some of these constants independently and also to evaluate some of the reported methods used. The two most commonly used methods for determining the equilibrium constants in Cr^{+6} solutions were the electrical methods (28, 113, 115, 116, 117) and the spectrophotometric method (30, 33, 115, 36, 116, 39) as described earlier.

Due to the fact that a spectrophotometer (SP1800) was available in the department and that the measurement of the absorption of light in solutions is straight forward, and involved less risk of interference from other ions in the solution when correct wavelengths are chosen, the choice of the spectrophotometric method was a matter of course.

Using spectrophotometry, the simplest way to determine the constants for the equilibrium in a Cr^{+6} solution would be to apply the Lambert Law: " The absorption of a solution is the sum of the absorption of the individual species, at any one wavelength." From the literature the following species are assumed to exist in acidic Cr^{+6} solutions (see section 2.3) in significant amounts.

CrO_4^{2-}, $HCrO_4^-$, H_2CrO_4, $Cr_2O_7^{2-}$, $HCr_2O_7^-$, $H_2Cr_2O_7$, and also CrO_3Cl^-

in the presence of chlorine ions. A mass balance may be written (mole/dm^3):

$[Cr] = C_T = [H_2CrO_4] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] + [CrO_4^{2-}] + [CrO_3Cl^-] +$ $2[H\ Cr_2O_7^-]$, or, in simplified notation:

$$[Cr^{6+}] = [A] + [B] + 2[C] + [D] + [E] + 2[F]. \qquad ......7.1$$

By the Beer-Lambert Law, the total absorption per unit length of solution for any given wavelength (λ) is:

$$A_\lambda = \bar{e}_\lambda C_T = e_{\lambda A}[A] + e_{\lambda B}[B] + e_{\lambda C}[C] + e_{\lambda D}[D] + e_{\lambda E}[E] + e_{\lambda F}[F]. \qquad .....7.2$$

Once the coefficients of molar absorptivity ($e_{\lambda X}$) are known the concentrations of various species in solution may be determined and hence the equilibrium constants. In fact, as is shown in the following sections determining the $e_{\lambda X}$ values is not straight forward, and results in the evaluation of some of the K values as a means to this end instead of vice-versa.

7.1 Materials and Equipment

7.1.1 Materials

a) De-ionised water; this was freshly prepared and used in all spectrophotometric experiments.

b) Hydrochloric acid; concentrated Analar grade acid was obtained from Hopkin and Williams (density 1.16 g/cm^3, 31 - 32% assay) was used and diluted to 1M according to the method outlined by Vogal(141); the actual strength was then determined by titrating against freshly prepared Borax solution using methyl orange as an indicator.

c) Nitric acid; concentrated Analar grade acid obtained from B.D.H. was used (sp. gr. 1.42 at 20°C, 69 - 71% assay): maximum limit of chloride, phosphate, silicates and sulphate $\not>$ 3.5 p.p.m.

d) Potassium chromate; Analar grade crystals obtained from Hopkin and Williams (> 99.5% assay. Maximum limit of insoluble matter ⊁ 0.003%).

e) Potassium nitrate; Analar grade crystals obtained from Hopkin and Williams (99.5% assay. Maximum limit of impurities ⊁ 0.003%).

f) Ammonia solution; Reagent for atomic absorption spectrophotometry obtained from Hopkin and Williams (sp. gr. 0.88 at 20°C assay 35%).

7.1.2 Equipment

Samples were made up in grade A volumetric flasks of volumes ranging from 1 dm^3 to 0.1 dm^3. The pH was measured with a Corning pH meter model 119, with a digital display readout, range 0 - 14 pH with a resolution of ± 0.01 pH and accuracy of ± 0.01 pH. Drift was found to be typically less than 0.005 pH/ K. It has a manual temperature compensator over the range 0 - 100°C. A Corning glass electrode in combination with a Corning calomel electrode (No. 476109) were used with the pH meter.

The absorptions were measured with a Pye-Unicam SP1800 UV Spectrophotometer, a description of which is given in section 4.1.2.

7.2 Experimental

All experiments were carried out by volumetrically preparing samples of various concentrations of pH and ionic strength from master solutions of potassium chromate, nitric (or hydrochloric acid), and potassium nitrate. The absorption of these solutions were measured in the SP1800 spectrophotometer. The procedure is described in the next section.

7.2.1. Preparation of Solutions

a) Solutions of potassium chromate (0.01M) were prepared as needed by weighing out accurately 1.942 g of potassium chromate,

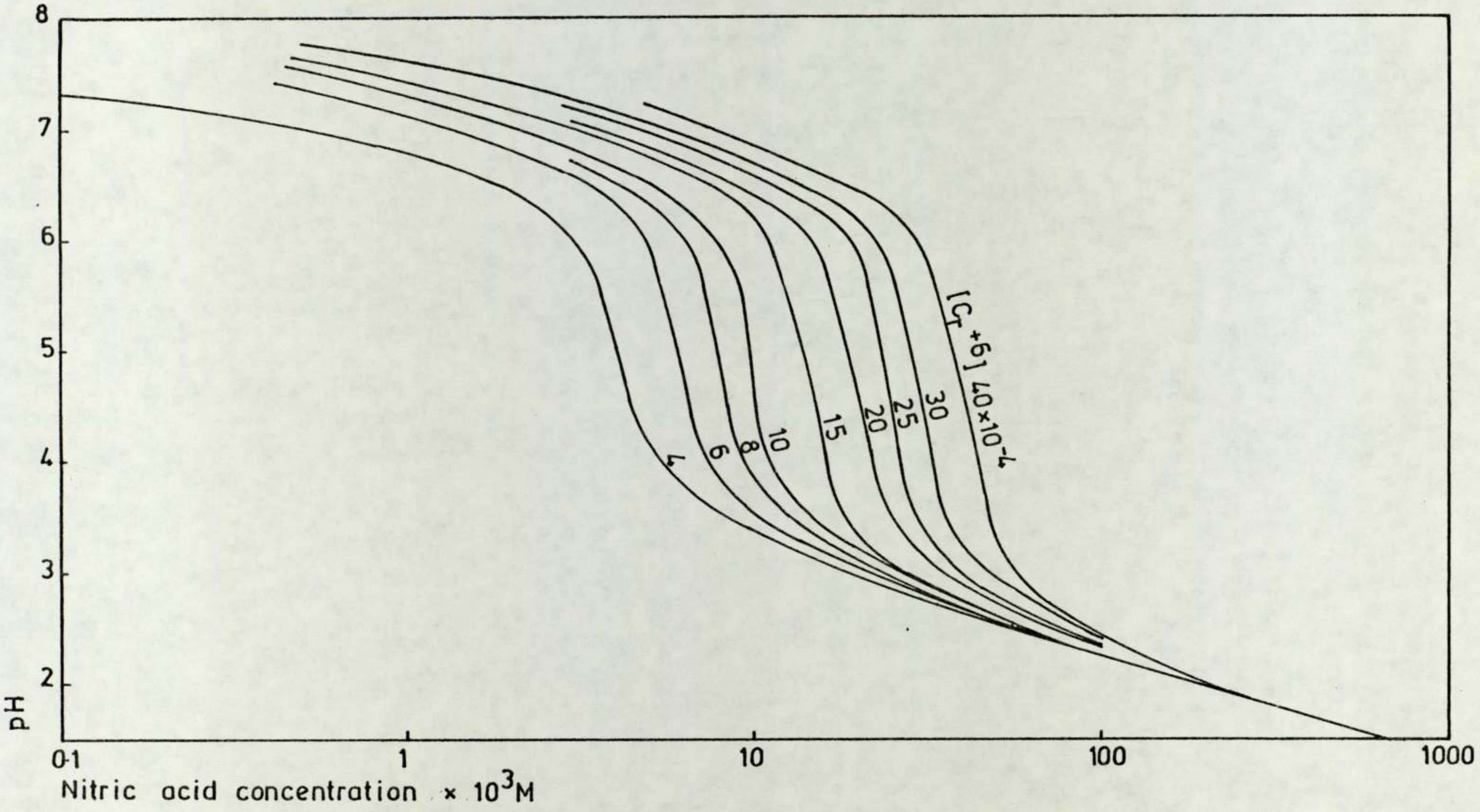


FIGURE 7:1 plot of change of pH of solutions of C_r^{+6} and nitric acid

dissolving in deionised water in a 1 dm^3 volumetric flask and making up to the mark.

b) Solutions of potassium nitrate (1M) were prepared as needed by weighing out accurately 1.11 g of salt and making up into solution in a 1 dm^3 volumetric flask.

c) Nitric and Hydrochloric acids of approximate strength 1M were first prepared by the method outlined by Vogal (141), they were then standardised against 0.01M borax solutions using methyl red as an indicator. Appropriate amounts were then pipetted from the 1M solutions to make up acid solutions of known strength ranging from 0.1M to 0.001M in 1 dm^3 flasks.

7.2.2 pH Calibration

Initial experiments showed that adding a constant amount of nitric acid (1 cm^3 of 0.1M HNO_3) to a series of 0.1 dm^3 solutions with different Cr^{+6} concentrations (varying from 2×10^{-4} to 5×10^{-3} M) gave solutions in the range $6.5 > pH > 3.2$.

This indicated that to be able to measure the effect of the increase in Cr^{+6} concentration without changing the pH it would be necessary to add different amounts of acid to the solution. It was, therefore, necessary to set up an experiment to determine the pH of solutions with different Cr^{+6} concentrations and nitric acid concentrations.

Solutions were prepared by pipetting 4 ml of 0.01 M potassium chromate solution into a 0.1 dm^3 volumetric flask. To these flasks varying amounts of nitric acid were added as shown in appendix 9. These solutions were left to stand for some 20 minutes in a water bath kept at 20°C. The pH of these solutions was then measured and the results are presented in appendix 9 for 4×10^{-4} M $< [Cr^{+6}] < 4 \times 10^{-3}$ M. The results plotted on a log-linear graph (figure 7.1) were used in absorption experiments to make up solutions of known pH. These results also indicate that in the range 2< pH <8 the protonated Cr^{+6} ions are not directly proportional to the unprotonated Cr^{+6} ions but for pH<2 the protonated Cr^{+6} ions are proportional to the unprotonated Cr^{+6} ion.

7.2.3 Ionic Strength Calibration

To keep the ionic strength constant in a series of solutions undergoing spectrophotometric measurements, varying amounts of potassium nitrate solution (1M) were added. This was necessary because each flask contained a different amount of Cr^{+6} and acid. The volume of potassium nitrate needed in each case was determined by calculation using the general ionic strength formula:

$$\mu_i = \frac{1}{2} \Sigma C_i Z_i^2$$

where μ is the ionic strength

C_i concentration of ionic species i

Z_i charge on ionic species i

Example:- To make a solution of $\mu = 0.25$:
Assuming that all the Cr^{+6} was in the form of CrO_4^{2-}, that the hydrogen ion concentration was constant at $[H^+] = 1 \times 10^{-5}$ M for $[Cr^{+6}] = 4 \times 10^{-4}$ M and that the required final ionic strength $\mu = 0.25$ M:-
Let x = concentration of KNO_3 needed to make the final solution $\mu = 0.25$ (assuming 100% ionisation):

?

$$0.25 = \frac{1}{2} ([CrO_4^{2-}] \times 4 + [K\ ] \times 2 + [H^+] + [NO_3^-] + 2 \overset{x}{\ } x) \qquad ....7.3$$

x x ?

$$\therefore \; 0.25 = \frac{1}{2} (4 \times 10^{-4} \times 4 + 4 \times 10^{-4} \times 2 + 1 \times 10^{-5} + 1 \times 10^{-5} + 2x)$$

hence, x = 0.249 M. in 1 dm³ = 249 cc of 1M
or 24.9 — — in 0.1 dm³ ✓

Therefore 24.9 cm^3 of 1M KNO_3 need to be added and the solution made up to 0.1 dm^3. The results for other $[Cr^{+6}]$ and ionic strengths are summarised in table 7.1. No significant difference was found for pH = 6,

Table 7.1: Calculated amount of M potassium nitrate solution to be added to 0.1 dm^3 of Cr^{+6} solution, at pH 5 and pH 6, to keep the stated ionic strength.

to be made up to - ?

Cr^{+6} Concentration (M) x 10^4	Ionic Strength		
	0.10	0.15	0.25
4	9.94	14.90	24.90
6	9.82	14.82	24.85
8	9.76	14.76	24.75
10	9.70	14.70	24.70
15	9.55	14.55	24.55
20	9.40	14.40	24.40
25	9.25	14.25	24.25
30	9.10	14.10	24.10
35	8.95	13.95	23.35
40	8.80	13.80	23.80

therefore, the same results were used for that pH value also.

7.2.4 Preparation of Samples

For all experimental analysis samples of solutions were prepared by pipetting the required amount of potassium chromate solution into a 0.1 dm^3 volumetric flask. To this was added the appropriate amount of acid (HNO_3/HCl), it required to adjust the pH. The amount of acid required was determined by interpolating from figure 7.1. Also added was the appropriate amount of potassium nitrate solution(as determined from table 7.1) to obtain the required final ionic strength. The volumetric flasks were then made up to the mark, shaken well and placed in a water bath at the required temperature (usually 20, 40 or 60°C) for 30 minutes. The pH of the sample was then measured, and if it varied from the required value by more than $\pm$ 0.02 pH units the sample was discarded and reprepared.

7.2.5 Absorption Measurements

The technique for absorption measurements was similar to that described in section 4.1.3, except that only the graph plotter was used and the absorption spectra of the solutions were only recorded between the wavelengths 260 and 390 nm, as shown in figure 7.2. It was noticed that when high concentrations of nitrate ions were used low energy output was registered in the wavelength regions, 280 to 310 nm, causing unstable measurement in that region, figure 7.2. This is probably due to the fact that the nitrate ion absorbed strongly in that region, figure 7.3.

The setting for the zero reading was slightly complicated in comparison to the method described in section 4.1.3. The zero reading shifts slightly as the wavelengths are scanned. It was important to record the zero reading before every test as the error (example given in table 7.2) could be as much as 10% of the absorption values for low concentrations.

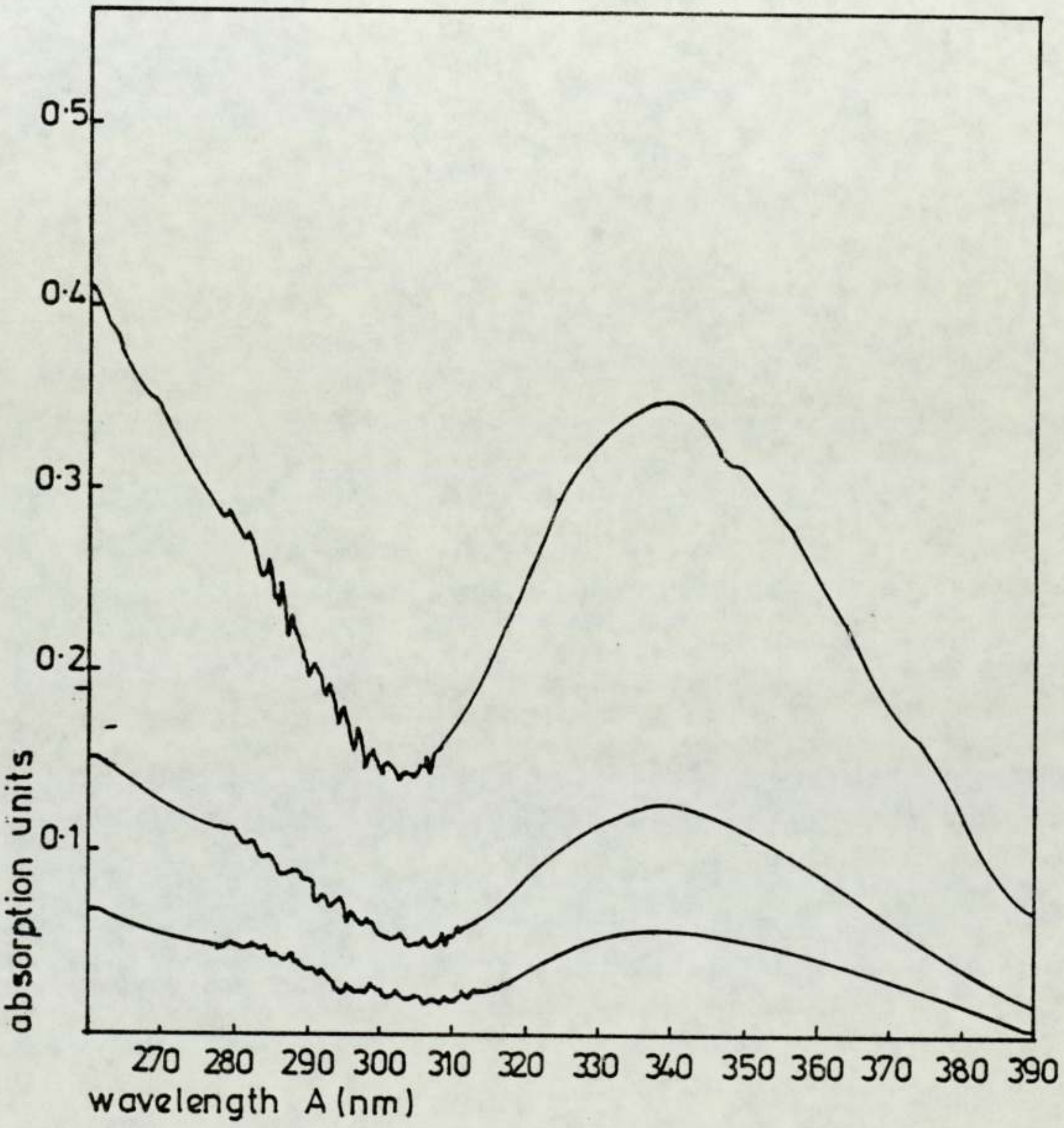


FIGURE 7:2 plot showing absorption curves of K_2CrO_4 in acid solutions at concentration 4×10^{-4}, 8×10^{-4}, and 20 10^{-4}M. It also shows an Interference in the range 280 – 310 nm

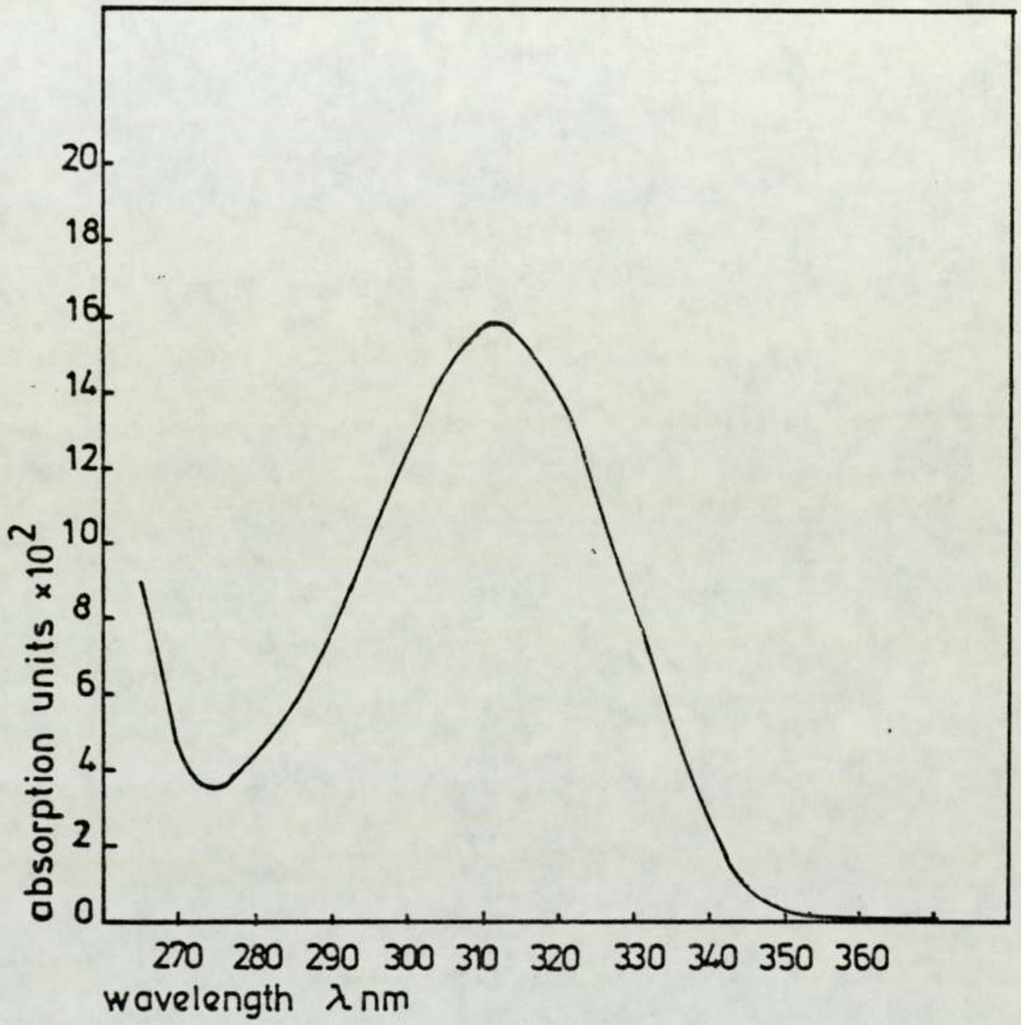


FIGURE 7:3 absorption curve for an 0·1M potassium nitrate solution measured at 20°C, through a 2mm path length cell, against reference solution of de-ionised water

Table 7.2: Zero Readings for $295 < \lambda < 430$ nm
at 5 nm intervals.

λ (nm)	Reading (Absorption Units)	λ (nm)	Reading (Absorption Units)	λ (nm)	Reading (Absorption Units)
295	0.008	345	0.000	395	0.001
300	0.008	350	- 0.001	400	0.001
305	0.008	355	- 0.001	405	0.001
310	0.007	360	- 0.001	415	0.000
326	0.006	370	0.000	420	0.000
325	0.001	375	0.000	425	0.000
330	0.001	380	0.001	430	0.000
335	0.000	385	0.002		
340	0.000	390	0.002		

Absorption values were obtained by reading the plotted graphs at 5 nm intervals; the values were then corrected for the zero errors to give the actual absorption A_{λ}, for the solution over the wavelength range. Each value of A_{λ} was then divided in path length of the solution and the $[Cr^{+6}]$ concentrations of the solution to give the overall coefficient of molar absorptivity, $\bar{e}_{\lambda}$.

Example:

For a solution of 4×10^{-4} M Cr^{+6} (pH = 4.92, $\mu = 0.25$) the absorption reading is $A_{295} = 0.105$. From table 7.2. the zero reading at that wavelength = 0.008 therefore $A_{295} = 0.105 - 0.008 = 0.097$, and $\bar{e}_{295} = 0.097 / (2 \times 0.0004) = \underline{121.2}$

The values of $\bar{e}_{\lambda}$ for all experiments are tabulated in appendix 10.

7.3 Determination of the Coefficients of Molar Absorptivities, e_{λ}

In evaluating the coefficients of molar absorptivity of a mixture of ions it is helpful if the individual ions absorbed light at different wavelengths. However, this is not the case with the complex ions of Cr^{+6} in acidic solutions. Figure 7.4. shows that, although in various acid concentrations different spectra are formed, no wavelength is found where only one of the species absorbs light. The method used here was to find pH regions in which only one or two of the complex ions exist and then attempt to separate them mathematically. As seen in section 3.2 a large number of ions are generated in the presence of hydrochloric acid. However, Haight et al.(38) claimed that in the presence of nitric and perchloric acids no similar complex ions are formed. This is probably due to the bigger ClO_4^- and NO_3^- ions being more difficult to attach to the CrO_4^{2-} ion. The use of perchloric acid was not possible as very special facilities are required (118) which were not available. Therefore, in the determination of e_{λ} for ions, other than CrO_3Cl^- and CrO_4^{2-}, solutions containing nitric acid were used.

7.3.1 Determination of $e_{\lambda D}$ for CrO_4^{2-}

It is established in the literature (31, 34, 35, 36) that in basic solutions (pH > 9.0) only the CrO_4^{2-} ion exists and hence for a unit length solution:

$$A_{\lambda} = e_{\lambda D}\,[D] \qquad .....7.4$$

samples of potassium chromate solutions of varying concentrations were prepared as described in section 7.2.4 but, instead of adding acid,

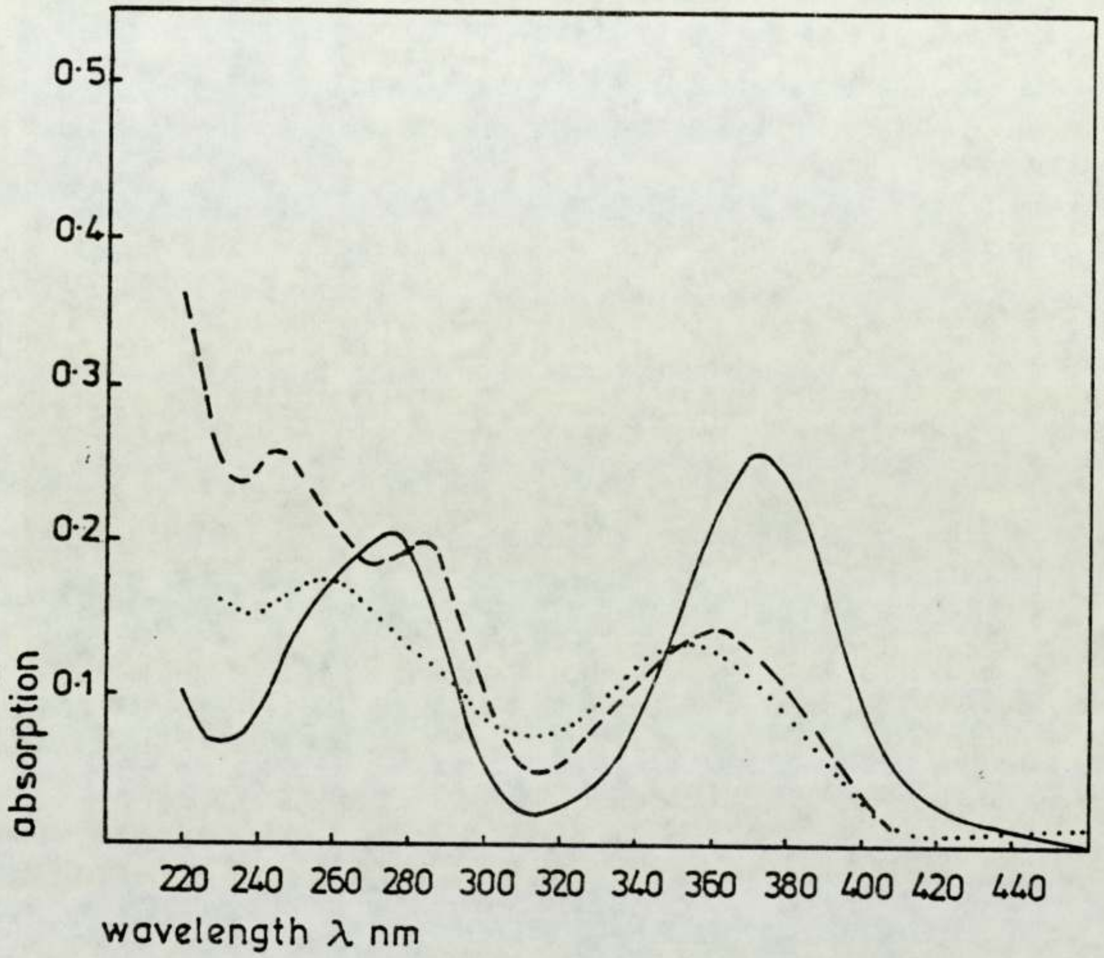


FIGURE 7:4 Plot of the absorption curves of a 5×10^{-4} M potassium chromate in various concentrations of hydrochloric acid and ammonia solution measured at 20°C

In ammonia solution ———

In 0·01 M HCl ....

In 5·0 M HCl — — — —

ammonia solution was added to adjust the pH of the solution to 9 - 10. The absorption of these samples at 20, 40 and 60°C was measured as described in section 7.2.5 and the values of $e_{\lambda D}$ are presented in tables A10.1, 2 and 3 respectively. It can be seen that although the Cr^{+6} concentration was varied from 1×10^{-4}M to 1.5×10^{-3} M no variation in the $e_{\lambda D}$ was found. The values were then averaged and tabulated in table 7.3. It was observed from these values that the varation with temperature was not the same at each wavelength. This confirms the findings of Linge and Jones. (36).

7.3.2 Determination of $e_{\lambda E}$ for $[CrO_3Cl^-]$

It has been claimed in the literature (38) that solutions of Cr^{+6} in hydrochloric acid solutions, with the acid concentrations between 1.0 and 8.0 M the U.V. spectrum for Cr^{+6} is invariant. On this basis the conversion of Cr^{+6} to CrO_3Cl^- was assumed to be essentially complete.

A series of solutions with the same concentration of Cr^{+6} (1×10^{-3}M), but different concentrations of hydrochloric acid from 0.1 M to 5.0 M were prepared as described in section 7.2.4 and the spectra of these were then measured and plotted.

These results (figure 7.5) show that, there is a distinct difference between the spectra of a solution with 0.1 M HCl and solutions with the hydrochloric acid concentration > 1.0 M which are all similar. They also show that only at acid concentrations > 3M was no detectable change noticed in the spectra. Complete conversion of all the Cr^{+6} was, therefore, assumed to take place at an acid concentration of 3M and hence the values of $e_{\lambda E}$ were calculated in the same manner as used to calculate $e_{\lambda D}$ in section 7.3.1. These values are given in table 7.4.

Measurements of $e_{\lambda E}$ at temperatures of 40°C and 60°C proved rather difficult as the spectrum of CrO_3Cl^- changed too rapidly with

Table 7.3: Values of $e_{\lambda D}$ (for CrO_4^{2-}) at 20, 40, and 60°C

Wavelength	Temperature (°C)		
(nm)	20	40	60
295	170.6	174.0	172.0
300	95.0	102.0	103.0
305	53.3	57.0	56.0
310	26.7	38.0	36.0
315	25.6	34.0	31.0
320	29.5	40.0	35.0
325	46.3	57.0	51.0
330	68.3	78.0	75.0
335	105.3	109.0	109.0
340	150.0	155.0	157.0
345	209.4	214.0	221.0
350	275.9	282.0	290.0
355	352.0	355.0	371.0
360	424.6	428.0	450.0
365	485.0	494.0	514.0
370	532.4	532.0	559.0
375	534.6	546.0	568.0
380	521.6	526.0	543.0
385	460.4	466.0	481.0
390	391.8	394.4	401.0
395	307.6	307.0	311.0
400	231.4	230.0	237.0
405	170.9	167.0	173.0
410	114.7	114.8	121.0

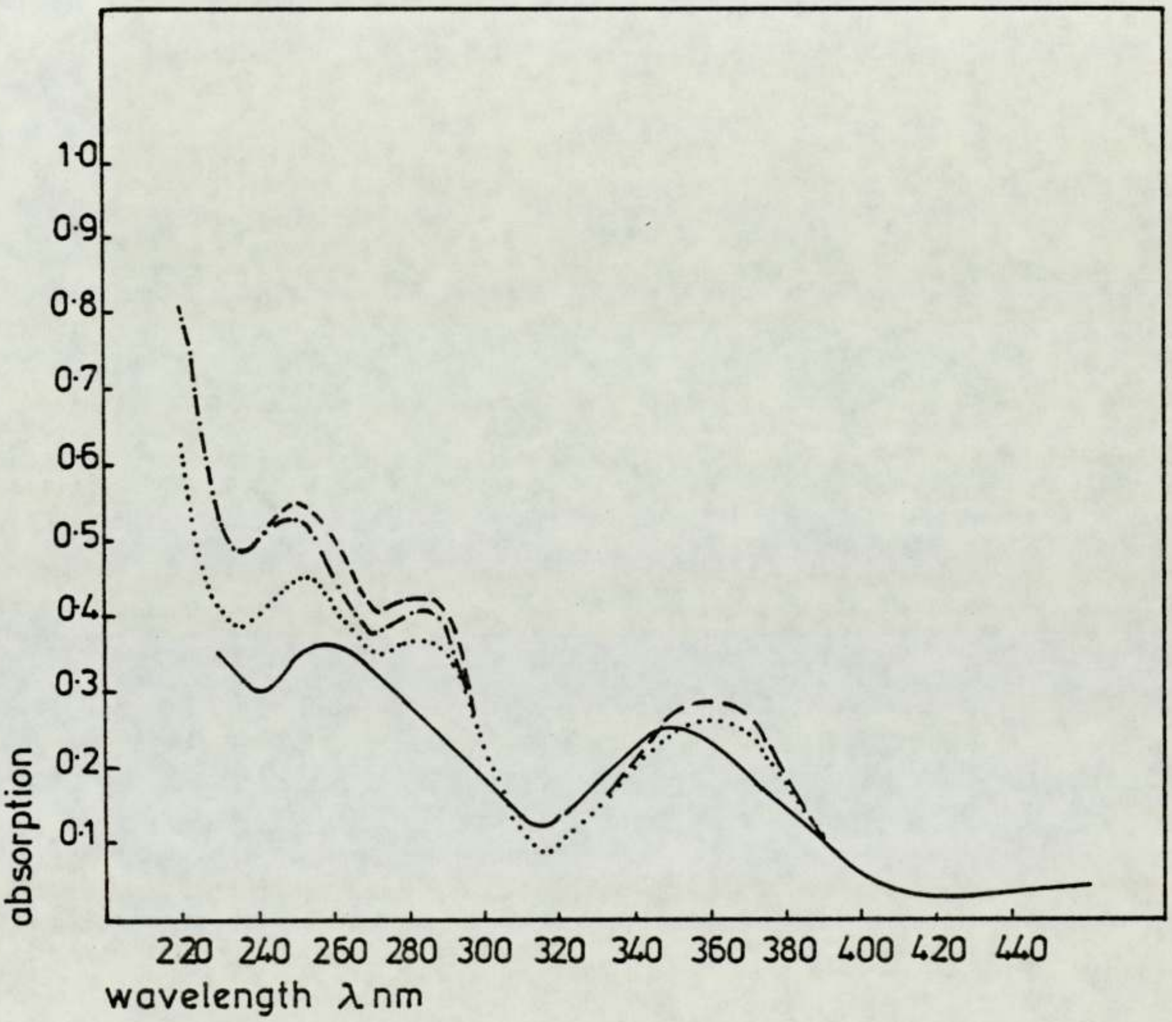


FIGURE 7:5 plot of the absorption curves of potassium chromate in Hydrochloric acid showing the formation of the CrO_3Cl^- ion

0·1M HCl ——————
1·0M HCl ·········
2·5M HCl —·—·—
3M and 5M HCl – – – – –

time (figure 7.6 for 20°C). Lukkari (39) and Haight et al.(38) claim that this is due to the change of Cr^{+6} to Cr^{+3} due to oxidising the Cl^-.

Table 7.4: Values of $e_{\lambda E}$ (for CrO_3Cl^-) at 20°C

Wavelength (nm)	$e_{\lambda E}$	Wavelength (nm)	$e_{\lambda E}$	Wavelength (nm)	$e_{\lambda E}$
230	255.0	300	113.0	370	142.0
235	244.8	305	77.5	375	104.5
240	245.0	310	58.0	380	87.5
245	250.0	315	47.0	385	70.0
250	245.7	320	47.5	390	56.0
255	235.0	325	57.5	395	38.0
260	215.0	330	70.0	400	28.0
265	190.0	335	76.0	405	20.0
270	180.0	340	94.0	410	15.0
275	185.0	345	112.0	415	13.0
280	190.0	350	146.0	420	13.5
285	587.0	355	157.0	425	13.5
290	177.0	360	156.0	430	14.0
295	150.0	365	154.0	435	15.0

7.3.3 Determination of $e_{\lambda B}$ (for $HCrO_4^-$)

7.3.3.1 Theoretical Considerations

For dilute solutions of Cr^{+6} (10^{-4}M) at a pH of 5 - 7 the probable reaction in the solution is

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad .....2.$$

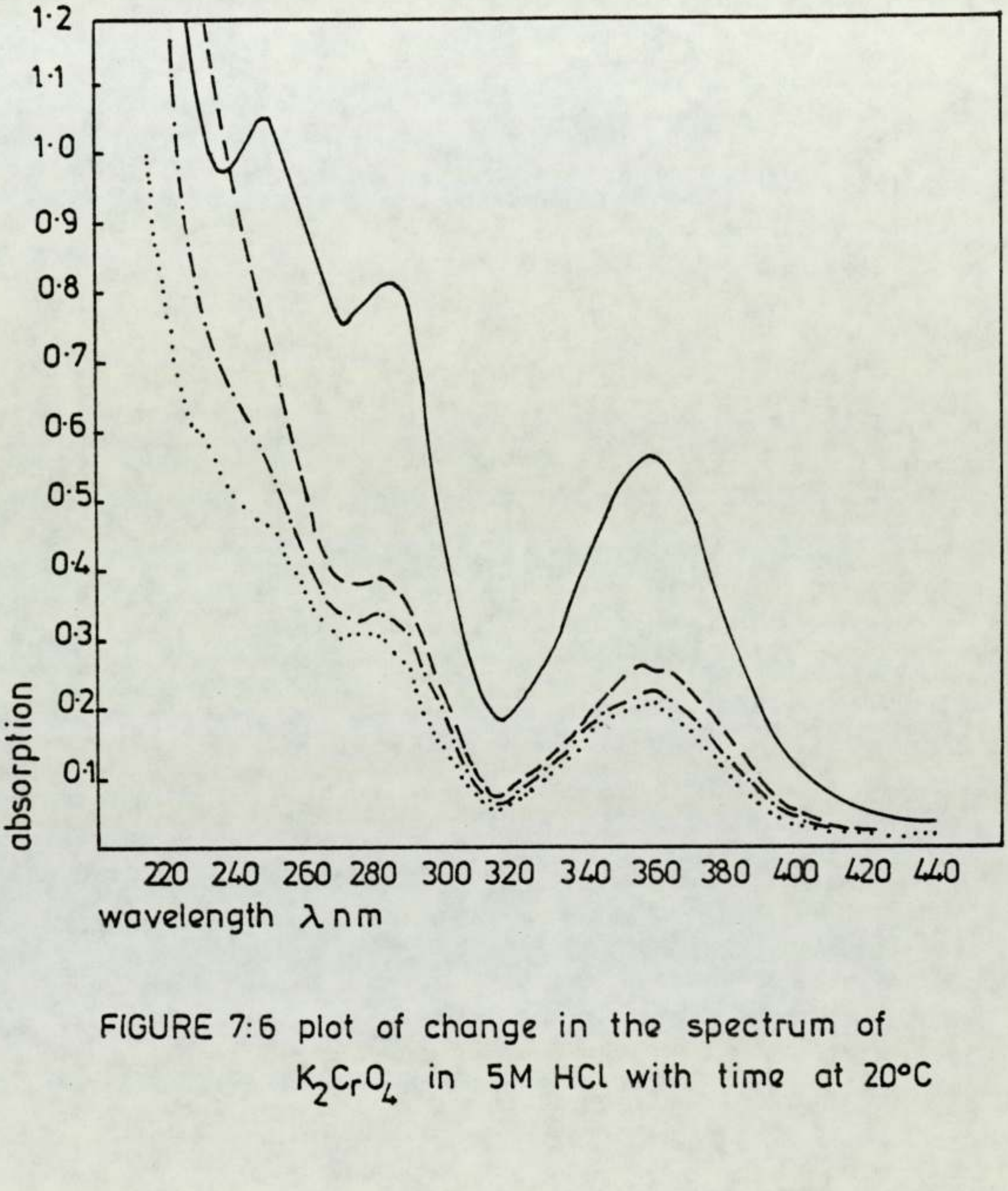


FIGURE 7:6 plot of change in the spectrum of K_2CrO_4 in 5M HCl with time at 20°C

Initial spectrum ————
After one hour – – – –
After two hours –·–·–
After twenty four hours ···········

with $$K_2 = \frac{[H][CrO_4^{2-}]}{[HCrO_4^-]} = \frac{H.D}{B} \qquad ......2.2$$

If this is the case a mass balance on Cr^{+6} would give,

$$C_T = B + D \qquad .....7.5$$

and the absorption balance would be,

$$A_\lambda/1 = e_{\lambda B}\,B + e_{\lambda D}\,D \qquad .....7.6$$

by substituting equation 2.2into 7.5,

$$B = \frac{C_T}{1 + K_2/H} \qquad .....7.7$$

and $$D = \left(\frac{C_T}{1 + K_2/H}\right) \cdot \frac{K_2}{H} \qquad .....7.8$$

substituting for B and D into equation 7.6,

$$A_\lambda\left(1 + \frac{K_2}{H}\right)/1 = C_T\ (e_{\lambda B} + e_{\lambda D}\frac{K_2}{H})$$

$$\therefore\ A_\lambda/C_T 1 = \frac{e_{\lambda B} + e_{\lambda D}\ K_2/H}{1 + K_2/H} \qquad .....7.9$$

if $H \approx 10^{-5}$ and $K_2 \approx 10^{-7}$ (see table 6.1) then $\frac{K_2}{H} \approx 10^{-2}$ and equation 7.9 simplifies (with an error of only 1%) to

$$A/1C_T = e_{\lambda B} + e_{\lambda D}\frac{K_2}{H} \qquad .....7.10$$

Hence, plotting $\frac{A_\lambda}{1C_T}$ against $\frac{1}{H}$ should give a straight line with a slope of $K_2\ e_{\lambda D}$ and intercept $e_{\lambda B}$.

7.3.3.2 Experimental

Two series of solutions of potassium chromate the concentrations ranging from 4×10^{-4} M to 4×10^{-3} M and $\mu = 0.25$ were prepared by the method described in section 7.2.3. The pH of the first series was set at about 5.5 by adding nitric acid in quantities interpolated from figure 7.1. Similarly, the second series of solutions were prepared but with pH set at 4.8. The absorption of these solutions were then measured at 20, 40 and 60°C as described in section 7.2.4 and the results are presented in tables A10.4 - 9.

7.3.3.3 Calculations

To determine the $e_{\lambda B}$ values an average value of K_2 was determined first, then this value was used to obtain the $e_{\lambda B}$ values. The following procedure was adopted.

(e.g.) Temperature 20°C, at the concentration of $Cr^{+6} = 4 \times 10^{-4}$ M

$$pH_1 = 5.52 \therefore \frac{1}{H} = 331131, \quad \bar{e}_{\lambda 1} = 124.7 \text{ (table A10.4) \& } (\lambda = 295 \text{ nm,})$$

$$pH_2 = 4.94 \therefore \frac{1}{H} = 83176, \quad \bar{e}_{\lambda 2} = 121.0 \text{ (table A10.7)}$$

Substituting these two pairs of data points into equation 7.10 yields.

$$e_{\lambda D} K_2 = 1.5 \times 10^{-5}$$

from table 7.3, $e_{\lambda D} = 170.6$ ($T = 20^0C$, $\lambda = 295$ nm),

$$\therefore \quad K_2 = 0.90 \times 10^{-7}.$$

These calculations were repeated and the results are presented in table A10.10. It is noticed from the results that when the value of the slope ($e_{\lambda D} K_2$) was small the values of K_2 varied considerably. It was, therefore, necessary to estimate the expected experimental error in the slope in order to eliminate those values of K_2 which are subject to greatest error.

7.3.3.4 Error Estimate

A relationship for the error in the slope was developed (Appendix 11) which shows that the error is dependent on the hydrogen ion concentration as follows,

$$\Delta(e_{\lambda D} K_2) = 5 \frac{1}{\bar{H}_1} - \frac{1}{\bar{H}_2} \qquad \text{.......A11.10}$$

substituting the values of $\frac{1}{\bar{H}_1}$ and $\frac{1}{\bar{H}_2}$

$\Delta(e_{\lambda D} K_2)$ at 20°C $= 2.0 \times 10^{-5}$

similarly $\Delta(e_{\lambda D} K_2)$ at 40°C $= 2.4 \times 10^{-5}$

and $\Delta(e_{\lambda D} K_2)$ at 60°C $= 1.5 \times 10^{-5}$

This shows that at certain wavelengths the value of the slope ($= e_{\lambda D} K_2$) is swamped by the estimated error. On this basis all the values of K_2 calculated from slopes with an error > 20% were disregarded and the remaining values were averaged as presented in table 7.5. The values of $e_{\lambda B}$ were then calculated from table A10.10 by substituting back into equation 7.10 the value of K_2. The results are given in table 7.6.

7.3.4 Determination of $e_{\lambda C}$ (for $Cr_2O_7^{2-}$)

7.3.4.1 Theoretical considerations

The results of the experiments described in section 7.3.3.2 showed that at a pH ≈ 5.5, in the Cr^{+6} concentration regions studied (table A10.3 - A10.5) the values of $\bar{e}_\lambda$ did not vary significantly with concentration, figure 7.7. While, the results at pH ≈ 4.8 (tables A10.7 - A10.9) the values of $\bar{e}_\lambda$ as seen in figure 7.8, changed noticably with change in concentration. This indicated that at pH ≈ 4.8 an equilibrium other than the one given by equation 2.1 is significant. This new

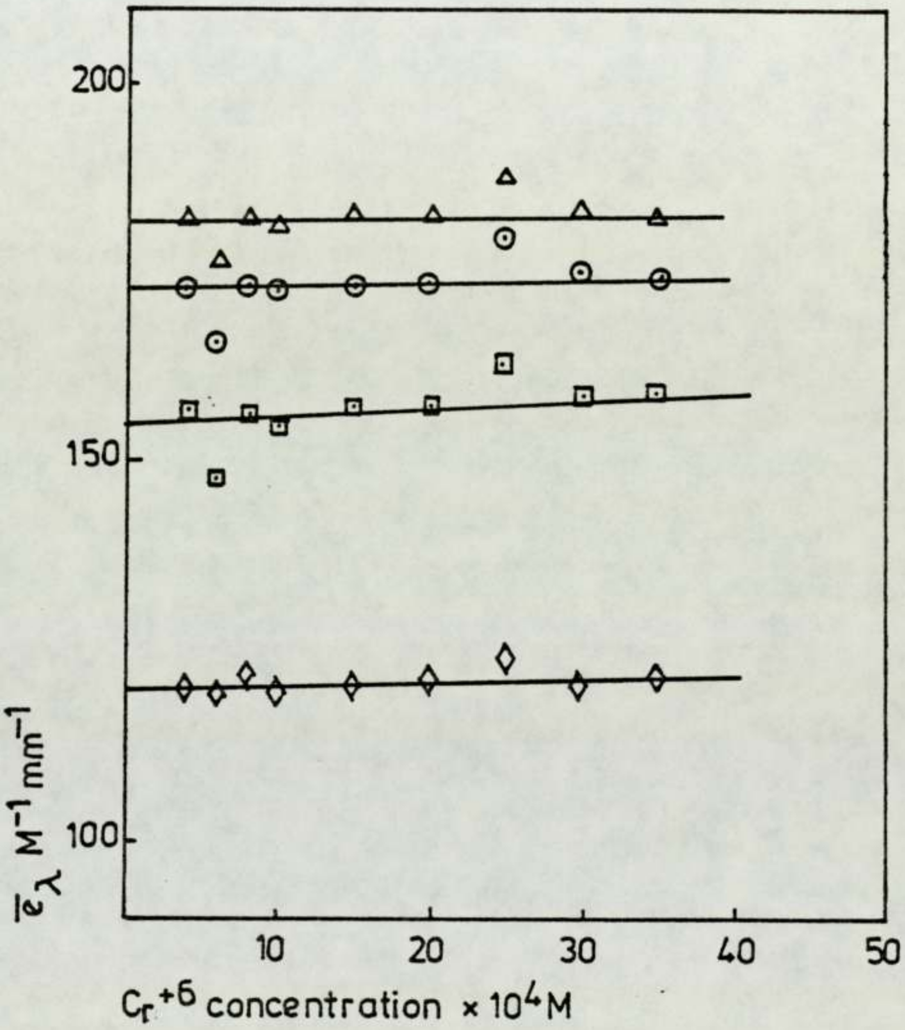


FIGURE 7:7 plot of $\overline{\varepsilon}_\lambda = \frac{A_\lambda}{lC_T}$ against the concentration C_T measured at 40°C and pH 5·45 with the Ionic strength $\mu = 0{\cdot}2$

△ wavelength $\lambda=370$
⊙ wavelength $\lambda=375$
⊡ wavelength $\lambda=380$
◊ wavelength $\lambda=335$

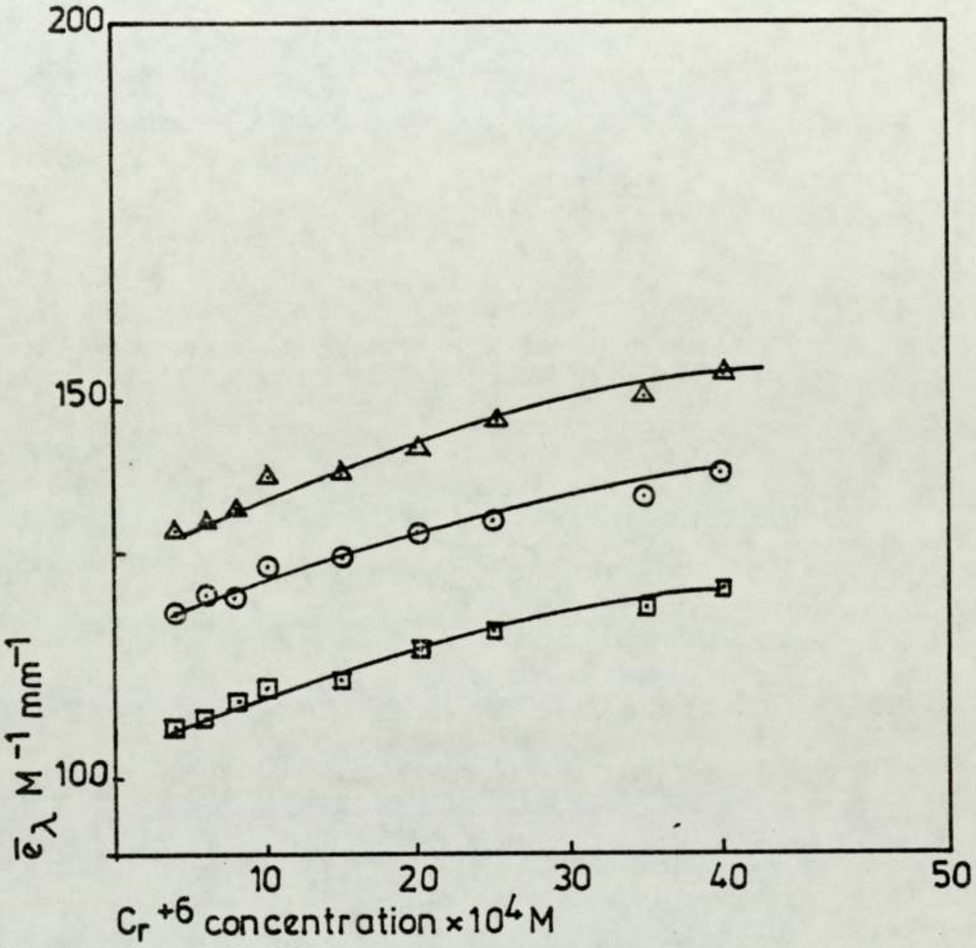


FIGURE 7:8 plot of $\overline{e}_\lambda = \frac{A_\lambda}{lC_T}$ against the concentration C_T measured at 40°C and pH 4·85 and Ionic strength $\mu = 0{\cdot}2$

△ wavelength $\lambda = 370$nm

⊙ wavelength $\lambda = 375$nm

⊡ wavelength $\lambda = 380$nm

equilibrium can only be due to the dimerisation reaction:

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad .....2.1$$

since, with all the other equilibria, change in concentration of Cr^{+6} while the $[H^+]$ concentration is constant will keep the ratios of the ions constant and hence the overall molar absorbtivity $\bar{e}_\lambda$ will not change. A simplified graphical approach similar to that in section 7.3.3.1 was tried to determine the $e_{\lambda C}$ and K_d values as follows.

From the mass balance of Cr^{+6}:

$$C_T = B + 2C + D \qquad .....7.14$$

From the absorption balance:

$$A_\lambda/1 = e_{\lambda B}B + e_{\lambda C}C + e_{\lambda D}D. \qquad .....7.15$$

But from equations 2.9 and 2.10

$$C = K_dB^2 \qquad .....7.16$$

and

$$D = \frac{K_2\ B}{H}. \qquad .....7.17$$

Substituting into 7.14

$$C_T = B + 2K_dB^2 + \frac{K_2\ B}{H}.$$

This is a quadratic equation in B the solution of which is:

$$B = \frac{-(1 + \frac{K_2}{H}) + [(1 + \frac{K_2}{H})^2 + 8K_dC_T]^{\frac{1}{2}}}{4K_d} \qquad .....7.18$$

and

$$B^2 = \frac{1}{16K_d^2}\left\{(1 + \frac{K_2}{H})^2 + (1 + \frac{K_2}{H})^2 + 8K_dC_T\right.$$

$$- 2\left(1 + \frac{K_2}{H}\right)\left(\left(1 + \frac{K_2}{H}\right)^2 + 8K_dC_T\right)^{\frac{1}{2}}\Bigg]$$

$$\therefore\ A_\lambda/l = \left(e_{\lambda B} + e_{\lambda D}\frac{K_2}{H}\right)\left(-\left(1 + \frac{K_2}{H}\right) + \left(\left(1 + \frac{K_2}{H}\right)^2 + 8K_dC_T\right)^{\frac{1}{2}}\right)\frac{1}{4K_d}$$

$$+ \frac{e_{\lambda C}}{8K_d}\left\{\left(1 + \frac{K_2}{H}\right)^2 + 4K_dC_T - \left(1 + \frac{K_2}{H}\right)\left(\left(1 + \frac{K_2}{H}\right)^2 + 8K_dC_T\right)^{\frac{1}{2}}\right\}\Bigg]$$

expanding the terms by binomial series and truncating

$$A_\lambda/l = \left(e_{\lambda B} - e_{\lambda D}\frac{K_2}{H}\right)C_T - \frac{e_{\lambda C}}{2}\,\frac{K_2\,C_T}{H} - \frac{e_{\lambda C}}{8K_d}\left(\frac{K_2}{H}\right)^2$$

rearranging,

$$\frac{A_\lambda}{lC_T} = e_{\lambda B} + \left(e_{\lambda D} - \frac{e_{\lambda C}}{2}\right)\frac{K_2}{H} - \frac{1}{C_T}\left(\frac{e_{\lambda C}}{8K_d}\left(\frac{K_2}{H}\right)^2\right) \qquad .....7.19$$

Hence, by plotting $\frac{A_\lambda}{lC_T}$ against $\frac{1}{C_T}$ a straight line should be obtained and from the intercept and slope $e_{\lambda C}$ and K_d can be extracted as they are the only unknowns in equation 7.19.

A calculator with a linear regression facility was used to calculate the slope and intercept for equation 7.19 using the data from table A10.8. The results of these calculations are given in table 7.7A below.

However, when these values were substituted into equation 7.19 negative values of $e_{\lambda C}$ were obtained (for example at wavelength λ = 385 nm). The intercept from (table 7.7), I = 109.0 from equation 7.19.

$$\therefore\ I = e_{\lambda B} + \left(e_{\lambda D} + \frac{e_{\lambda C}}{2}\right)\frac{K_2}{H} = 109.0 \qquad .....7.20$$

since,

$e_{\lambda B}$ (Table 7.6) = 75.5

$e_{\lambda D}$ (Table 7.3) = 466.0

K_2 (Table 7.5) = 4.3×10^{-7}

$\frac{1}{H}$ = 70795.0

substituting into 7.20

$$\therefore \; e_{\lambda C} = 2\,((109 - 75.5) \times 32.8 - 466) = -\,1269.0$$

As, this is physically not possible, a second look at the mathematical problem indicated that very severe constraints apply for the binomial expansion and consequent truncation of the terms in the square root in equation 7.18. These constraints being (Appendix 6)

$$0 < \alpha \ll 0.1716 \qquad \text{.....A6.6}$$

which under the conditions of the experiment would not be possible. It was necessary to develop a method of solving for K_2 and $e_{\lambda C}$ which would not simplify the basic equation.

If the $[CrO_4^{2-}]$ ion is assumed negligible in amount the mass balance on Cr^{+6} becomes:-

$$C_T = B + 2C \qquad \text{.....7.21}$$

and the absorption balance:-

$$A_\lambda / 1 = \bar{e}_\lambda C_T = e_{\lambda B}B + e_{\lambda C}C. \qquad \text{.....7.22}$$

Assuming the fraction of $[HCrO_4^-]$ in the mass balance is $(1 - \alpha)$ and the fraction of $[Cr_2O_7^{2-}]$ is $(\frac{1}{2}\alpha)$.

Substituting for B and C, in equation 7.22, in terms of α it can be shown that:-

$$\bar{e}_{\lambda} = \left(\tfrac{1}{2}\, e_{\lambda C} - e_{\lambda B}\right)\alpha + e_{\lambda B} \qquad .....7.23$$

$$\text{where } \alpha = \frac{4K_d\, C_T + 1 - \sqrt{(1 + 8K_d C_T)}}{4K_d C_T} \quad . \qquad .....7.24$$

Lukkari (39) and Tong and King (30) solved this by assuming values of K_d, solving for $e_{\lambda B}$ and $e_{\lambda C}$ (using an averages method) then re-evaluating $\bar{e}_{\lambda}$ and optimising on the difference between experimental and calculated $\bar{e}_{\lambda}$. However, the averages method is dependent on the choice of groupings and different choices could lead to different answers. (119).

An analytical approach, which did not depend on optimisation was considered here. This method developed in appendix 12, gives a function $F(K_d)$ which should give the value of K_d when $F(K_d) = 0$. A computer programme was written (appendix 7), which solved for K_d at different wavelengths using the Reguli-Falsi iteration method. The values of K_d obtained from 10 wavelength evaluations were then averaged as shown in table 7.7A. The choice of these wavelengths was dependent on the fact that for these $\bar{e}_{\lambda}$ showed greatest variation with the concentration C_T.

The estimated error that could arise in the values of the molar absorptivity $\bar{e}_{\lambda}$ was shown (appendix 8) to be not greater than ± 1% in the region of measurements carried out. Although, this was considered to be a small error, when some of the values of $\bar{e}_{\lambda}$ were varied by that percentage the values of K_d varied by as much as 100% at some of the wavelength as seen in table 7.8. This indicates that the calculation of K_d is very sensitive to the absorption measurements and great accuracy is required in the measurements of $\bar{e}_{\lambda}$. As the obtained values of K_d were consistent within themselves and are in the same region as the values found in the literature, it is most likely that the estimated error in $\bar{e}_{\lambda}$ is in fact greater than the actual experimental error in these experiments.

The coefficients of molar absorptivity $e_{\lambda C}$ of $(Cr_2O_7^{2-})$ were calculated from the data in tables A10.7 to A10.9 by substituting the calculated values of K_d and the previously obtained values of $e_{\lambda B}$ into equation 7.24 and 7.23. At each wavelength a value of $e_{\lambda C}$ was calculated for each concentration by the computer programme SK7 given in appendix 7. The values were averaged and tabulated in table 7.9. These values are reasonably consistent only with the range $405 > \lambda > 380$ nm showing a dependency on temperature, contrary to the claim of Linge and Jones (36) However, the values in the wavelength range $375 > \lambda > 340$ nm show a random variation. This could have arisen due to the negligence of the (CrO_4^{-2}) ion in this region in the calculations. As can be seen in figure 7.4 this is the region where the (CrO_4^{2-}) ion has a high absorption peak.

Table 7.5: Value of K_2 ($\times 10^{+7}$)M at various wavelengths and temperatures 20, 40 and 60°C

Wavelength λ nm	Temperature °C		
	20	40	60
360	3.2	3.6	2.7
365	3.5	3.8	3.1
370	3.8	4.4	3.0
375	3.9	4.4	3.2
380	4.0	4.5	3.4
385	4.3	4.7	3.2
390	4.7	4.8	3.6
395	4.9	4.9	3.6
400	4.5	5.4	3.7
Average Value	4.1	4.5	3.3
σ_{n-1}	± 0.5	± 0.5	± 0.3

Table 7.6: Values of $e_{\lambda B}$ (for $HCrO_4^-$) at temperatures 20, 40 and 60°C.

Wavelength λ nm	$e_{\lambda B}$ at Temperatures		
	20	40	60
295	100.8	99.0	94.5
300	86.2	83.7	76.8
305	71.3	67.7	62.3
310	61.0	59.3	52.0
315	59.2	56.4	49.7
320	64.9	61.5	58.1
325	77.4	74.2	71.0
330	92.0	90.9	88.7
335	111.0	108.4	107.0
340	120.2	122.5	122.3
345	136.6	134.0	133.5
350	141.7	139.1	139.0
355	141.2	139.9	138.9
360	135.8	133.8	132.9
365	128.5	126.2	122.5
370	115.4	114.1	113.9
375	105.8	103.9	104.6
380	90.9	90.1	90.1
385	79.4	78.6	80.6
390	65.1	64.8	67.7
395	53.3	52.6	55.1
400	41.8	42.3	44.3
405	32.4	33.0	34.1

Table 7.7: Values of Slope and Intercept calculated for equation 7.19 using data from table A10.8.

Wavelength nm	Slope	Intercept	Regression coeff.
295	- 0.015	131.8	- 0.90
300	- 0.014	109.0	- 0.88
305	- 0.013	89.0	- 0.90
310	- 0.011	75.5	- 0.90
315	- 0.010	70.4	- 0.93
320	- 0.005	72.9	- 0.90
325	- 0.002	86.5	- 0.59
330	0.0005	104.1	- 0.21
335	- 0.0001	124.3	- 0.03
340	- 0.0001	141.1	- 0.06
345	- 0.0002	155.8	0.09
350	0.0003	162.7	0.15
355	- 0.0015	166.8	- 0.54
360	- 0.004	163.9	- 0.84
365	- 0.005	158.7	- 0.83
370	- 0.008	148.1	- 0.90
375	- 0.008	137.7	- 0.88
380	- 0.008	122.3	- 0.86
385	- 0.009	109.0	- 0.85
390	- 0.008	90.1	- 0.86
395	- 0.008	73.9	- 0.84
400	- 0.008	59.5	- 0.88
405	- 0.005	45.3	- 0.81

Table 7.7A : Values of K_d Side 6 obtained by using programme SK6 with data in Tables A10.7 - A10.9.

Wavelength λ nm	Temperature °C		
	20	40	60
295	74.9	67.2	52.9
300	71.7	65.5	51.1
370	75.7	56.7	54.5
375	74.9	59.2	46.6
380	72.8	60.6	49.8
385	74.5	62.2	49.4
390	78.4	66.8	55.1
395	66.3	57.3	52.2
400	70.4	52.0	52.3
405	69.7	57.1	51.1
Average Value of K_d	72.9	61.2	51.5
σ_{n-1}	3.5	4.0	2.5

Table 7.8: Values of K_d (20°C) calculated by subjecting $\bar{e}_\lambda$ values to an error of ± 1% Calculated from data in table A10.7.

Wavelength λ nm	% Change $\bar{e}_\lambda$		
	+ 1%	0	- 1%
295	133.8	74.9	28.0
300 *	-	71.7	-
370	224.0	75.7	12.9
375	180.8	74.9	22.8
380	128.2	72.8	28.4
385	116.0	74.5	44.8
390	114.3	78.4	51.4
395	95.0	66.3	38.8
400	97.5	70.0	48.4
405	96.7	69.7	48.7

* For Wavelengths 365 > λ > 305.
The computer programme failed due to attempting to calculate the square root of a negative number, obtained as a result of the iteration procedure.

Table 7.9: Values of $e_{\lambda C}$ (for Cr_2O_7) from tables A10.7 - A10.3 using programme SK7.

Wavelength λ nm	Temperature °C		
	20	40	60
295	618.7	462.4	564.8
300	477.2	316.7	544.9
305	402.6	218.9	443.5
310	347.4	149.3	413.4
315	316.1	132.5	369.6
320	331.0	226.0	337.8
325	386.4	338.1	409.0
330	418.0	486.9	474.9
335	518.7	525.6	591.1
340	673.3	606.0	663.6
345	641.2	697.0	727.7
350	981.0	768.0	738.3
355	722.4	770.9	799.8
360	718.9	737.9	796.5
365	699.4	750.2	836.1
370	709.3	693.4	738.3
375	665.5	649.9	658.8
380	602.1	597.6	591.0
385	536.1	495.7	472.3
390	412.8	400.1	368.8
395	332.2	295.8	272.7
400	268.1	223.2	214.1
405	200.0	165.6	225.5

CHAPTER 8

Crystallisation Literature

8.0 Introduction

Since barium chromate has a very low solubility in aqueous solution two special problems arise in its crystallisation :-

i) To obtain a reasonable crystal yield from a given volume of solution (i.e. reasonable plant capacity) it is necessary to continuously balance the loss of chromate by crystal growth with either the production of more chromate in solution, or if the material had a reasonably high solubility the reduction of chromate solubility in order to maintain the supersaturation necessary for growth to continue.

ii) If the supersaturation is maintained by adding soluble chromate and barium salts there is serious risk of local concentration fluctuations and gradients causing fresh ("homogeneous") nucleation rather than growth on existing crystal seed.

Although very high turbulance in the solution may be a useful way of avoiding problem (ii), it encourages secondary nucleation. Also, even a highly turbulent solution must necessarily contain high local concentration gradients around the feed points of the make up solutions. There will, therefore, always be a risk of nucleation of more seed crystals.

The literature here is, therefore, reviewed from the point of view of the methods of crystal growth study, and the method of generating the chromate chemically analogous to the method used to produce the sulphate ion from sulphamic acid (121).

8.1 Crystal Growth Methods

The crystal growth literature is extensive even when the field is restricted to solution growth only. The references quoted are therefore typical rather than exhaustive. A concise, although somewhat dated review of the whole field is given by White (122), and Bostaris et al.(125, 126). In the main the literature has been concerned with growing sound, inclusion free, crystals of the order of 1 cm size. Since the kinetics are not usually investigated, one or more critical parameters are often not measured, let alone controlled. It is necessary to know (or to be able to deduce) in addition to the linear growth rate (dr/dt), the system temperature (T), supersaturation (ΔC), and relative velocity (v) between the crystal and the solution. Hence, for example some of the ingenious techniques reported by Petrov et al.(123) cannot be made use of here. Even the sophisticated apparatus described by Novotny (124) which includes a knowledge of the Reynolds' Number of the agitator, does not give the value for the suspended crystal nor the relative velocity.

The different types of apparatus for measuring crystal growth kinetics may be conveniently divided into two groups; single crystal techniques and those involving crystal suspensions.

8.1.1 Single Crystal Methods

The advantages of this method are direct optical or mass measurements of the growth rate; virtually constant supersaturation even in the batch situation when relatively small amounts of solution are used, and thirdly, independent control of the relative velocity.

Against this must be considered the fact that two apparently identical crystals may grow at different rates under the same conditions and (in the < 50 μM region) large crystals grow faster than small ones (this is quite a separate phenomenon from the low growth rate of crystals of ~1 μM size due to their increased solubility)and no satisfactory explanation has been offered . The second consideration against, is the difficulty of handling supersaturated solutions when pumping and metering them. Thirdly, the mounting of the crystal, especially in the case of those smaller than 50 μM as in the case of barium chromate.

Even in the very careful work of Bennema (127, 128) the solution was only stirred and no relative velocity measurements could be made. Moving crystals through nearly static solution is a possible alternative but complicates the technique for size measurement (129, 408). Only in a few papers are all the variables under independent control (131, 132, 133, 134). In a further two papers (135, 136) the relative velocity can be deduced from separate calibration tests. With very small crystals ($\sim 10\mu$M the diffusion flux is so great that the relative velocity is probably unimportant and Walton's **epitaxial** microscopic method may be suitable (137). For larger crystals and high growth rates, however, even this apparatus needs to be modified to a flow cell (138).

8.1.2 Crystal Suspension Methods

An important advantage of suspension methods is that the industrially important average growth rate for the population is determined. The masses of the initial and final beds of crystals can be determined with relative ease. The system can also be measured easily under steady state conditions.

There are many disadvantages which may or may not be significant depending on the particular circumstances. The change in supersaturation may be significant especially in a stirred batch cell. Using a fluidised bed may overcome this problem either by having a complicated re-supersaturation system (139) or simply having a very large hold up of supersaturated solution (140). Further, not only is the relative velocity now a dependent variable but it will vary with the seed size distribution (142) and also throughout the course of an experiment. For consecutive (B.S.) sieves the size ratio of the apertures is $2^{\frac{1}{4}}$ therefore for small crystals in the laminar flow regime the ratio of the relative velocities of the extreme seed sizes ~ 1.4. For large crystals in the turbulent flow regime the situation is not so serious and the relative velocity ratio is ~ 1.1. In fact, unless agitation is very intense, the Frossling (123) equation may be used to demonstrate that the velocity effect is negligible for these ratios and that the growth rate would be expected to be inversely proportional to the crystal size raised to the power ¼.

There are also two theoretical requirements which may not be met: the calculation of growth rate assumes that neither nucleation of new seeds nor elutriation (in a flow system) occurs and also that the growth rate is independent of crystal size (i.e. the "McCabeΔL. Law"). Inspite of these possible difficulties the suspension method is a popular one. For a continuously monitored system the supersaturation change may in fact be advantageous, enabling a series of growth rates against supersaturation data to be collected from one test (144, 145).

Assuming relative velocity and size effects of growth rate to be negligible then a relatively new technique is available which does not involve the assumption of no nucleation. This method is referred to as "Mixed Suspension, Mixed Product Removal" (MSMPR), and not only is it not necessary to assume no nucleation, but the nucleation rate is determined (146, 147, 151). The MSMPR technique has been successfully used on both soluble materials (148) and relatively insoluble calcium sulphate (149). However, due to the large crystal surface areas involved in the MSMPR technique the system tends to be one of low supersaturation, which might cause difficulties with solutions that are stable at high supersaturation, for example $SrSO_4$ have been found to be stable at concentrations up to at least twice the solubility value (150).

8.1.2.1. MSMPR Theory (140, 151,152)

The MSMPR crystalliser (see figure 8.1) is assumed to operate as an "ideal" mixed vessel (hold up volume = V) so that its liquid concentration and crystal suspension is constant throughout. The other

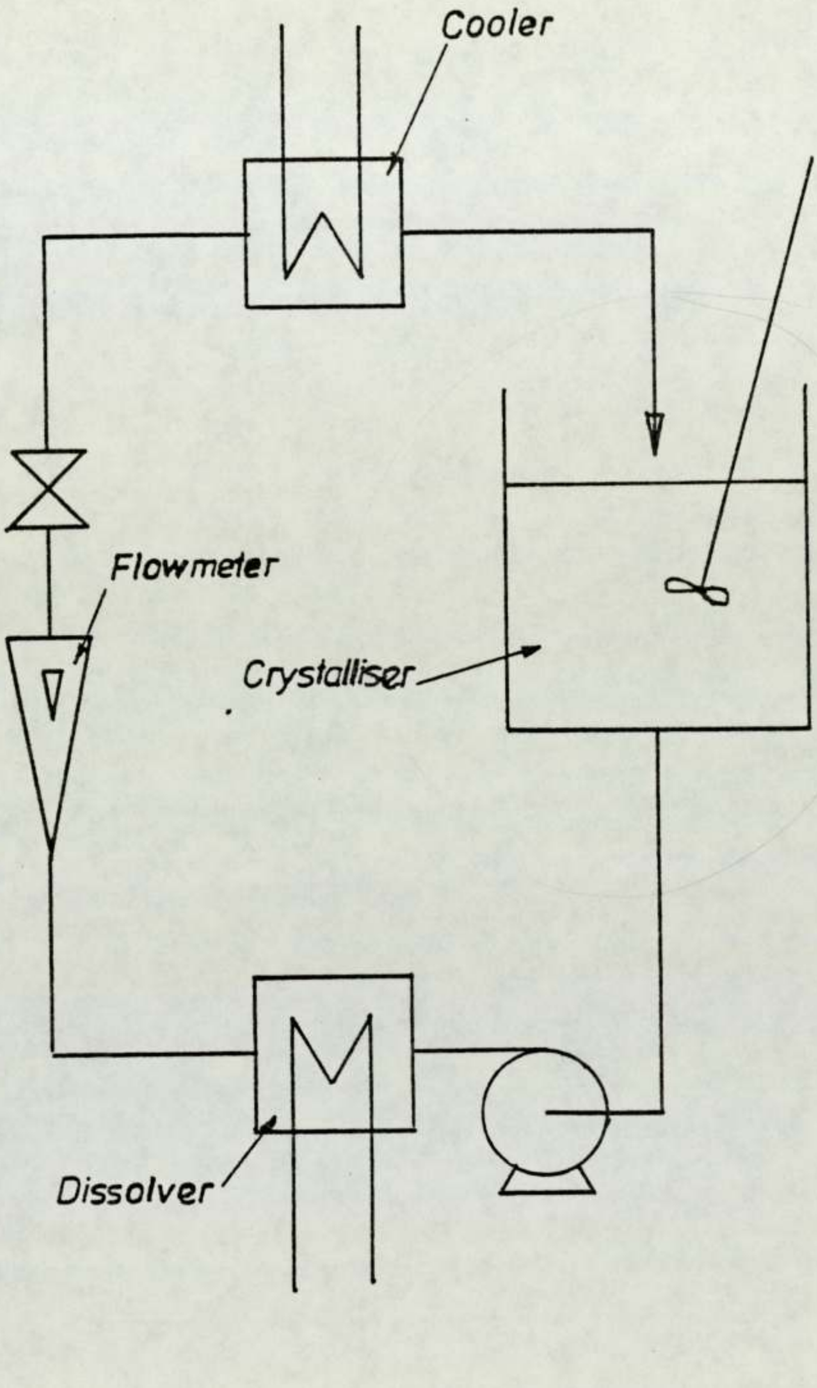


FIGURE 8.1. Basic flow sheet for the MSMPR crystal growth rate apparatus

assumptions made are a) steady state operation, b) no particles in the feed, c) no attrition of particles, d) growth rate independent of size. Then by setting up a population balance $^{(153)}$ in the system for an arbitrary size range L_1 to L_2 and time interval Δt, it can be shown that:

$$\frac{V\, d(\dot{r}\, n)}{dr} + Qn = \text{zero} \qquad ....8.1$$

where Q = rate of removal of crystal magma

$\dot{r}$ = growth rate (dr/dt).

n = population density (dN/dr).

and N = number of crystals per unit volume.

Since it is assumed that the growth rate is independent of crystal size $(d\dot{r}/dr = 0)$ then equation 8.1 solves to,

$$n = n_o \exp\left(- rQ/\dot{r}V\right) \qquad ....8.2$$

where n_o is the number of crystals per unit volume of "zero" size or the nucleation population density. Hence a plot of the size distribution at equilibrium in the form of $\ln (\Delta N/\Delta r)$ vs. r should give a straight line of slope = $- Q/\dot{r}V$ and intercept n_o. Using the value of $\dot{r}$ extracted from the slope and since the nucleation rate,

$$\frac{dN_o}{dt} = \frac{dN_o}{dr} \cdot \frac{dr}{dt} = n_o \dot{r} \qquad ....8.3$$

the nucleation rate can also be found.

Canning $^{(147)}$ mentions that deviations from a straight line form of equation 8.2. might occur due to:

1) Differential fines dissolution which occur in evaporative crystallisers, and also in cooling crystallisers if hot undersaturated solutions are added to the cooler vessel.

2) Bulk diffusion limited growth which causes the growth to be size dependent.

3) Crystal breakage. This would be expected to appear as (and be indistinguishable from) nucleation but there is evidence that small chips may behave differently from nuclei in their growth rate behaviour and so cause a build up in the very fine particle region of < 10 μM sizes (54, 155).

A number of papers (156, 157, 158, 159) have been published in connection with the problem of systems that violate the "McCabeΔL Law" suggesting models that fit the experimental data for such systems.

8.2 Generation of Supersaturation

The basic problem with growing barium chromate crystals is that it has a low solubility ≈ 0.02 - 0.3 g/dm^3 at 20°C. This implies pH ~ 3.5. 4 that most of the conventional methods of growing the crystals such as evaporative cooling crystallisation are not, at any rate industrially, viable, because of the small amounts of material involved. There are therefore, three main systems that may be considered for the growing of barium chromate crystals.

a) The double decomposition method of mixing a soluble barium salt with a soluble chromate salt. This method, as seen in the discussion in section 8.0 has the disadvantage of local concentration gradients.

b) Electrochemical process to generate chromate ions in the presence of barium ions by oxidizing Cr^{3+} in the solution electrochemically (160). Although, a process of this type could promise ease of control, there is a risk of the electrode causing nucleation (161), and therefore, introducing the problem of fresh ("homogeneous") nucleation in the solution.

c) Homogeneous Precipitation from solutions: The precipitating component is slowly generated throughtout the solution by a chemical reaction, allowing the crystals to grow while the

cipitation From Homogeneous Solution"
PFHS

undesirable effect of high concentration gradients is eliminated.

8.2.1 Homogeneous Precipitation:-

The precipitation of metal hydroxides and basic metal salts by carefully controlled change of the pH of a solution is a well established method in the literature. Vogal (162) gives a detailed method of precipitating barium chromate by forming an acidic solution of barium and chromate ions in solution then adding urea $[(NH_2)_2CO]$ to the solution and raising the temperature to 90 - 100°C. The urea hydrolysis giving ammonia and carbon dioxide which neutralises the acid and precipitates barium chromate. Hobart and Gordon (164) in the separation of thorium in monazite sand used the hydrolysis of methyl oxalate in acid solutions to precipitate the thorium as oxalate The authors also used the hydrolysis of urea to precipitate thorium oxide by changing the pH of a solution from 4.5 to about 5.5. Although the authors mention that the solution was boiled for 95 - 97 minutes no actual temperatures were given and no attempt was made to actually measure the precipitate rate. They also did not give any reasons as to why they used formic acid. Gordon and Wroczynski (165) precipitated calcium oxalate by mixing methyl oxalate and calcium carbonate and reacting for 2 1/2 hours at 90°C. Their results again give no rates, only stating that the crystals obtained were readily filtered and easy to wash (and therefore large).

Barrus (166) when precipitating calcium hydrogen phosphate from homogeneous solution by the hydrolysis of urea found the rate of precipitation was directly dependent on the rate of hydrolysis of urea, hence on the concentration of urea. Further, by employing this technique he managed to vary the mean crystal size from about 3.7μm to 22μ m. Gordon et al. (167) precipitated silver chloride crystals of size 2 to 8μm by the hydrolysis of ethylene and propylene chlorohydrins in the presence of the silver ion at 60°C. However, they also found that if the silver ion was also released by hydrolysis of an ammonia complex of silver by the action of the hydrogen ion released from the hydrolysis of ethylene chlorohydrin, crystals of silver chloride of size up to 200 μm where obtained. No data or information on rate was given.

Sheldon (168) found that when precipitating ferric hydroxide by the hydrolysis of urea the addition of carboxilic acids such as formic acid modify the rate of hydrolysis of urea to give a more even hydrolysis rate as seen in figure 8.2. Tong (169) found that when precipitating aluminium hydroxide by the hydrolysis of urea ammonium chloride regulated the decomposition of urea figure 8.3.

Gordon and Firsching (163) precipitated barium chromate from an acidic solution (pH 1.7 to 1.8) of barium chloride and potassium dichromate by the hydrolysis of urea at 95°C in the presence of ammonium acetate and formic acid. However, they do not give any rates of, or the effect on the rates of, hydrolysis and precipitation, of the ammonium acetate and formic acid.

It is therefore, necessary to consider the hydrolysis of urea and the factors that affect it in more detail.

8.2.2 Hydrolysis of Urea:

It has been suggested by Warner (170) that urea hydrolyses according to the following two reactions:

$$CO(NH_2)_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} NH_4 + OCN^- \qquad \text{....8.4}$$

$$\text{and} \quad OCN^- + H_3O^+ \xrightarrow{K_3} NH_3 + CO_2 \qquad \text{....8.5}$$

When the pH <5 the hydrolysis of the cyanate ion is so rapid that its concentration is negligible and only the first reaction is the rate determing reaction. Hence, the kinetics may be assumed to approximate to the first order equation.

$$\frac{d\,[\text{urea}]}{dt} = -K_1\,[\text{urea}] \qquad ....8.6$$

Values of K_1 at 100°C in the presence of HCl are given in table 8.1.

Table 8.1: Values of K_1 at 100°C (170)

pH	K_1 (h^{-1})
- 0.59	0.0221
- 0.22	0.0386
0.08	0.0603
0.41	0.0885
0.71	0.120
1.03	0.126
1.5 to 5.0	0.145

The velocity constant is very much temperature sensitive and at 66°C it was found to be some three orders of magnitude smaller.

Werner (171) stated that the reaction rate is greater in the presence of sodium hydroxide than hydrochloric acid, because the proportion of free urea in solution is greater in the former case.

Bergman and Kuznetsova (172) found that fatty acids react with urea to give $CO(NH_2)_2 \cdot 2RCO_2H$ the stability of which decreases with the increase in the size of R.

Vanda Velde(173) found that the chloride salts of sodium and potassium accelerated the rate of hydrolysis of urea while ammonium chloride retarded the reaction rate.

These effects really need to be investigated quantitatively owing to the prime importance of the hydrolysis rate and its effect on the rate of generation of supersaturation.

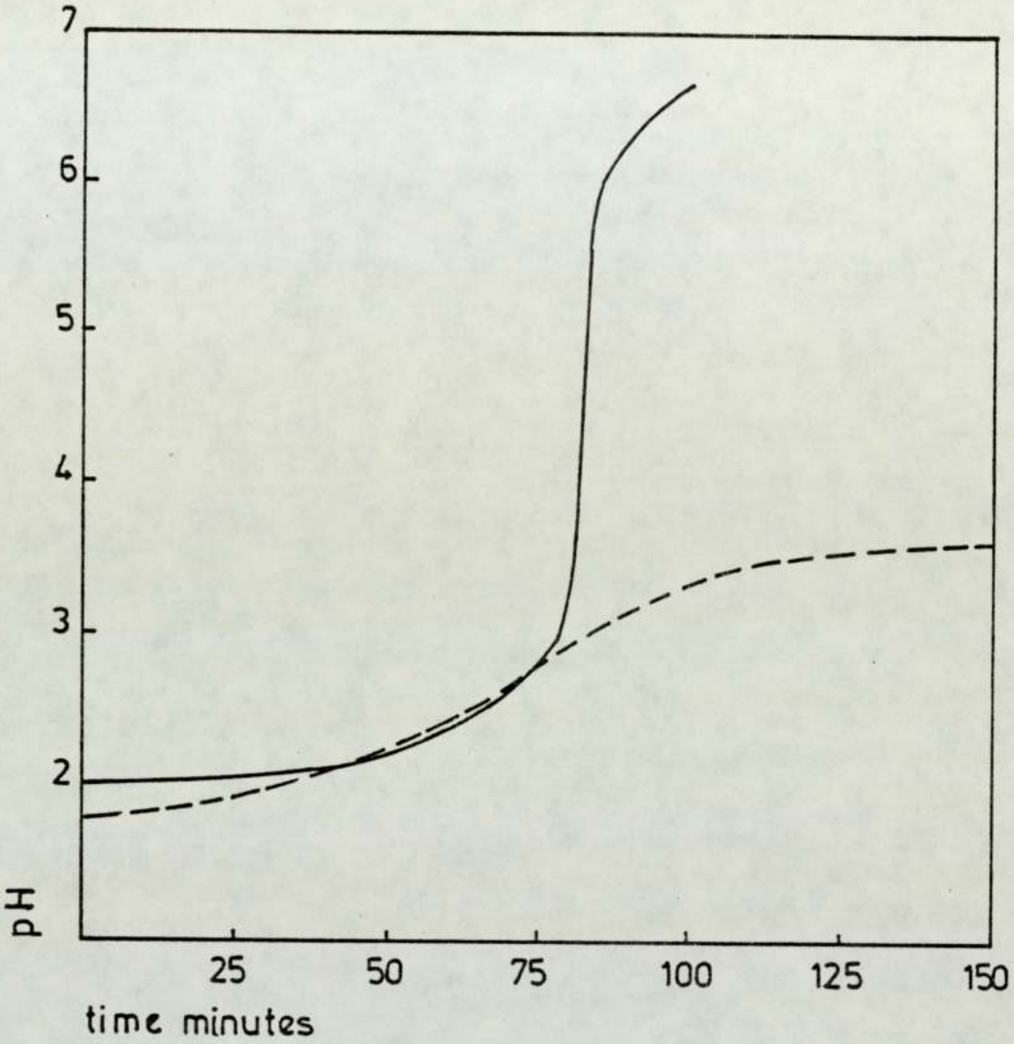


FIGURE 8:2 change of pH of a solution due to the hydrolysis of 4g of urea with and without formic acid *in 0.4 dm^3* (taken from reference 168)

without formic acid ————

with 2ml conc formic acid – – – – –

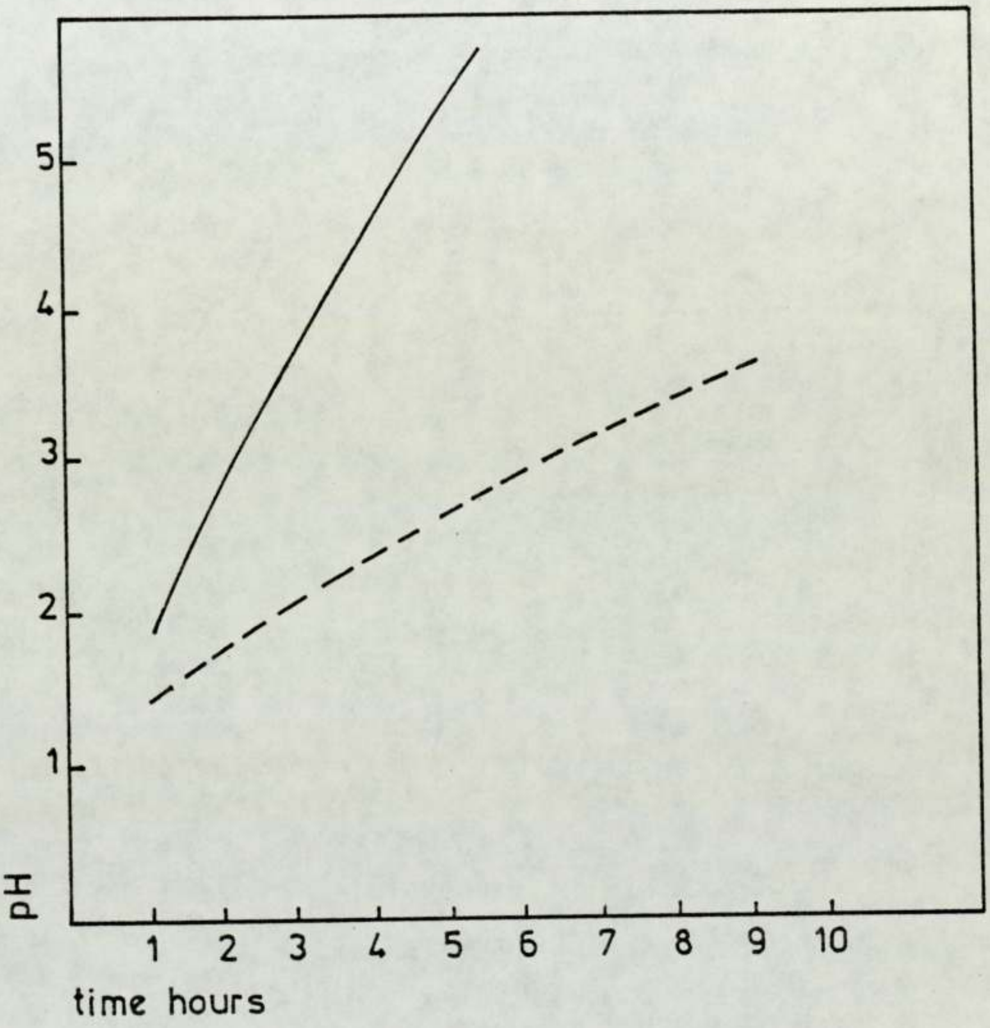


FIGURE 8:3 effect of Ammonium Salt on the rate of hydrolysis of urea. pH change.
(taken from reference 169)

M/8 urea solution ———

M/8 urea solution and
M ammonium chloride ---- ?

CHAPTER 9

Crystallisation Experiments

9.0 Introduction

Two distinct areas of study can be recognised from the literature in connection with the study of growth rates of barium chromate crystals.

Firstly, precipitation of barium chromate from homogenous solutions; although Gordon and Firsching (163) precipitated barium chromate from acidic solutions, they did not give any data on the precipitation rates or crystallisation rates or what factors control the process. This chapter reports the attempts which were made to determine the feasibility of producing barium chromate crystals from acidic solutions by the hydrolysis of urea.

Secondly, growth rate of barium chromate crystals; various papers have been published in the literature regarding the growth rate of barium chromate in aqueous solutions (20,43,73,102). However, no one appears to have studied the growth rate in acid solution or by precipitation from homogeneous solutions.

At the outset of experimentation the "Mixed Suspension and Mixed Product Removal" technique was considered the most appropriate for measuring the growth rate of barium chromate crystals at low pH.

9.1 Materials and Equipment

9.1.1 Materials

a) De-ionised water; description in section 4.1.1.

b) Barium Chromate; description in section 4.1.1.

c) Urea; Analar grade crystals from Hopkin and Williams (assay $\nless$ 99.5%).

d) Formic Acid; concentrated Analar grade reagent from

Hopkin and Williams, specific gravity at 20°C 1.216 - 1.220 and assay ≮ 98%.

9.1.2 Equipment

9.1.2.1 MSMPR Crystalliser

The MSMPR crystalliser (figure 9.1 flow diagram, fig 8.1) comprised of two circuits. A primary circuit for the circulation of the solution under study, and a cooling circuit. Construction was entirely from standard QVF glassware.

i) Primary Circuit: This was made up of a crystallisation compartment (1) which is a 10 dm^3 QVF sphrical vessel (No. VS10/M), the solutions were stirred with a polypropylene coated agitator driven by a variable speed motor. The solution magma drops into a dissolver (2) in which the temperature is raised by an immersion heater (rated at 1kw). The solution next passes to the peristaltic pump (3) (Watson Marlow No. 8210) which pumps the hot solutions to QVF heat exchangers (4) (No. HE2) joined in series. In these heat exchanges the solution is cooled to below the equilibrium temperature and is then supersaturated. The supercooled solution then returned to the crystallisation compartment through an insulated pipe.

ii) Cooling Circuit: This comprised mainly of a closed loop again of 5/8" QVF pipework in which water is circulated by a Schuco centrifuge pump (No. 3MD). The temperature of the cooling water was kept constant by controlling the outlet from the heat exchangers with aid of an on-off solenoid action valve. (Alexander Controls No. ACONP25), and an Ether controller.

Temperatures were measured at four points:

a) In the crystallisation compartment,

b) Just after the dissolver,

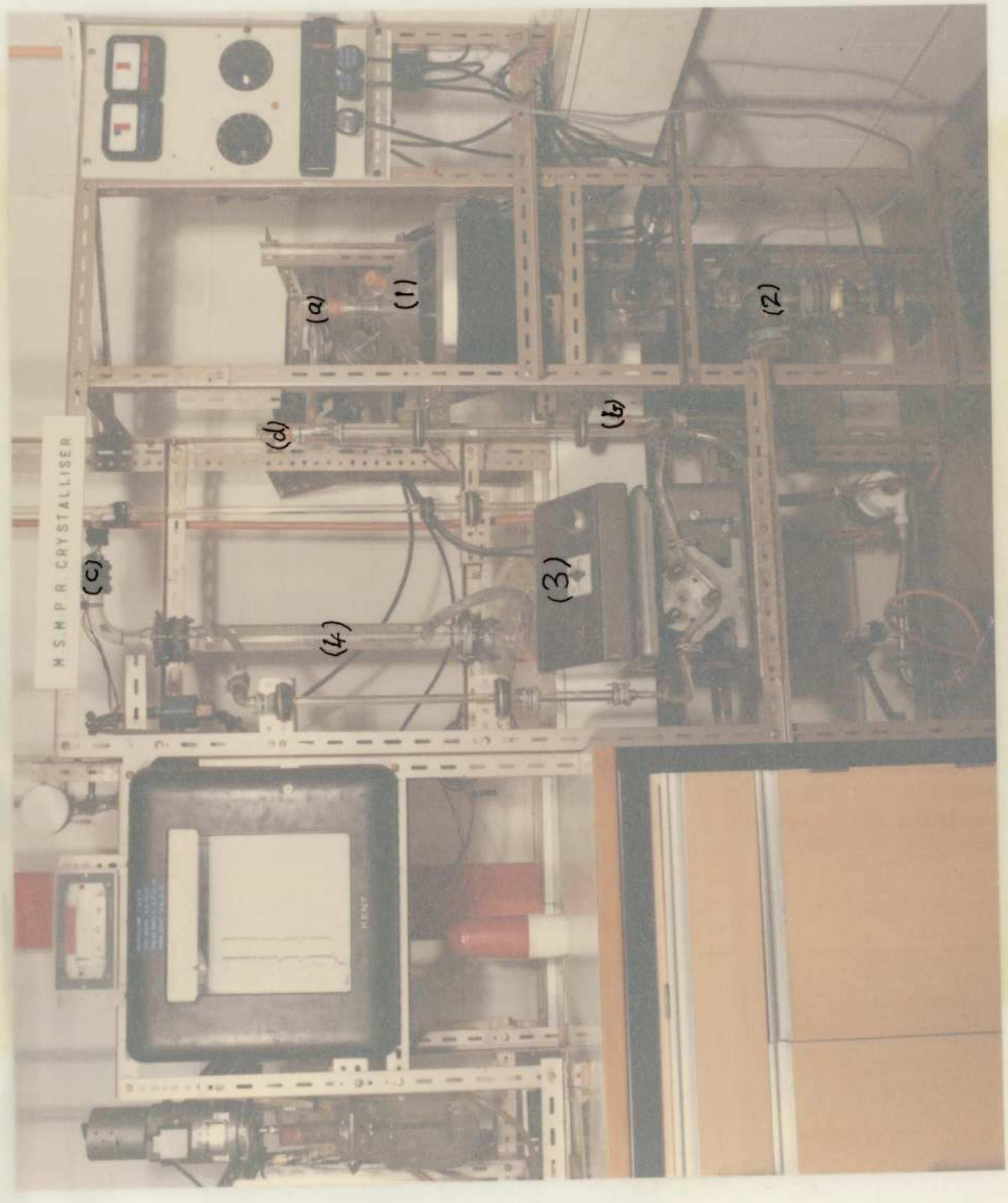


FIGURE 9·1: M.S.M.P.R. crystalliser

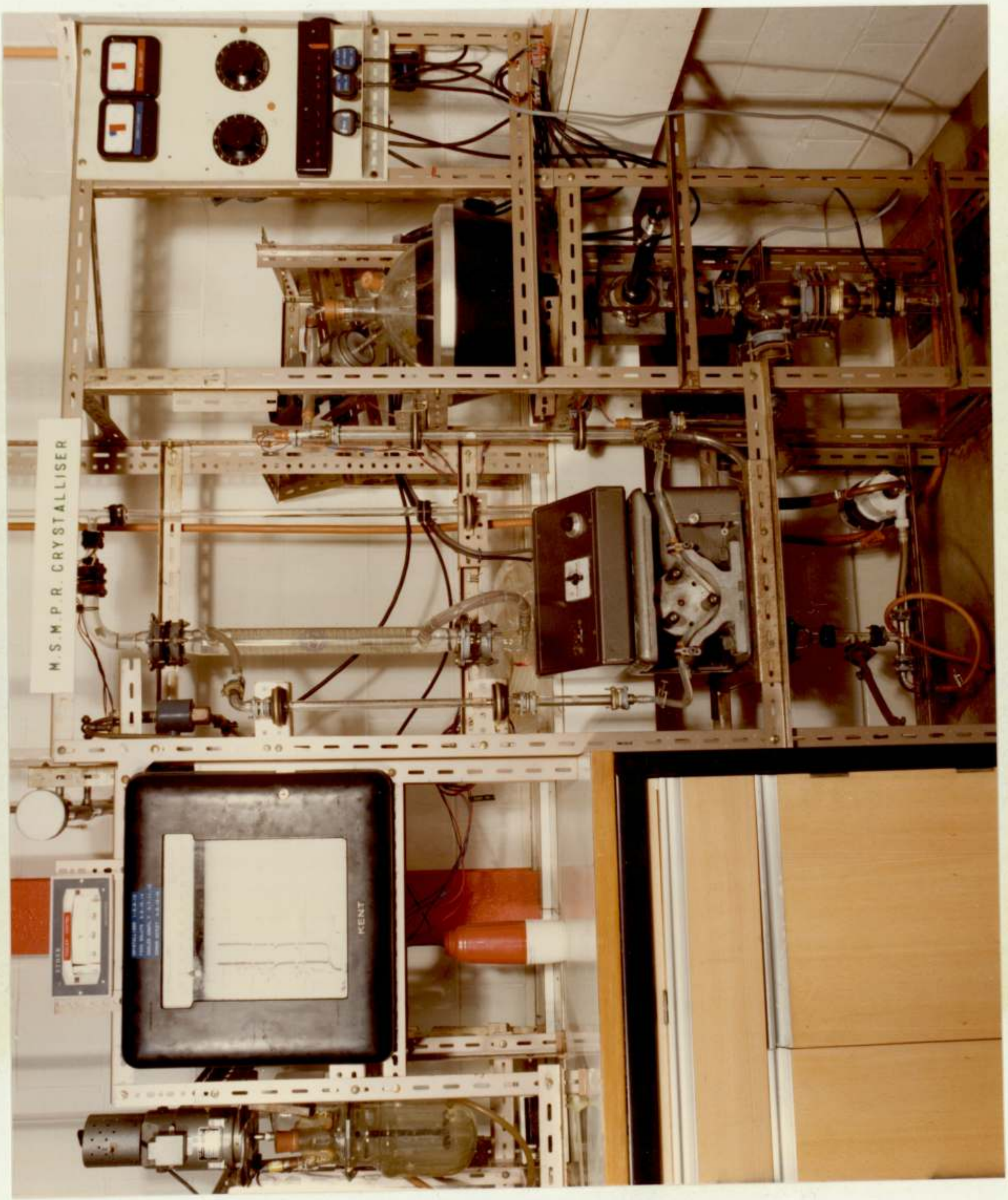


FIGURE 9·1: M.S.M.P.R. crystalliser

c) The outlet cooling water from the heat exchanger and,

d) The inlet feed to the crystallisation compartment. These temperatures were recorded using a 16 point Kent instrument Mark 3 chart recorder.

The heat supply to the dissolver was controlled with a variable transformer and the current was monitored by an ammeter.

9.1.2.2 Batch Crystalliser

This crystalliser (figure 9.2) consisted of a 1 dm^3 QUICKFIT Jacketed Reaction Vessel (No. JRVIL), covered with a Multi-Socket Flange Lid (No. MAF 2/2). This was fitted to a Handi-angle frame by a specially made coller fitted to the Multi-Socket Flange Lid with araldite. The Jacketed Reaction Vessel was further insulated by surrounding with a cardboard box filled with glass wool.

Boiling water was circulated using a Townson and Mercer Thermo-circulator.

The pH was monitored with a Pye Universal pH meter range 0 - 14pH with a discrimination of ± 0.02 pH units. It has a manual temperature compensator. A specially made Pye combination pH electrode (No. 11067) was used with the Instrument.

9.1.2.3 Crystal Size Measurement

Crystal size distributions (CSD) of suspensions were measured on a Coulter Counter Model A. The electrolyte used was a 0.9% NaCl solution saturated with barium chromate. Two orifice tubes were used, these were a 140 μm tube and a 280 μm tube. The tubes were calibrated with monosized lycopodium powder (28 μm)obtained from Coulter Counter. The calibration and use of the Coulter counter is outlined in the manual for Model A.

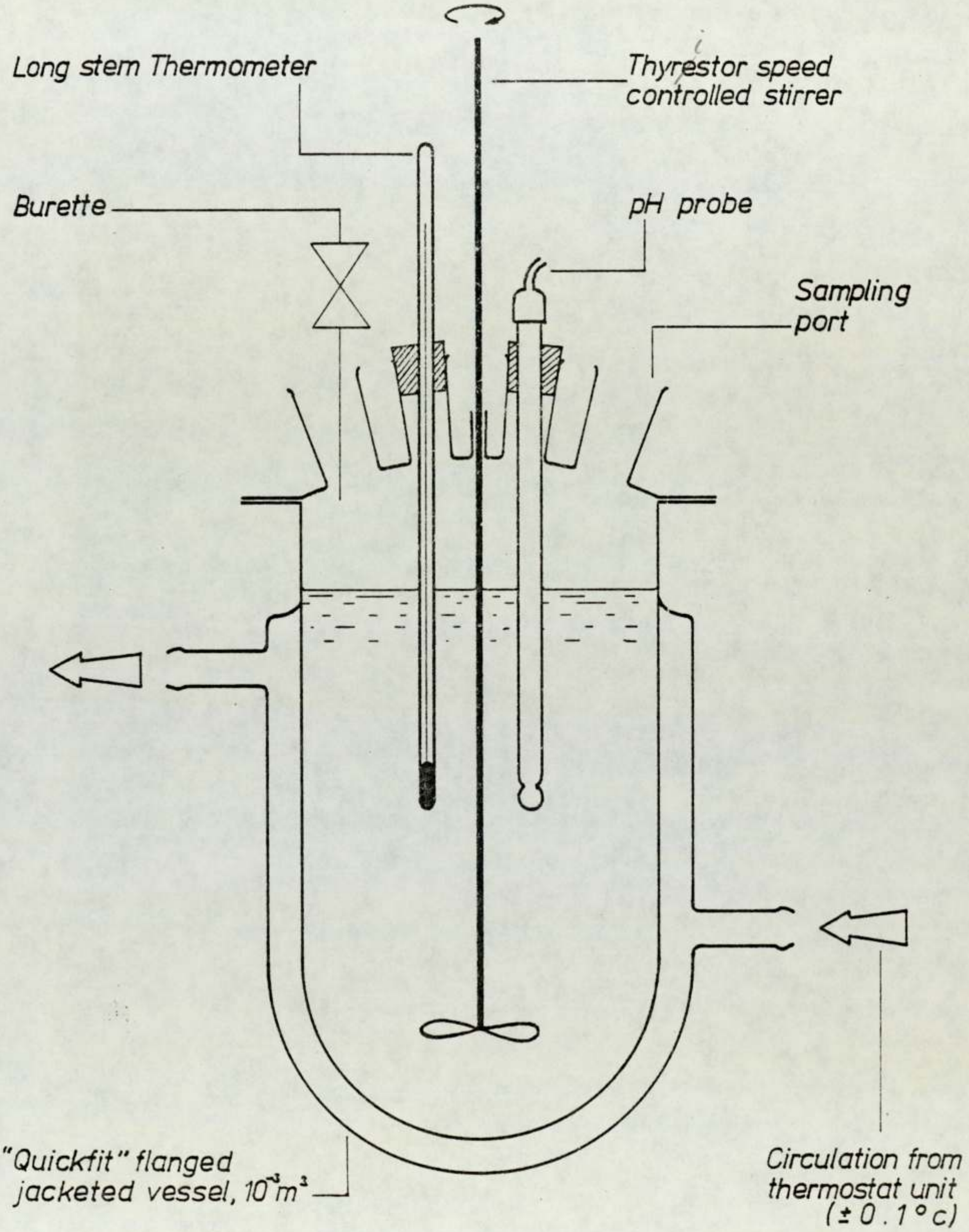


FIGURE 9.2: Batch crystalliser.

Sieve analysis were also carried out on crystals obtained from the batch experiments.

9.2 Experimental Procedure

Before any crystallisation experiments were carried out a number of initial tests and calitrations were necessary as indicated in the following three sections.

9.2.1. Calibration of Stirrer Speed

The scale setting an the thyristor controller of the motor was calibrated by measuring the shaft speed with a stroboscope.

9.2.2. Design and Use of Sampler

To obtain a representative sample of crystals from the suspensions in the crystalliser, and to avoid non-isokinetic sampling a special J-tube and sampling probe (figure 9.3) was made from 5 mm glass tubing. This was connected to an ordinary 10 cm^3 syringe which was then modified to give limited travel for reproducible sample size.

The sample probe was tested with a suspension of known mean, skewness and kurtosis and the results (table 9.1) showed that for a stirrer speed range of (310 - 880 rpm) the sample was reproducible to within ± 4%.

9.2.3. Choice of Stirrer

Because of the nature of solutions being handled in the batch and MSMPR crystalliser (hot concentrated acid), great care needs to be taken in the choice of material the stirrer was made of.

The commercially available stirrers were either glass or stainless steel propeller or polypropylene coated paddle stirrers.

Table 9.1: Results of analysis of samples withdrawn from batch crystalliser at various speeds of stirrer.

Speed r.p.m.	Mean Size (μm)	Skewness	Kurtosis
120	15.5	2.4	6.6
310	17.5	2.2	5.5
500	17.3	2.2	5.7
690	17.3	2.2	5.6
880	17.5	2.2	5.4
1070	16.9	2.3	6.0
Original Sample	17.6	2.2	5.6

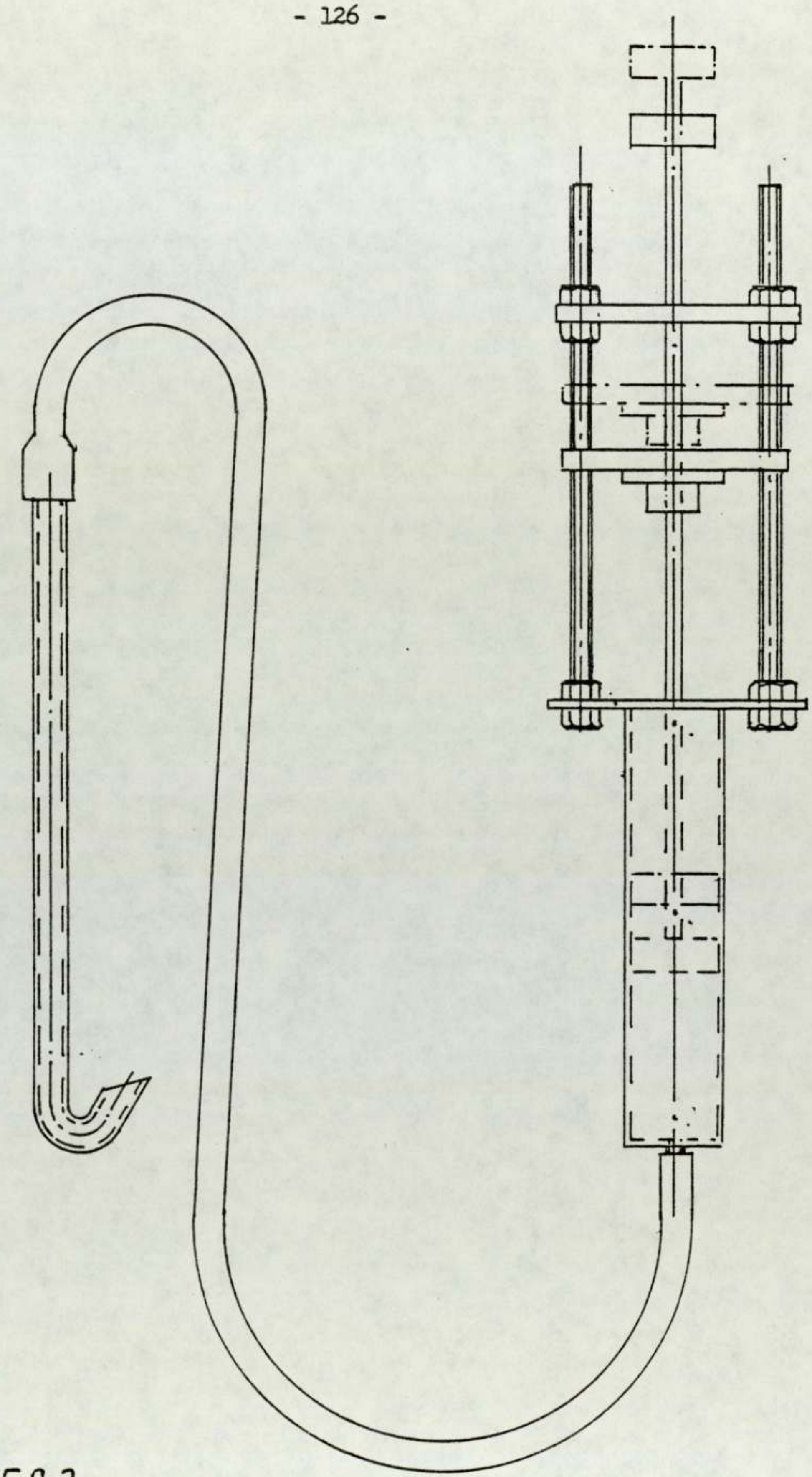


FIGURE 9-3

J-tube sampling probe connected to syringe with limited travel

Since hot HCl was involved stainless steel shafts were out of the question as the corrosion products could act as an impurity, changing the crystal growth rate. However, shafts made from polypropylene coated steel were too pliable and caused whipping at high speeds (> 200 rpm). Glass stirrers were considered unsuitable and not used.

Initially, shafts were made from stainless steel (5mm in diameter) and were coated in latex rubber and tested. This type of stirrer showed stability up to speeds of 800 rpm, but at 100°C the latex rubber soon stripped off within a period of one hour. Subsequent examination of the stripped shaft showed that in any case the coating had contained pin holes and spots of corrosion were visible.

A stainless steel shaft was coated by a local firm with an expoxy based resin containing special fillers in the hope of preventing corrosion. This coating lasted for a period of some 27 hours running. It then started to break up and disintegrate. Throughout this period signs of chemical attack were evident on the stem and propeller blades. It was also noticed that crystal habit changed to needle shape as discussed in section 9.4.3.3. It was therefore, concluded that this type of coating would not be suitable.

Although the paddle type stirrer did not give as effective mixing as the propeller stirrer, these were the only suitable stirrers available at the time the work was carried out and therefore had to be used.

9.3 Experimental

9.3.1. MSMPR Crystalliser

9.3.1.1. Procedure

The crystalliser was filled with 10 - 12 dm^3 of de-ionised water The pH of the solution was adjusted by adding 1M, hydrochloric acid.

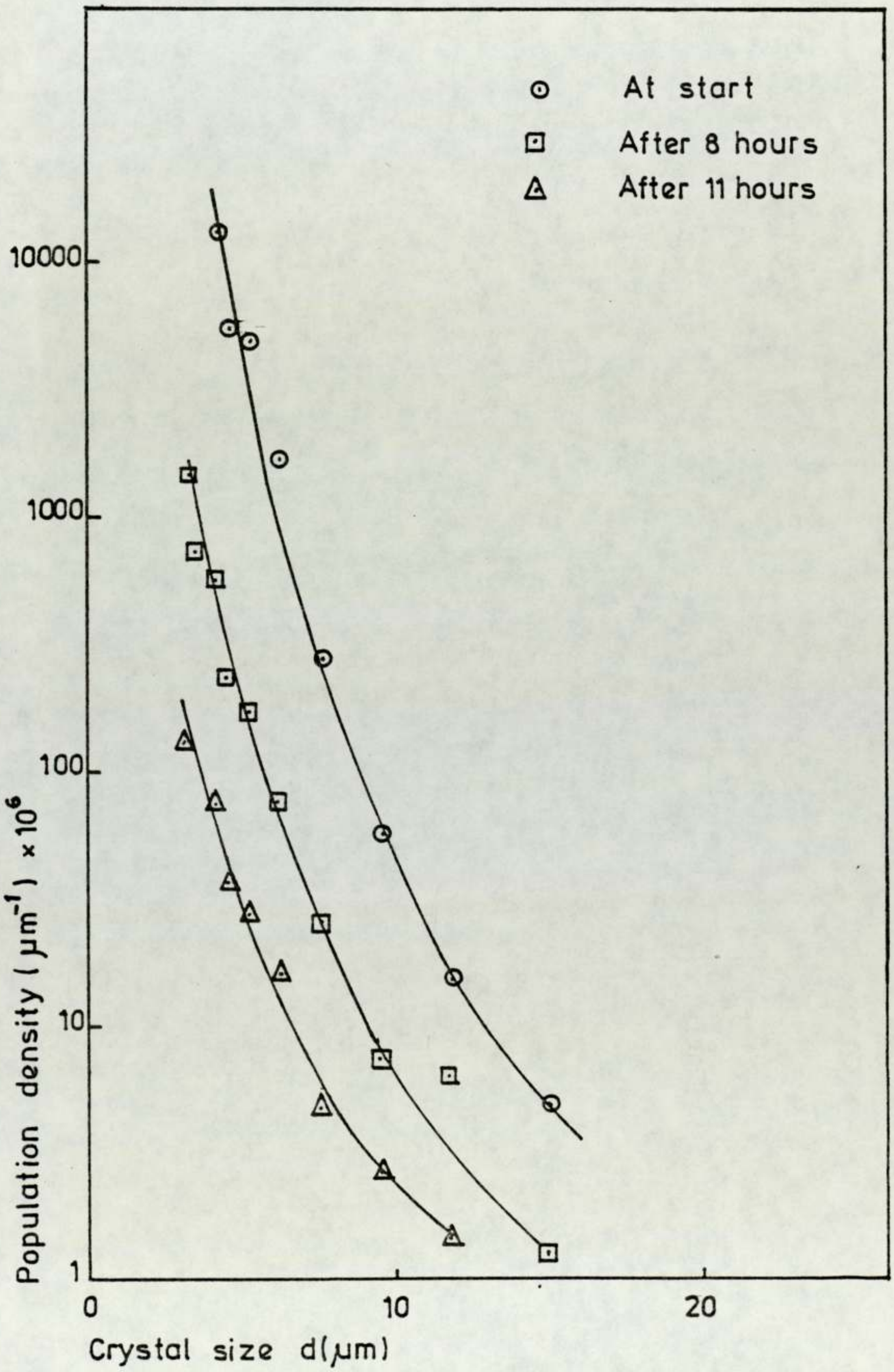
The system was then switched on by first starting the stirrer followed by the peristaltic pump, and the water cooling circulation pump. Finally, the heating element was switched on and set to give a temperature of between 85 to 95°C while the controller was adjusted to give a temperature of solution of about 30°C in the crystalliser. The system was then left running for about 60 minutes to reach thermal equilibrium. Barium chromate crystals of the required weight to give a supersaturated solution (obtained by interpolating the solubility from figure 5.2 plus a pre-determined amount) were accurately weighed and carefully added to the crystalliser over a period of 10 - 15 minutes. Samples of 1 cm^3 volume were removed at hourly intervals to measure solution concentration on the SP1800 spectrophotometer (as described in section 4.2), samples of 4 cm^3 were also removed to measure the crystal size distribution (CSD) on the Coulter Counter. The results from the Coulter Counter measurements were plotted on a log-linear graph.

9.3.1.2. Results of the MSMPR Experiments

Tests on the MSMPR crystalliser at 30°C and $0.1 < pH < 1.0$ indicated that the crystalliser appeared to be operating in an unstable mode, and did not reach equilibrium. Over a 10 h period the seed crystals seemed to be slowly but continuously dissolving (figure 9.4) with little indication of having reached a steady size distribution, and the liquid concentration fluctuated at around the solubility value of barium chromate with a period of about half to one hour.

The usual reason for unstable operation of this type of crystalliser is low crystal growth rate. Since, in principle the system is a low supersaturation one it is probable that insufficient supersaturation was being achieved by the dissolution method used. In order to maintain a constant low supersaturation, very great precision in

FIGURE 9:4 CHANGE OF POPULATION DENSITY OF BARIUM CHROMATE CRYSTALS WITH TIME IN THE MSMPR CRYSTALLISER



temperature control would be required. In round figures, if the supersaturation was 0.1% an error of 10% in this value would be caused by temperature fluctuations of ± 0.001°C. Temperature fluctuations in any case will alter the pH of the solution to which the solubility is very sensitive.

Since this degree of precision in temperature control was quite unobtainable (only ± 0.1 °C was possible), this method of crystal growth rate measurement had to be abandoned.

9.3.2. Batch Crystalliser

9.3.2.1. Procedure

A solution was made up in the (1.0 dm^3) batch crystalliser containing where appropriate barium chromate (c.a. 20g) and approximately 20g urea. The pH of the solution was adjusted to pH ~ 1.0 with 1M hydrochloric acid. Concentrated formic acid (1 or 2 cm^3) was added depending on the experiment. The temperature of the solution was brought to approximately 95°C. The pH and temperature were monitored and recorded every 30 minutes, over the first 3 hours of the experiment. The measurements were then recorded every 5 - 10 minutes for the remaining time until the pH of the solution did not change. Crystals obtained from solutions with barium chromate were filtered, dried, weighed and sieved. In experiments where growth rates were measured samples of (ca 2 cm^3) were removed at regular 30 minute intervals and the particle size distribution was measured using the Coulter Counter.

9.3.2.2. Batch Crystalliser Results

9.3.2.2.1. Preliminary Tests

Initial experiments carried out in a nominal 1 dm^3 beaker on a hot plate showed that precipitation from homogeneous solutions (by the urea hydrolysis method) of barium chromate was possible. These preliminary tests contained 10 g of barium chromate and 15 g of urea added to 1 dm^3 solution of hydrochloric acid of initial pH = 1.0 The duration of the precipitation was about 6 hours to a final pH 5.50. It may be noted that 3.0 g of urea are equivalent to 1 dm^3 0.1N (= pH of 1) acid.

The final precipitate contained crystals ranging in size from about 10 μm to 350 μm. A typical sieve analysis is given in table 9.2.

Table 9.2. Typical sieve analysis of final precipitate of barium chromate crystals from hydrolysis of urea preliminary tests.

Size μm	Mass % oversize	f(d) (mass %/μm) x 10^2
212	1	2.6
180	1	3.1
150	1	3.3
106	18	40.9
90	14	87.5
75	13	87.6
53	24	109.1
45	22	275.9
pan	6	13.3

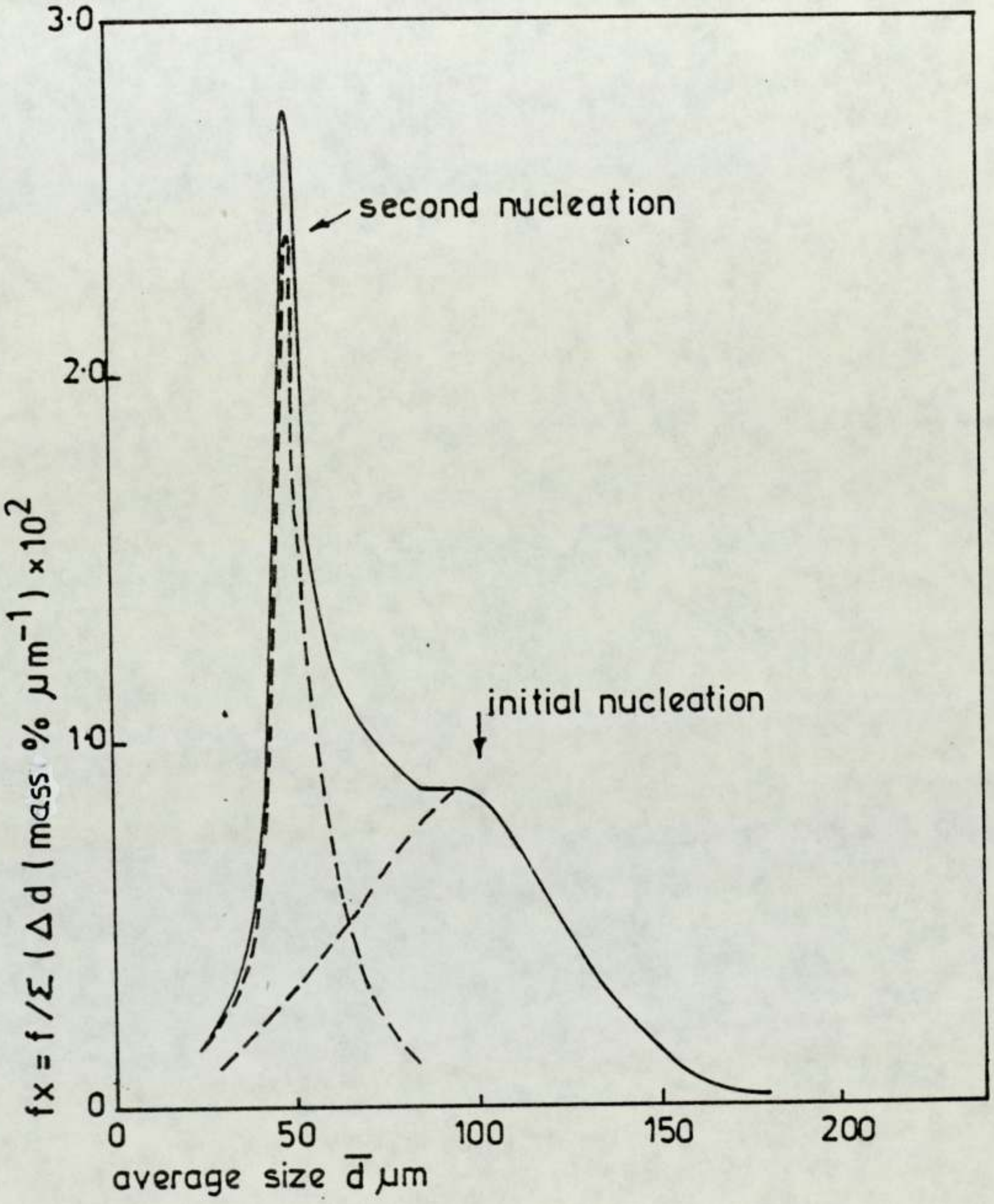


FIGURE 9:4A frequency plot of size analysis on C.D.S. of final precipitate from initial tests

solid line showing actual analysis
dashed line showing actual analysis ?
of bi modal distribution

The third column in table 9.1 represents the value of the % weight of crystals in a size range per unit length.

$$f(d) = \text{frequency } (f) \,/\, [\Sigma f \times (d_j)] \qquad \ldots.9.1$$

where $d_j = d_{j-i} - d_j$ at the j-T point.

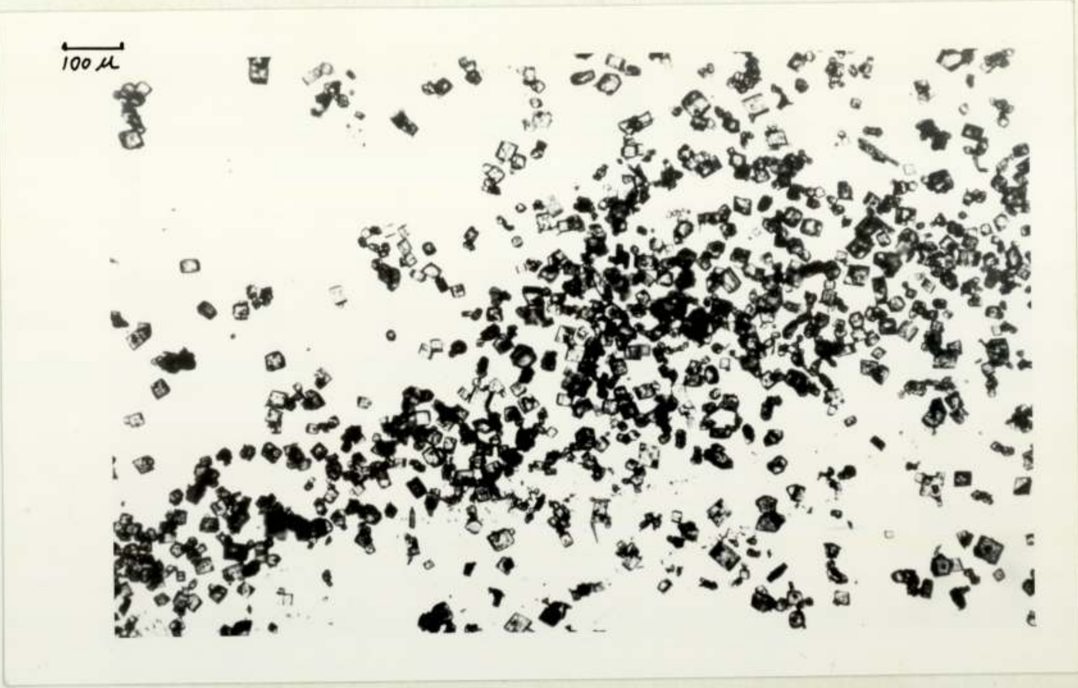
A plot of $(f(d)_j, d_j)$ figure 9.4A shows the distribution to have a plateau in the size range 80 μm to 100 μm. This could be caused by the sum of two unimodal distributions as shown by the dashed line in figure 9.4. This was probably caused by the initial nucleation being followed by a second nucleation due to the growth rate of crystals being slower than the rate of formation of supersaturation by the hydrolysis reaction thus causing the supersolubility limit to be exceeded.

The crystals obtained from these preliminary tests ranged from pale yellow to amber in colour. When the darker coloured crystals were crushed the final colour was a pale yellow, indicating that the change in colour was a light effect. Figures 9.5. and 9.6. show crystals obtained in the preliminary tests photographed under a microscope. Although the literature gives the structure of barium chromate crystals grown from the melt as orthorombic (2,3), it can be seen from figure 9.7 that the crystal has not taken an orthorombic habit. It is probable that the (001) faces have grown faster than the (010) and the (100) faces of the crystal leaving the (111) faces as shown in figure 9.8.

9.4 Feasibility Experiments on Urea Hydrolysis Method

9.4.1. Experimental

The preliminary tests showed that barium chromate crystals could be grown under controlled release of the chromate ion in the solution. However, there was also a strong indication that further



Scale

Figure 9.5: Barium chromate crystals obtained from preliminary urea hydrolysis tests. Fraction retained on 45 μm seive.

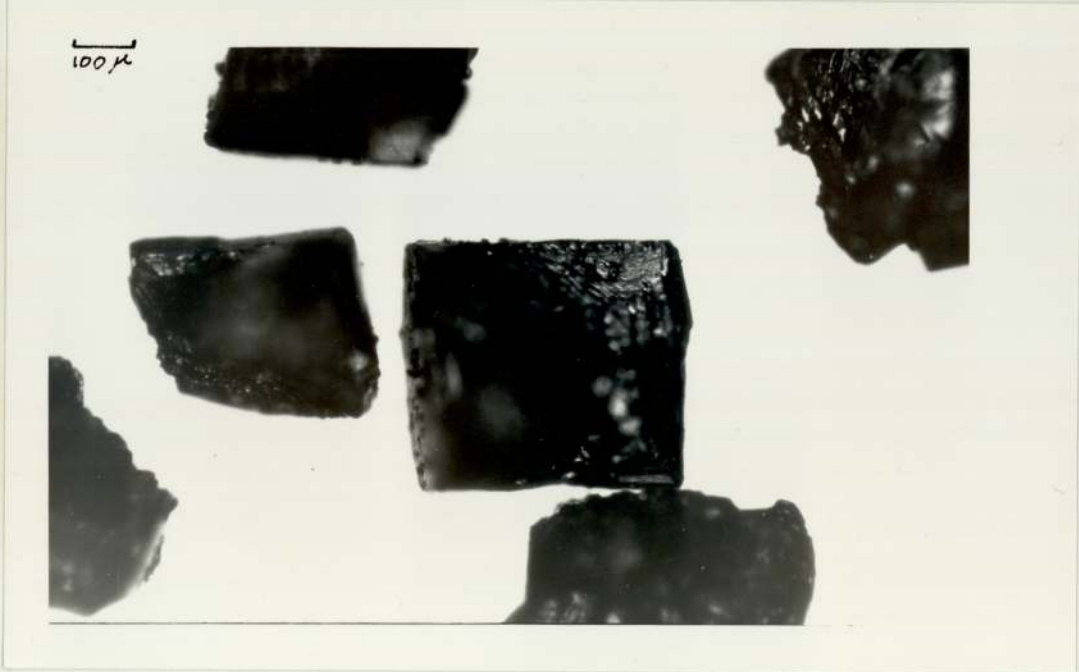


Figure 9.6: Barium chromate crystals obtained from preliminary urea hydrolysis tests. Fraction retained 300 μm seive.

Figure 9.7: Barium chromate crystal obtained from preliminary urea hydrolysis test enlarged X 150.

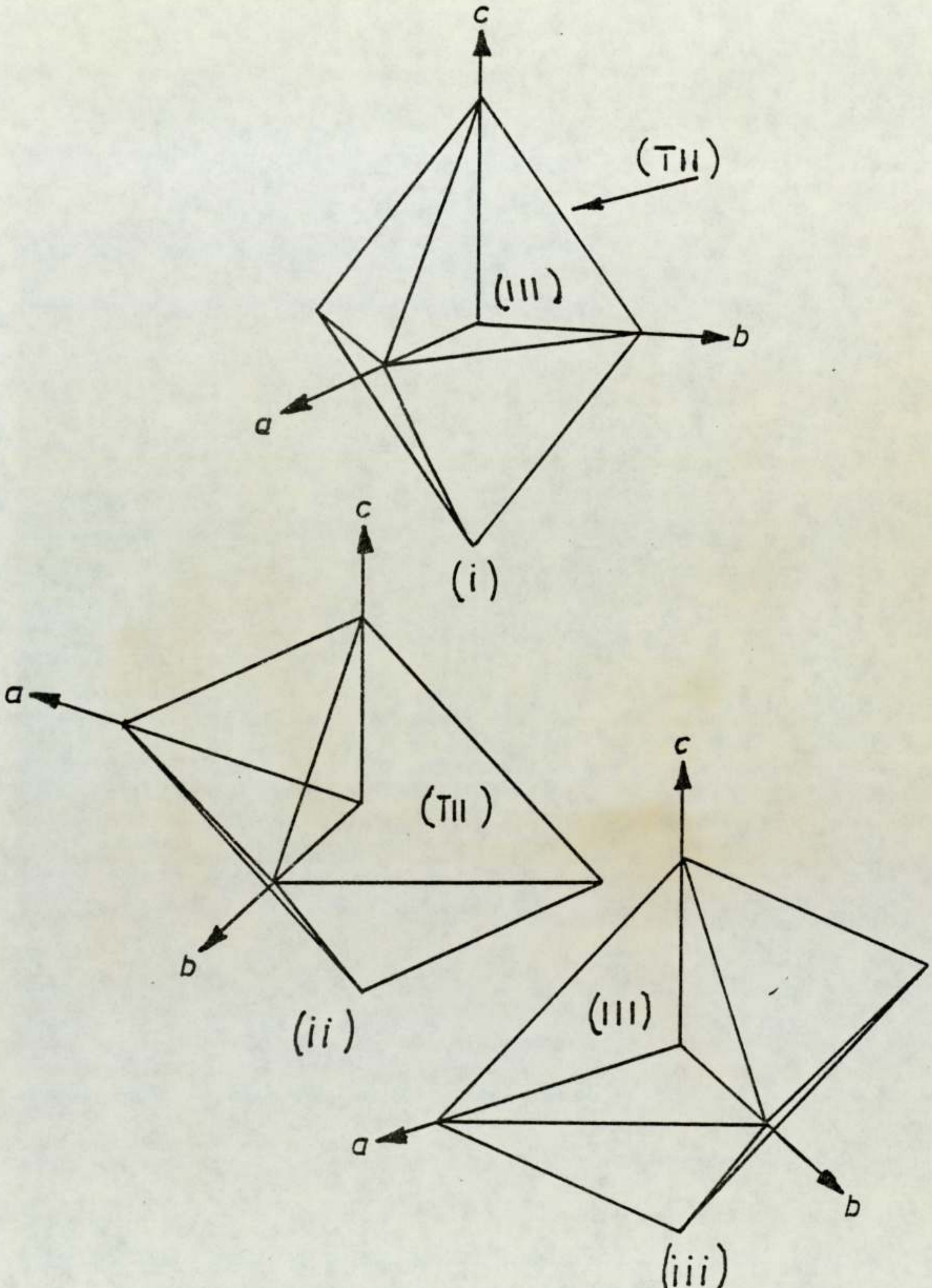


FIGURE 9.8: Scale drawing of the (111) form of a barium chromate crystal (i) Clinographic projection
(ii) & (iii) Views of the $(\bar{1}11)$ and (111) faces, which are mirror images, as seen by a microscope and showing the true shapes of these two faces

nucleation occurred when ever the supersaturation exceeded the metastable region.

To avoid further nucleation would require the control of the hydrolysis of urea such that the metastable limit is not exceeded.

Sheldon (168) has shown that the addition of formic acid in the precipitation of ferric hydroxide by the hydrolysis of urea changed the rate of hydrolysis giving rise to a coarser precipitate. A feasibility study was, therefore, carried out to find the effect of formic acid on the rate of hydrolysis of urea in the precipitation of barium chromate.

These tests were carried out by monitoring the change in pH with time of solutions of hydrochloric acid and urea with the addition and exclusion of barium chromate and formic acid, as shown in table 9.2.

Table 9.2A Experimental design for feasibility studies

Experiment No.	$BaCrO_4$ (g)	Urea (g)	Formic Acid (cm^3)
CUF010	-	20	-
CUF011	-	20	2
CUF110	20	20	-
CUF111	20	20	2

9.4.2 Results and Discussion

The results of the pH measurements from the hydrolysis of urea (table 9.3) can be divided into separate sections:

i) hydrolysis without formic acid and,

ii) hydrolysis with formic acid.

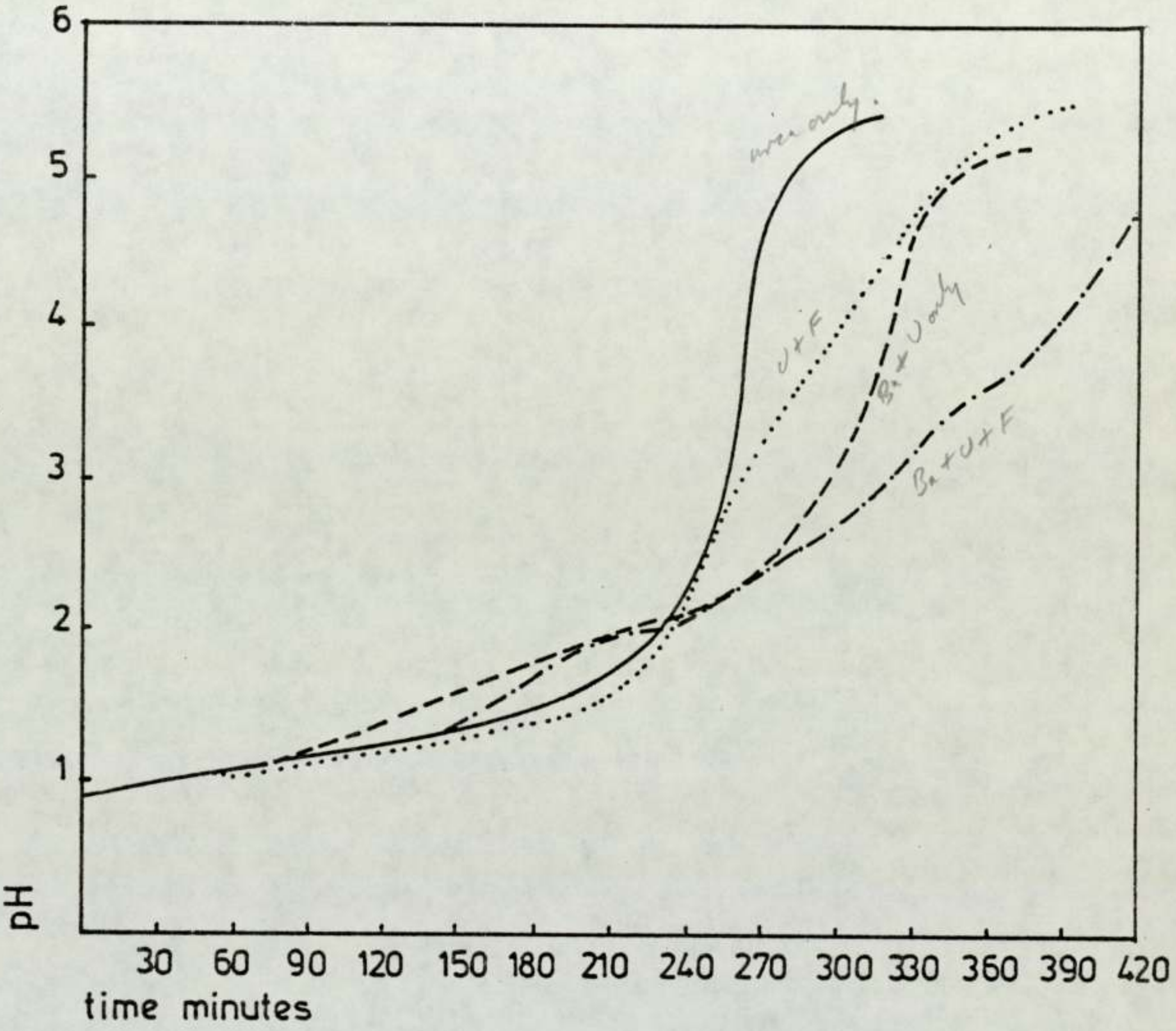


FIGURE 9:9 graph showing the change in pH due to the Hydrolysis of Urea and the effect of barium chromate and formic acid.

expt. no.	
CUF 010	————————
CUF 011	....
CUF 110	— — — — —
CUF 111	—·—·—·—

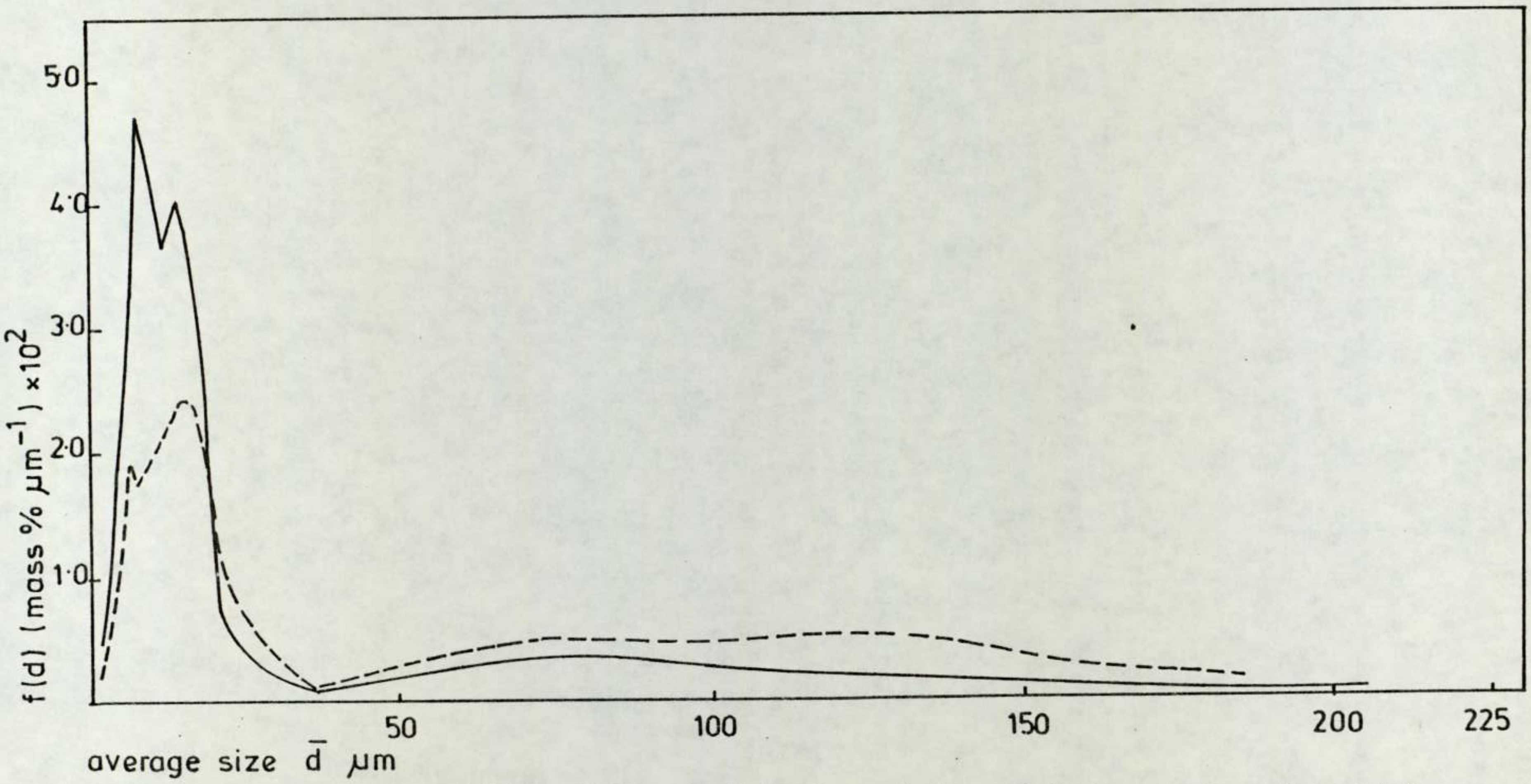


FIGURE 9:*10* plot of % weight/ unit length of final crystal precipitate vs. size of crystal

——— CUF 110 - - - - - CUF 111

9.4.2.1. Hydrolysis without formic acid

As predicted from the literature the pH change, due to the hydrolysis of urea, changes slowly for the first 3 1/2 hours over the pH range 1 to 2; then a rapid change occurs in a period of 1 hour over the pH range 2 to 5. On repeating the test with the addition of 20g of barium chromate a slight increase was noted in the rate of pH change over the first 3 hours but this rate was almost constant for a further 1 1/2 hours up to pH = 2.0 followed by a much faster rate of change, (figure 9.9). This shift to the right indicates that the presence of Cr^{+6} and Ba^{+2} has a direct effect on the rate of hydrolysis of urea. However, this slight decrease in the rate of hydrolysis was not sufficient to stop the occurance of further nucleation as seen by the solid line in figure 9.10.

9.4.2.2. Hydrolysis with formic acid

The addition of 2 cm^3 of formic acid to the reacting solutions showed that a slower rate of hydrolysis could be achieved over the pH range 2 to 5 which is emphasised in experiment CUF111 with barium chromate being precipitated as seen in figure 9.9. Although, with 2 cm^3 of formic acid added the rate of change of pH altered significantly, it is apparent that even the 2 cm^3 added was not sufficient to stop further nucleation as may been seen in figure 9.10 (dashed line).

It is, however, noticed that a definate improvement has occured. With the crystals from the second nucleation showing an increase in size and the percentage of crystals caused by fresh nucleation decreasing by as much as 50%.

The results of the CSD from the preliminary tests (figure 9.4A) showed a different distribution pattern, than those obtained from the feasibility (figure 9.10). The latter giving rise to at least 3 distinct peaks where as the former showed only 2 distinct peaks. This could be a possible indication that 3 or more, homogeneous nucleations occured. As the feasibility experiments were carried out with more barium chromate (20g compared to 10g) and more urea (20g compared to 15g) the compounding effect of both the rate of hydrolysis and increase in supersaturation could have given rise to this phenomenon.

9.4.3.3. Effect of Impurities on the crystal habit

When barium chromate crystals were grown in the batch crystalliser, using the epoxy resin coated stirring shaft, the crystals grown were needle shape, figure 9.11. However, on the polypropylene coated paddle the crystal shape (figure 9.12) was similar to that grown in the preliminary tests figure 9.7).

This effect on the crystal habit is probably caused by the impurities leached out of the resin.

Figure 9.11: Barium chromate crystals grown by the hydrolysis of urea using a mild steel stirring shaft coated with ~~PTFE~~. epoxy resin.

Figure 9.12: Barium chromate crystals grown by the hydrolysis of urea using a mild steel stirring shaft coated with ~~PTFE~~.

polypropylene.

?

Table 9.3: Change of pH with time during the hydrolysis of urea in the feasibility experiments.

Time Minutes	pH			
	CUF010	CUF011	CUF110	CUF111
0	0.90	0.90	0.88	0.90
30	0.98	0.98	0.95	0.98
60	1.04	1.05	1.08	1.05
90	1.15	1.10	1.20	1.15
120	1.25	1.20	1.35	1.23
150	1.30	1.30	1.60	1.35
165	1.39	-	1.70	-
180	1.48	1.40	1.80	1.70
195	1.55	-	1.88	1.85
210	1.68	1.55	1.95	2.00
225	1.82	1.85	2.00	2.05
240	2.15	2.20	2.05	2.10
255	2.85	2.80	2.20	2.35
270	4.60	3.25	2.40	2.40
285	5.15	3.65	2.70	2.55
300	5.30	3.99	3.15	2.70
315	5.40	4.30	3.65	2.90
330	-	4.75	4.65	3.20
345	-	5.08	5.02	3.50
360	-	5.28	5.15	3.60
375	-	5.40	5.20	3.80
390	-	5.50	-	4.10
405	-	-	-	4.43
420	-	-	-	4.81
435	-	-	-	5.05
450	-	-	-	5.22

Table 9.4: Crystal size distribution of precipitates from experiments CUF110 and CUF111

Crystal size (μm)	% oversize (mass basis)	
	CUF110	CUF111
600	2.0	-
422	3.5	0.5
355	1.9	0.1
300	1.8	0.6
180	6.0	4.4
150	2.9	7.2
105	8.6	25.8
90	4.0	6.1
53	13.4	18.6
23	1.0	3.4
18	3.5	5.3
15	9.6	6.9
12	12.2	6.9
9	11.0	5.9
7	8.3	3.5
6	4.7	1.9
5	2.6	1.2
4	1.6	1.0
3	0.9	0.5
2	0.5	0.2

CHAPTER 10

Discussion

The principle objective of this study, to produce barium chromate crystals of the order of 10^{-4}m in size, was achieved and the feasibility of this was demonstrated (Chapter 9). The method used was to dissolve the barium chromate in hydrochloric acid solutions (~0.1M) and recrystallise by the controlled homogeneous generation of supersaturation (by the release of ammonia from the hydrolysis of urea at temperature of about 100°C). The use of small quantities of formic acid, which has a buffering effect on the pH change, was found to reduce the amount of fines. In order to study the process quantitatively it was necessary to know not only the growth rate of the crystals but also the prevailing driving force. This requires a knowledge of the solubility and also the chromate ion concentration. This in turn requires a knowledge of the relevant equilibrium constants.

The results obtained (Chapter 5) showed that it is possible to increase the overall solubility of barium chromate by ~3 orders of magnitude by lowering the pH. Although this only increases the dissolved barium chromate to ~20g/dm^3 of solution, it poses the possibility of producing barium chromate crystals by the urea hydrolysis method as an alternative to the double-decomposition method used in industry, which in any case only gives crystals of the size of ~ 2×10^{-6}m.

The solubility in neutral solution was found to be higher than published values determined electrochemically by a factor of ca.2.

It is considered that the electrochemically determined results may be low as they are sensitive to impurities. The only known chemical analysis method (of Waddel (14)) does give a result which approaches the values found in the present work. The solubility was found to increase from 5×10^{-5} M/dm^3 at 30°C to 28.5×10^{-5} M/dm^3 at 90°C. The consequence of this higher solubility is that the solubility product (by extrapolation to 20°C) is $1.9 \times 10^{-9} (M/dm^3)^2$, which is some five times greater than the published values.

The effect of pH on solubility is quite dramatic for pH < 4. This is attributed to the shift in the solubility equilibrium due to the protonation and dimerisation of the chromate ion. The solubility at 30°C increases from 0.118×10^{-3} M/dm^3 at pH = 4.18 to 39.8×10^{-3} M/dm^3 at pH = 0.6. This is consistent with data which appears in the International Critical Tables (22). At 90°C the solubility increases from 0.461×10^{-3} M/dm^3 at pH = 4.50 to 106.9×10^{-3} M/dm^3 at pH = 0.75.

A theoretical equation was derived for the solubility in terms of the equilibrium constants. This was a cubic equation in terms of solubility (equation 5.2). However, possibly due to the large number of unknowns in this equation, attempts to extract values for the equilibrium constants were unsuccessful.

A mathematical model was developed to predict the concentration of the chromate ion (appendix 13) giving:

$$\left[CrO_4^{2-} \right] = \frac{-(1 + H/K_2 + H^3K_c/K_2) + \sqrt{((1 + H/K_2 + H^3K_c/K_2)^2 + 8HK_3C_T/K_2^2)}}{4\ H^2\ K_d/K_2^2} \quad \ldots \text{A13}$$

In order to use this equation the equilibrium constants must be known as well as the pH value.

The values of the equilibrium constants in the literature were found to be variable (Chapter 6). Therefore, the most critical ones, the dimersation equilibrium constant K_d and the protonation equilibrium constant K_2 were determined independently (Chapter 7) using spectrophotometry and applying a different mathematical approach to that used by other authors. The values of K_d determined in this work (figure 10.1) are within reasonable agreement with that of Pladziewiezet et al. (174) but are higher than those of Gelea et al. (44) and Linge and Jones (36). The value of K_2 obtained here (figure 10.2) is lower than those obtained by Galea (44) and Linge and Jones (38), but agrees with the value obtained by Sasak (31).

Since these equilibrium constants were needed to calculate the chromate ion concentration at 100°C, it was necessary to extrapolate the values found. Based on the Van't Hoff equation this was done by straight line extrapolation of log K vs. 1/T as indicated by the dotted lines in figures 10.1 and 10.2.

These values of equilibrium constants were used to calculate (programme SK10, appendix 13) the concentration of the chromate ion for the special case when the total concentration of Cr^{+6} is equal to the solubility. The results (figure 10.3) show that, although the overall solubility increased with a decrease in pH, the chromate ion concentration decreased by over an order of magnitude. Further, these results are noticeably different from concentrations calculated from the solubility product. The dashed line (figure 10.3) is based on the solubility product obtained from the present work; the dotted line is based on a solubility product value from the literature. This discrepancy is probably due to (a) the solubility product changing over the pH range, (b) the effect of ionic strength, and (c) the fact that the solubility product theory only holds with slightly soluble salts.

It is noted that when the solubility product is calculated from the chromate ion concentration, the value changes with pH (table 10.6). The concentration of CrO_3Cl^-, $HCrO_4^-$ and $CrO_2O_7^{2-}$ increased with (H^+) (tables 10.1 to 10.5). The most significant increase is that of CrO_3Cl^- which increased from $< 10^{-11}$ M/dm^3 at pH = 4.18 and to 7×10^{-3} M/dm^3 at pH = 0.6, at 30°C. This indicates that 20% of the solubility increase is due to the formation of the CrO_3Cl^- ion.

FIGURE 10:1 EFFECT OF TEMPERATURE ON THE CONSTANT K_d ($\mu = 0$)

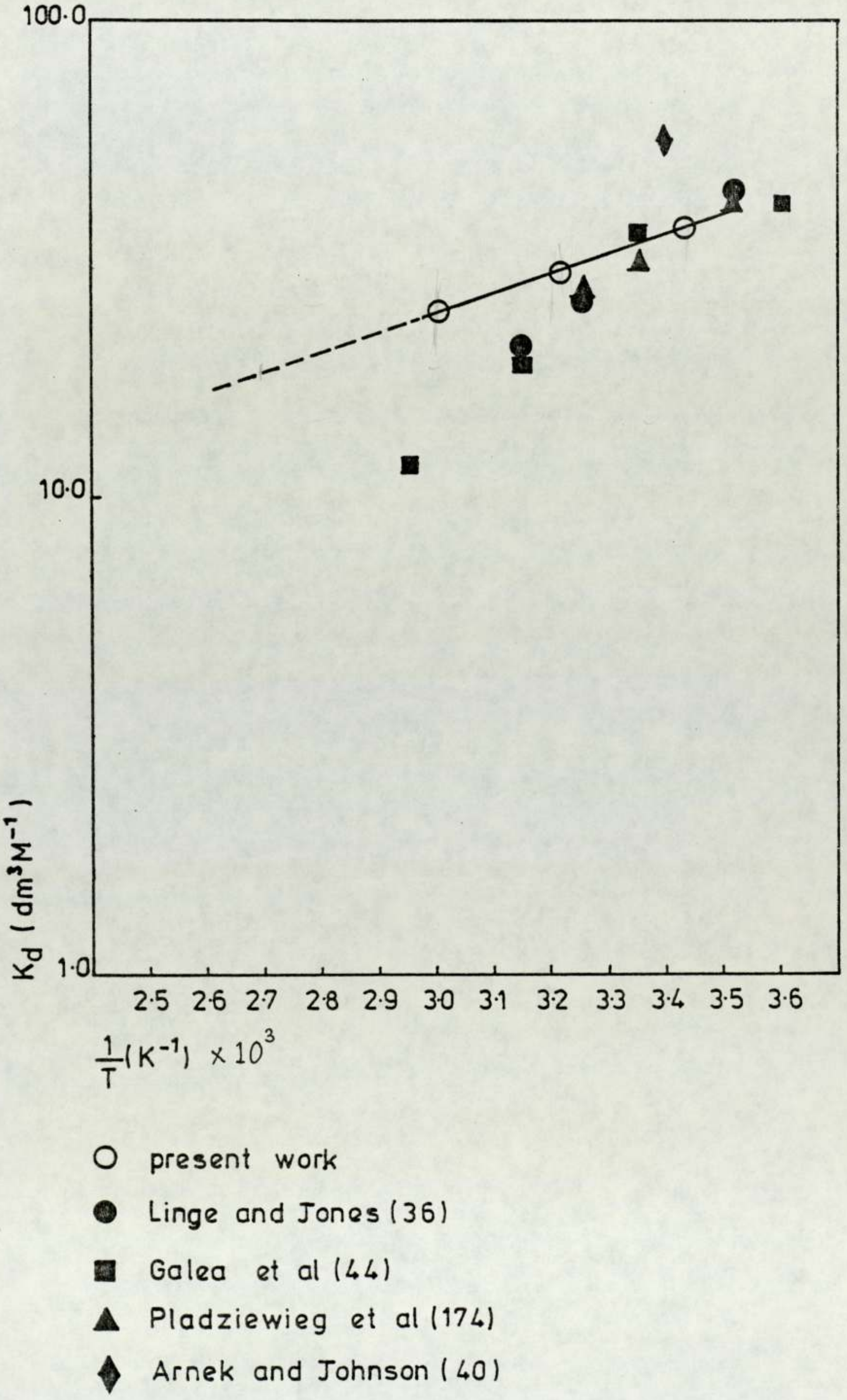
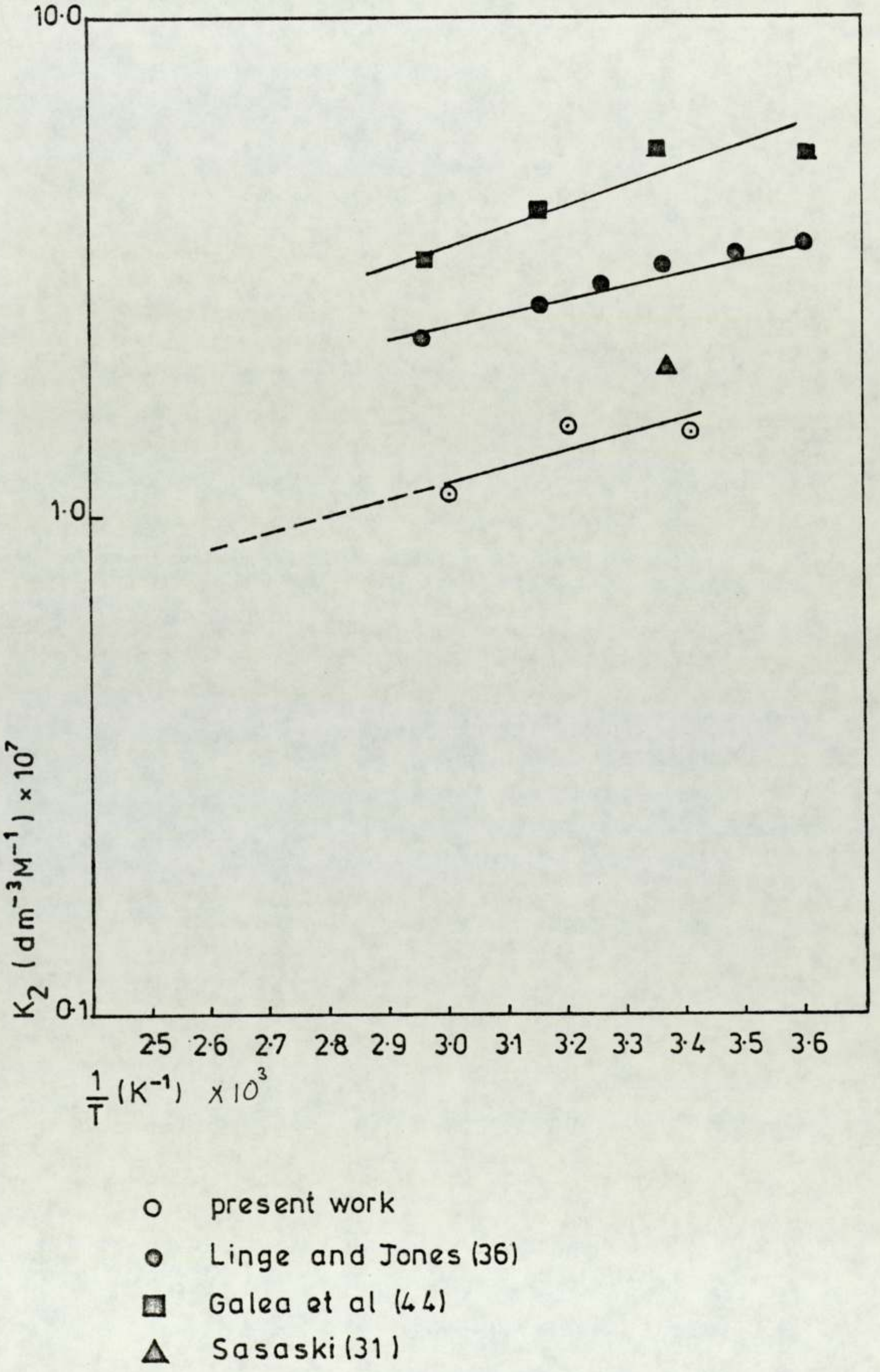


FIGURE 10:2 EFFECT OF THE TEMPERATURE ON THE CONSTANT K_2 ($\mu = 0$)



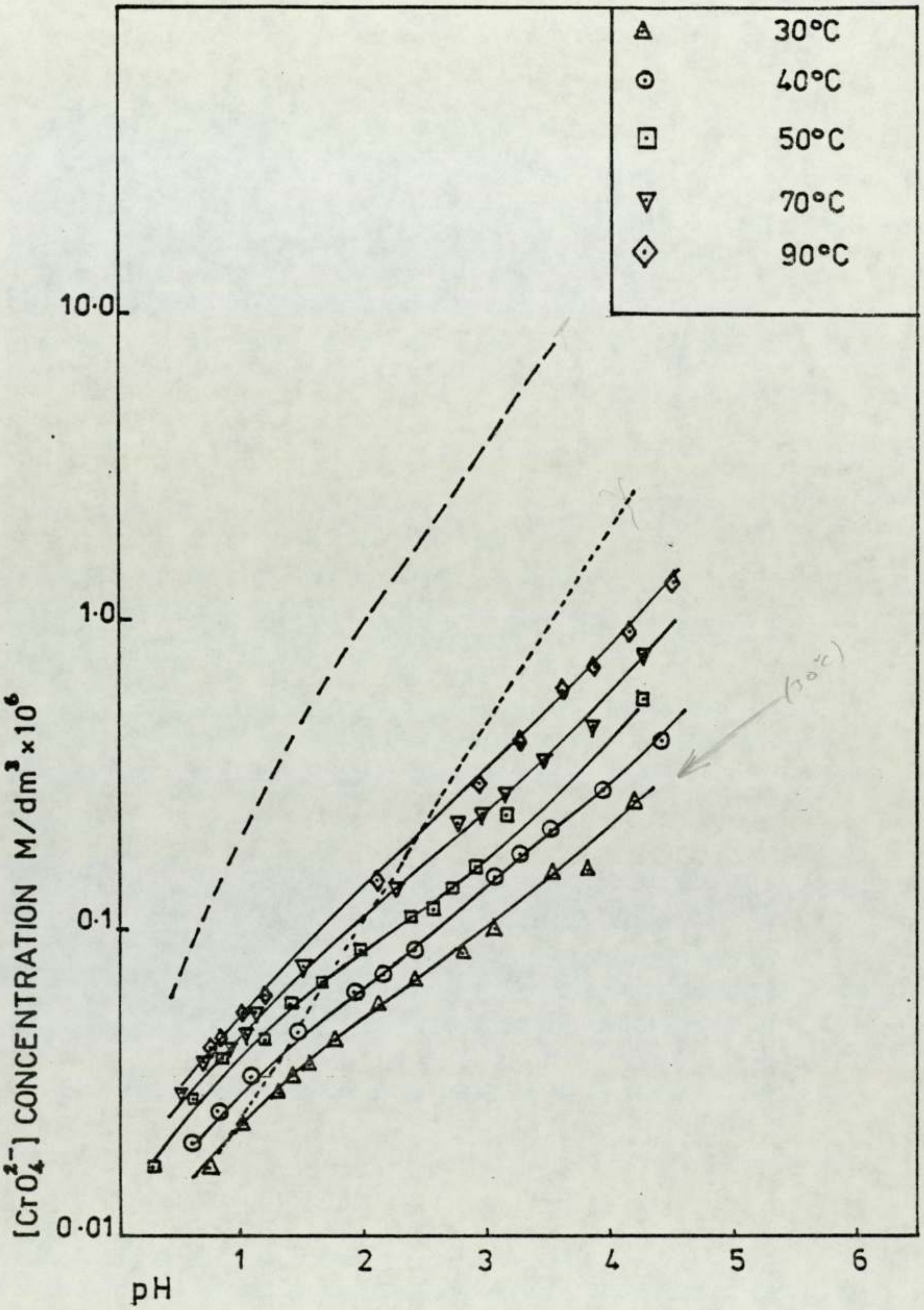


FIGURE 10: 3 PLOT OF CHANGE OF CONCENTRATION OF $[CrO_4^{2-}]$ WITH pH IN A SATURATED SOLUTION OF BARIUM CHROMATE–HYDROCHLORIC ACID

– – – – $[CrO_4^{2-}]$ CONCENTRATION CALCULATED FROM PRESENT WORK K_{sp} VALUE AT 30°C

-------- $[CrO_4^{2-}]$ CONCENTRATION CALCULATED FROM VALUE OF K_{sp} AT 30°C

Table 10.1: "The effect of pH on the concentration of various Cr_{VI} ions in $BaCrO_4$ - HCl solutions at 30°C.

pH	Concentration (M/dm^3) x 10^6			
	$HCrO_4^-$	CrO_4^2	$Cr_2O_7^=$	CrO_3Cl^-
4.18	116.8	0.2577	0.4483	$< 10^{-5}$
3.80	163.1	0.1525	0.8820	3×10^{-5}
3.50	321.9	0.1538	3.486	21×10^{-4}
3.05	558.3	0.0986	10.78	0.0030
2.80	803.3	0.0828	22.82	0.0137
2.40	1510.0	0.0667	84.88	0.1680
2.10	2365.0	0.0567	219.5	1.007
1.75	3513.0	0.0424	525.1	8.393
1.55	4193.0	0.0348	791.1	25.89
1.40	5313.0	0.0336	1336.0	67.33
1.30	5540.0	0.0293	1503.0	113.4
1.00	7321.0	0.0232	3922.0	2351.0

Table 10.1: Continued.

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	CrO_4^2	$Cr_2O_7^=$	CrO_3Cl^-
0.75	7984.0	0.0168	3922.0	2351.0
0.60	12240.0	0.0206	10010.0	756.70

Table 10.2 **"The effect of pH on the concentration of various ions in $BaCrO_4$ - HCl solutions at 40°C.**

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
5.50	66.0	2.78	0.128	$< 10^{-5}$
4.75	84.9	0.648	0.213	$< 10^{-5}$
4.40	119.7	0.405	0.425	$< 10^{-5}$
3.90	254.8	0.278	1.95	3×10^{-5}
3.50	469.3	0.210	6.74	3.4×10^{-4}
3.25	694.8	0.178	15.00	0.0016
3.05	898.0	0.149	25.4	0.0052

Table 10.2: Continued

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
2.55	1815.0	0.078	111.1	0.200
2.40	2055.0	0.085	143.2	0.247
2.20	2561.0	0.070	229.7	0.787
1.90	4093.0	0.062	626.4	5.180
1.45	7144.0	0.047	2174.0	77.30
1.05	10248.0	0.033	5196.0	761.0
0.80	12013.0	0.026	7959.0	3009.0

Table 10.3: "The effect of pH on the concentration of various ions in $BaCrO_4$ - HCl solutions at 50°C.

pH	Concentration $(M/dm^3) \times 10^6$			
	$HC4O_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
4.25	243.2	0.544	1.617	1×10^{-5}
3.15	1227.0	0.236	43.39	0.005
2.90	1398.0	0.155	57.31	0.017
2.70	1834.0	0.136	106.4	0.058
2.55	2225.0	0.117	151.0	0.139
2.35	3154.0	0.110	313.6	0.502
1.95	5416.0	0.085	1003.0	5.681

Table 10.3: Continued.

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
1.65	7616.0	0.068	2149.0	33.24
1.40	10140.0	0.057	4137.0	146.5
1.20	10830.0	0.043	5041.0	408.1
0.95	13510.0	0.035	8705.0	1710.0
0.85	16990.0	0.038	14550.0	3524.0
0.60	18840.0	0.028	20000.0	13230.0
0.35	16560.0	0.016	17290.0	39510.0

Table 10.4 : **"The effect of pH on the concentration of various ions in $BaCrO_4$ - HCl solutions at 70°C.**

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	$CrO_4^{=}$	$Cr_2O_7^{=}$	CrO_3Cl^-
4.25	402.8	0.759	3.704	1×10^{-5}
3.80	664.1	0.453	10.21	14×10^{-5}
3.45	1122.0	0.352	29.71	0.001
3.15	1665.0	0.270	66.88	0.007
2.85	2224.0	0.234	121.4	0.024
2.75	3214.0	0.222	260.2	0.088
2.25	5428.0	0.132	797.6	1.548

Table 10.4: Continued

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
1.85	7869.0	0.086	1822.0	14.82
1.50	12930.0	0.075	5514.0	129.9
1.15	16430.0	0.051	10050.0	886.5
1.15	16500.0	0.051	10140.0	890.5
1.05	17240.0	0.045	11490.0	1507.0
0.90	19730.0	0.040	16090.0	3581.0
0.60	23150.0	0.029	25370.0	18180.0

Table 10.5: **"The effect of pH on the concentration of various ions in $BaCrO_4$ - HCl solutions at 90°C.**

pH	Concentration $(M/dm^3) \times 10^6$			
	$HC4O_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
4.50	451.7	1.315	4.000	$< 10^{-5}$
4.15	706.3	0.934	9.887	3×10^{-5}
3.85	1071.0	0.723	23.04	19×10^{-5}
3.60	1582.0	0.615	51.03	91×10^{-5}
3.25	2262.0	0.405	106.5	0.007
2.95	3131.0	0.292	209.2	0.037
2.10	9402.0	0.153	2171.0	5.980

Table 10.5: Continued

pH	Concentration $(M/dm^3) \times 10^6$			
	$HCrO_4^-$	$CrO_4^=$	$Cr_2O_7^=$	CrO_3Cl^-
2.00	10640.0	0.143	2848.0	10.87
1.85	12030.0	0.120	3771.0	25.02
1.60	14150.0	0.088	5567.0	96.41
1.20	19350.0	0.058	11920.0	898.7
1.10	23190.0	0.060	18030.0	1760.0
1.00	24800.0	0.054	21480.0	3055.0
0.75	29050.0	0.042	32870.0	12090.0

Table 10.6: Change in K_{sp} with pH calculated from the solubility data at 30°C and the concentrations of CrO_4^{2-} at 30°C not corrected for ionic strength.

pH	$K_{sp} \times 10^{11}$	pH	$K_{sp} \times 10^{11}$
4.18	3.0	1.75	19.2
3.80	2.5	1.55	20.3
3.50	4.9	1.40	27.4
3.05	5.7	1.30	25.1
2.80	7.1	1.00	31.9
2.40	11.3	0.75	30.9
2.10	16.0	0.60	83.6

CHAPTER 11

Conclusions and Recommendations for Future Work

11.1 Conclusions

1. Crystals of barium chromate of the order of 10^{-4} m in size can be produced by precipitation from homogeneous solution.

2. The solubility of barium chromate in neutral aqueous solution was found to be approximately twice that of the values usually found in the literature.

3. The solubility of barium chromate was found to increase by ~ 3 orders of magnitude as the pH of the solution changed from pH = 4 to pH = 1.

4. In the presence of chloride ion the formation of (CrO_3Cl^-) ion has a significant effect in increasing the solubility.

5. The equilibrium constant for the dimerisation of the $(HCrO_4^-)$ ion was found to be of similar magnitude to those values found in the literature but was temperature sensitive.

6. The equilibrium constant for the protonation of the $(CrO_4^=)$ ion was found to be lower than those values found in the literature.

11.2 Recommendations for Future Work

1. The effect of urea on the solubility of the barium chromate should be determined.

2. The kinetics of barium chromate crystal growth in low pH solutions should be studied.

3. The effect of additives such as ammonium salts on (a) the solubility of barium chromate, (b) the rate of hydrolysis of urea, should be studied.

4. The crystallisation of barium chromate process using urea hydrolysis to produce a large crystal product of narrow size distribution should be optimised.

APPENDIX 1

The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration in the system.

$$\mathrm{pH} = -\log_{10}[H^{+}] \qquad \ldots\ldots\ldots \quad \text{A1.1}$$

Let the final pH of any sample be - log [X] therefore the hydrogen ion concentration in that solution = x.

Let y be the hydrogen ion concentration required in sample bottle.

Let z be the hydrogen ion concentration of the acid used.

$$\text{Sample volume} = 1\ \mathrm{cm}^3$$

$$\text{volumetric flask volume} = 25\ \mathrm{cm}^3$$

On adding sample to volumetric flask and making up amount of hydrogen ion in volumetric flask:

$$[H^{+}] = x/25 \qquad \ldots\ldots\ldots \quad \text{A1.2}$$

Amount of acid needed to make the hydrogen ion conc. y is:

$$y = x/25. \qquad \ldots\ldots\ldots \quad \text{A1.3}$$

Volume of acid of conc. z needed to be added before the volumetric flask is made up is:

$$Va = 25(y - x/25)/z\ . \qquad \ldots\ldots\ldots \quad \text{A1.3}$$

Taking $z = 1.0\ \mathrm{M/dm}^3$,

if the pH of the sample is 1.0 then $x = 0.1$ and taking the final pH = 1.0 $y = 0.1$ then $Va = 25(0.1 - 0.1/25)/1.0 = 2.4\ \mathrm{cm}^3$ from titrations the acid concentration was found = $0.995\ \mathrm{M/dm}^3$.

$$\therefore\ Va = 2.4/0.995 = \underline{\underline{2.41\ \mathrm{cm}^3}}$$

Similarly table A1.1 was constructed.

Table A1.1

Calculation of acid added to make up pH to 1.0

pH of Sample	x	x/25	y-x/25	Va $(dm^3) \times 10^3$	Va $(dm^3) \times 10^3$
0.4	0.398	0.016	0.084	2.10	2.11
0.5	0.316	0.012	0.088	2.20	2.21
0.6	0.251	0.010	0.090	2.25	2.26
0.7	0.1995	0.00798	0.092	2.30	2.31
0.8	0.158	0.0063	0.0937	2.35	2.36
0.9	0.1259	0.00504	0.095	2.38	2.39
1.0	0.10	0.004	0.096	2.40	2.41
1.5	0.0366	0.00146	0.0987	2.46	2.47
2.0	0.01	0.00040	0.0996	2.49	2.50
2.5	0.00316	0.00013	0.09987	2.497	2.51
3.0	0.0010	0.00004	0.09996	2.499	2.51

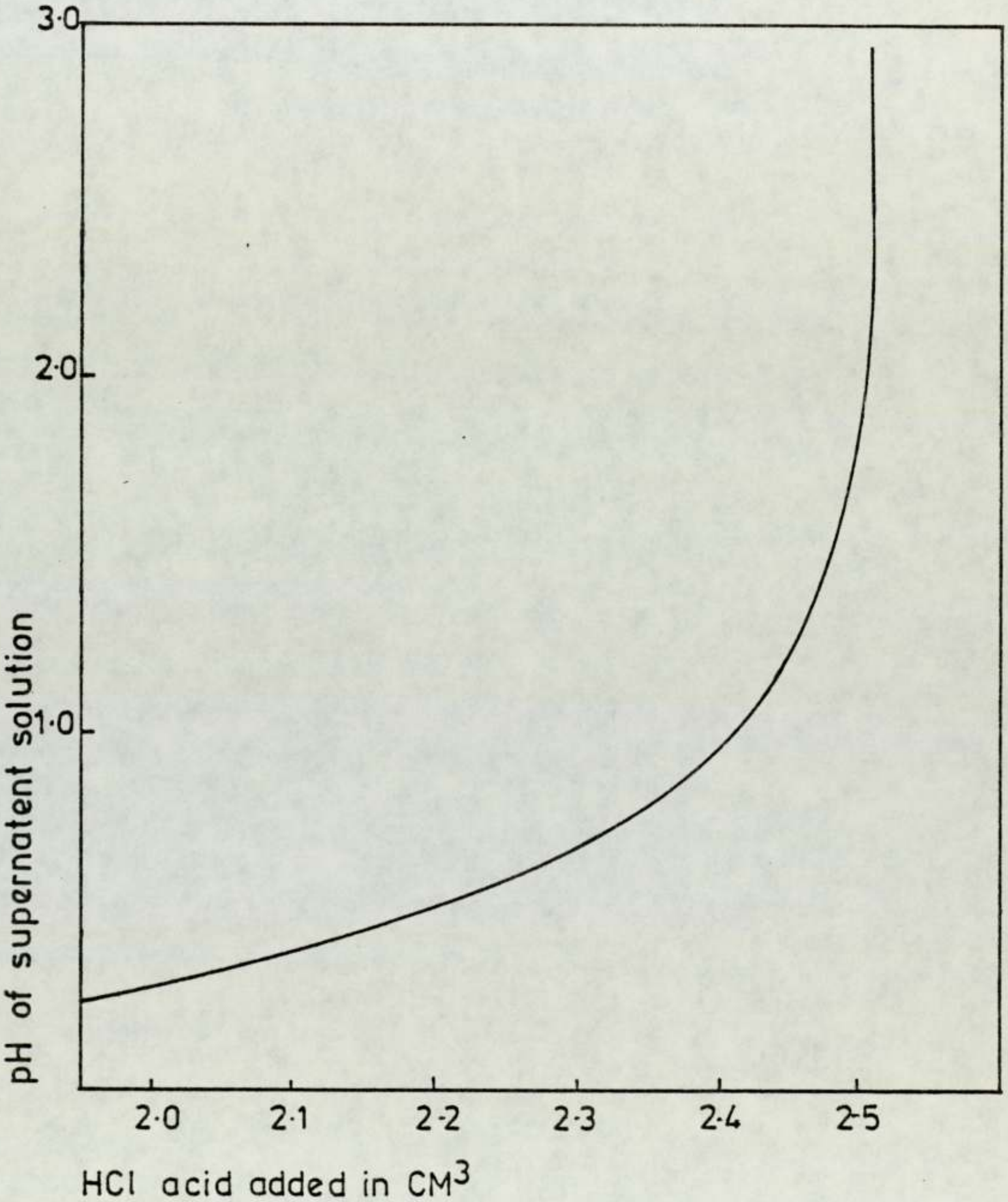


FIGURE A1: 1 plot of amount of HCl necessary to add to solution to make pH = 1·25

APPENDIX 2

Correction of equilibrium constants for ionic strength.

In any equilibrium reaction

$$aA + bB \rightleftharpoons cC + dD \qquad \text{A2.1}$$

the thermodynamic equilibrium constant can be defined as

$$K^{o} = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \qquad \text{A2.2}$$

where a is the activity of the constituents of the reaction. Further,

$$a_i = f_i \; C_i \qquad \text{A2.3}$$

where f_i = the activity coefficient of i

C_i = the molar concentration of i

Defining a second equilibrium constant in terms of the concentration of the reactants and products.

$$K = \frac{C_C^c \times C_D^d}{C_A^a \times C_B^b} \qquad \text{A2.4}$$

equation A2.2 can then be written as follows,

$$K^{o} = K \; \frac{(f_C^c \times f_D^d)}{(f_A^a \times f_B^b)} \qquad \text{A2.5}$$

The activity coefficient of any species i can be defined by the Debye-Huckle equation (32).

$$- \log fi = \frac{Az_i^2 \sqrt{\mu}}{1 + Ba\sqrt{\mu}} \qquad \text{A2.6}$$

where A is a constant dependent on the solvent and the temperature of the system and is given by (46):

$$A = 1.823 \times 10^b/(DT)^{3/2} \qquad \text{A2.7}$$

where T = absolute temperature K

D = dielectric constant of solvent that temperature.

and B can be defined as (47):

$$B = 5.0_4 \times 10^9(1/DT)^{1/2} \qquad \text{A2.8}$$

a is defined as the mean distance of approach of ions, and

Z_i is the charge of ion i.

Table A2.2 Variation of D, A and B with temperature when the solvent is water, (175) for the Debye-Huckle equation.

Temp (K)	D	A	B
273	88.15	0.488	0.325×10^8
288	82.23	0.500	0.328×10^8
298	78.54	0.509	0.330×10^8
303	76.76	0.514	0.331×10^8
313	73.75	0.525	0.333×10^8
323	70.10	0.535	0.335×10^8

Table A2.3

The values of "a" for various ions of interest are tabulated in table A2.3 (32).

Ion	a (cm) x 10^8
H^+	9.0
Ba^{2+}	5.0
CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$	
$HCrO_2O_7^-$, CrO_3 Cl^-	4.0
Cl^-	3.0

Taking the equilibrium reaction

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad 1.1$$

$$K_2^o = \frac{[CrO_4^{2-}]\,(H^+)\;f_D f_B^{-1}}{[HCrO_4^-]} \qquad 1.9$$

where [ ] indicates concentration and ( ) indicates activity using equation A2.4.

$$K_2^o = K_2 \; f_D f_B^{-1} \qquad A2.9$$

substituting equation A2.6 into equation A2.9

$$\log K_2^o = \log K_2 - \frac{4A\sqrt{\mu}}{1 + a_D B\sqrt{\mu}} + \frac{A\sqrt{\mu}}{a + a_B B\sqrt{\mu}} \qquad A2.10$$

as $a_B = a_D$

$$\therefore \quad \log K_2^{\circ} = \log K_2 - \frac{3A\sqrt{\mu}}{1 + a_D B\sqrt{\mu}} \qquad \text{A2.11}$$

inserting the values of A, B and a at the appropriate temperatures, the following relations for the six equilibrium constants at temperatures 30°, 40°, 50°, 70°, 80° and 90°C were formed.

Table A2.4:

Values of the constants for equation A2.11

Temperature ^{o}C	Equilibrium Constant	3A	a_4 B
30	K_1^0	0.514	1.324
	K_2^0	1.542	1.324
	K_c^0	0.514	0.993
	K_d^o	1.028	1.324
	K_{d1}^o	0.514	1.324
	K_{d2}^o	1.542	1.324
40	K_1^o	0.525	1.332
	K_2^o	1.575	1.332
	K_c^o	0.525	0.999
	K_d^o	1.05	1.332
	K_{d1}^o	0.525	1.332
	K_{d2}^2	1.575	1.332
50	K_1^o	0.535	1.340
	K_2^o	1.605	1.340
	K_c^o	0.535	1.010
	K_d^o	1.07	1.340
	K_{d1}^o	0.535	1.340

Table A2.4: Continued

Temperature ^{o}C	Equilibrium Constant	3A	a_4 B
50	K^{o}_{d2}	1.605	1.340
70	K^{o}_{1}	0.555	1.356
	K^{o}_{2}	1.665	1.356
	K^{o}_{c}	0.555	1.017
	K^{o}_{d}	1.11	1.356
	K^{o}_{d1}	0.555	1.356
	K^{o}_{d2}	1.665	1.356
80	K^{o}_{1}	0.565	1.364
	K^{o}_{2}	1.695	1.364
	K^{o}_{c}	0.565	1.023
	K^{o}_{d}	1.130	1.364
	K^{o}_{d1}	0.565	1.364
	K^{o}_{d2}	1.695	1.364
90	K^{o}_{1}	0.576	1.368
	K^{o}_{2}	1.728	1.368

Table A2.4: Continued

Temperature ^{o}C	Equilibrium Constant	3A	a_4 B
90	K_c^o	0.576	1.026
	K_d^o	1.152	1.368
	K_{d1}^o	0.576	1.368
	K_{d2}^o	1.728	1.368

APPENDIX 3

When barium chromate crystals are in suspension in water, Ba^{2+} and CrO_4^{2-} ions go into solution according to the equilibrium:

$$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{-2} \qquad A3.1$$

Defining the fraction of crystal surface covered by the barium ions as z, the fraction covered by the chromate ions is then 1 - z. The rate r_1 at which barium ions leave the surface is proportional to z and can be expressed as

$$r_1 = k_1 z \qquad A3.2$$

where k_1 is a rate constant. The rate r_2 at which barium ions are deposited from solution is proportional both to the concentration of barium ions in solution and the remaining available space,

$$r_2 \ z = k_2 (1 - z) [Ba^{2+}] \ , \qquad A3.3$$

at equilibrium

$$k_1 z = k_2 (1 - z) [Ba^{2+}] \ , \qquad A3.4$$

rearranging

$$[Ba^{2+}] = k_1 z / k_2 (1 - z) \ , \qquad A3.5$$

similarly

$$[CrO_4^{2-}] = \frac{K_3 (1 - z)}{k_4 z} \ . \qquad A3.6$$

$$\therefore \quad [CrO_4^{2-}] [Ba^{2+}] = \frac{k_1 \ k_3}{k_2 \ k_4} = K_{sp} \qquad A3.7$$

where K_{sp} is the solubility product of the ions in solution. On adding HCl the equilibria given in (section 2.3) are formed.

These equilibria can be represented mathematically as follows:-

$$K_1 = [HCrO_4^-]\,(H^+) / [H_2CrO_4] \qquad A3.8$$

$$K_2 = [CrO_4^{2-}]\,(H^+) / [HCrO_4^-] \qquad A3.9$$

$$K_d = [Cr_2O_7^{2-}] / [HCrO_4^-]^2 \qquad A3.10$$

$$K_{d1} = [H_2Cr_2O_7^-]\,(H^+) / [H_2Cr_2O_7] \qquad A3.11$$

$$K_{d2} = [Cr_2O_7^{2-}]\,(H^+) / [HCr_2O_7^-] \qquad A3.12$$

$$K_c = [CrO_3Cl^-] / [HCrO_4^-]\,(H^+)(Cl^-) \qquad A3.13$$

Defining S as the total solubility of Cr(VI) in the solution and assuming that not all the $BaCrO_4$ is ionised a mass balance on Cr(VI) gives:-

$$S = [BaCrO_4] + [CrO_4^{2-}] + [HCrO_4^-] + [H_2CrO_4]$$
$$+ 2[Cr_2O_7^{2-}] + 2[HCr_2O_7^-] + 2[H_2Cr_2O_7]$$
$$+ [CrO_3Cl^-] \qquad A3.14$$

A mass balance on barium gives,

$$S = [BaCrO_4] + [Ba^{2+}] = \Sigma\, Ba\,. \qquad A3.15$$

Defining β as the fraction of $\mathrm{BaCrO_4}$ not ionised.

$$\beta = \frac{[\mathrm{BaCrO_4}]}{\Sigma \mathrm{Ba}} \qquad \text{A3.16}$$

$$\therefore\ [\mathrm{Ba}^{2+}] = S(1 - \beta) \qquad \text{A3.17}$$

from equations A3.9

$$[\mathrm{HCrO_4^-}] = [\mathrm{CrO_4^{2-}}]\,(\mathrm{H}^+) / K_2 \qquad \text{A3.18}$$

similarly modifying equation A3.8 and equation A3.10 to A3.13 and substituting into equation A3.14.

$$\begin{aligned} S = {} & [\mathrm{BaCrO_4}] + [\mathrm{CrO_4^{2-}}] + [\mathrm{CrO_7^{2-}}]\,(\mathrm{H}^+)/K_2 + [\mathrm{CrO_4^{2-}}](\mathrm{H}^+)^2/K_2\,K_1 \\ & + 2[\mathrm{CrO_4^{2-}}]^2\,(\mathrm{H}^+)^2\,K_d/K_2^2 + 2[\mathrm{CrO_4^{2-}}]^2\,(\mathrm{H}^+)^3\,K_d/K_2\,K_{d2} \\ & + 2[\mathrm{CrO_4^{2-}}]^2\,(\mathrm{H}^+)^4\,K_d/K_2^2\,K_{d2}\,K_{d1} \\ & + [\mathrm{CrO_4^{2-}}]\,[\mathrm{Cl^-}]\,(\mathrm{H}^+)^2.\ K_c/K_2 \end{aligned} \qquad \text{A3.19}$$

from equation A3.7

$$[\mathrm{CrO_4^{2-}}] = K_{sp} / [\mathrm{Ba}] = K_{sp} / S(1 - \beta) \qquad \text{A3.20}$$

substituting A3.20 into A3.19

$$\begin{aligned} S = {} & \alpha S + K_{sp} / (1 - \beta)\,S + K_{sp}\,(\mathrm{H}^+)/K_2\,(1-\beta)\,S \\ & + K_{sp}\,(\mathrm{H}^+)^2 / K_2\,K_1\,(1 - \beta)\,S + 2\,K_{sp}^2\,K_d\,(\mathrm{H}^+)^2/K_2^2\,(1 - \beta)^2\,S^2 \\ & + 2\,K_{sp}^2\,K_d\,(\mathrm{H}^+)^3 / K_2^2\,K_{d2}\,(1 - \beta)^2\,S^2 \end{aligned}$$

$$+ 2\, K_{sp}^2\, K_d\, (H^+)^4 \,/\, K_2^2\, K_{d2}\, K_{d1}\, (1 - \beta)^2\, S^2$$

$$+ K_{sp}\, (H^+)\, (Cl^-)\, K_c \,/\, K_2\, (1 - \beta)\, S \qquad \text{A3.21}$$

taking the $[Cl^-]$ concentration to equal (H^+) and rearranging equation A3.21 the following equation is obtained:

$$S^3\, (1 - \beta)^3 \; - \; S\, (1 - \beta)\, A \; - \; B \; = \; 0 \qquad \text{A3.22}$$

where,

$$A \; = \; K_{sp}\, (1 + (H)\, /K_2 + (H)^2\, (1/K_1 K_2 + (H)\, K_c \,/\, K_2)) \qquad \text{A3.23}$$

and,

$$B \; = \; \frac{2\, K_{sp}^2\, K_d}{K_2^2}\; (H)^2 + (H)^3\, /K_{d2} + (H)^4 \,/\, K_{d1}\, K_{d2}) \qquad \text{A3.24}$$

APPENDIX 4

SK22

```
10    REM PROGRAM FOR HURESTIC APPROACH
20    PRINT
30    DIM E [5], G [5], W [5], X [5], Y [5]
40    DIM H [5], S [5], C [5], D [5]
50    PRINT " INPUT DATA H & S "
60    FOR 1 = 1 TO 2
70    INPUT H [1], S [1]
80    NEXT 1
90    PRINT " INPUT KC, K1 & K2"
100   FOR J = 1 TO 3
110   INPUT X [J], D [J], E [J]
120   NEXT J
130   PRINT "INPUT KSP, KD1 & KD2 "
140   FOR 1 = 1 TO 2
150   INPUT C [1], W [1], Y [1]
160   NEXT 1
170   PRINT "INPUT KD "
180   FOR 1 = 1 TO 5
190   INPUT G [1]
200   NEXT 1
210   FOR P = 1 TO 2
220   FOR 1 = 1 TO 2
230   FOR J = 1 TO 3
240   FOR K = 1 TO 2
250   FOR L = 1 TO 2
260   FOR M = 1 TO 5
270   FOR N = 1 TO 3
280   FOR O = 1 TO 3
290   GOSUB 400
300   GOSUB 510
310   NEXT O
320   NEXT N
330   NEXT M
340   NEXT L
350   NEXT K
360   NEXT J
370   NEXT I
380   NEXT P
```

```
390   STOP
400   A1 = H[P]/E [N]
410   A2 = (H [P]  2)/(E [N] * D [O])
420   A3 = X [J] * (H [p[  3)/)E [N])
430   A = C [1] * (1 +A1 +A2 + A3)
440   B1 = 2 * ((C [1]  2) * G [M])/(E [N]  2)
450   B2 = H [P]  2
460   B3 = (H [P]  3)/W [K]
470   B4 = (H [P]  4)/(W [K] * Y [L])
480   B = B1 * (B2 + B3 + B4)
490   F = (A * S [P] + B)/(S [P]  3)
500   RETURN
```

YVAL

```
      FUNCTION YVAL (H,W)
C
C     EVALUATE CORELATION
C
      DIMENSION V(10),M(10),W(10)
      REAL K1,K2,K3,KSP,M,K4,K5,K6
      DO 5 I=1,6
      IF(ABS(W(I)).GT.150.)W(I)=SIGN(W(I),150)
      V(I)=EXP(W(I))
    5 CONTINUE
      K=1
      M(K)=0.0
      V(7)=(2.28E-09) * V(1)/(V(1) * 1. E-07)
   10 F1=ALOG(V(1)) * 514 * (M(K) ** (.5))/(1. + 1.324 * M(K) ** (.5))
      F2=ALOG(V(2)) * 542 * (M(K) ** (.5))/(1. +1.324 * M(K) ** (.5))
      F3=ALOG(V(3))-.514 * (M(K) ** (.5))/(1. + 933 * M(K) ** (.5))
      F4=ALOG(V(4)) +1.028 * (M(K) ** (.5))/(1. + 1.324 * M(K) ** (.5))
      F5=ALOG(V(5)) +514 * (M(K) ** (.5))/(1. +1.324 * M(K) ** (.5))
      F6=ALOG(V(6)) +1.542 * (M(K) ** (.5))/(L. +1.324 * M(K) ** (.5))
      F7=ALOG(v(7)) +4. * (M(K) ** (.5))/(1.+M(K) ** (.5))
      K1.EXP(F1)
      K2=EXP(F2)
      K3=EXP(F3)
```

```
      K4=EXP(F4)
      K5=EXP(F5)
      K6=EXP(F6)
      KSP=EXP(F7)
      C=1./(K1 * K2) + H * K3/K1
      A=-KSP * (1. +H/K1 + (H ** 2) * C)
      B1=2.* (KSP ** 2)/(K2** 2)
      B2=(H**3)/K6
      B3=(H**4)/(K5*K6)
      B=-B1 * (H * * 2 + B2 + B3)
      R=(A/3.) * * 3 * (B/2.)**2
      IF (R,GE.O.O.) GO TO 100
      P=ACOS (((B**2)*27./(-(A**3)*4,))** (.5))
      S=2.*(-A/3.)**(.5))*COS(P/3)
      TO TO 40
 100  A1=(-A/2.+SQRT(R))**(1./3)
      A2=(-A/2.-SQRT(R))**(1./3.)
      IF(R,GT,0,0) GO TO 20
      S=-5* (A1 + A2)
      TO TO 40
  20  S=A1 + A2
  40  C1=KSP/S
      C2=C1 * H/K1
      C3=C2*K3*H**2
```

```
      C4=K4*C2**2
      C5=C4*H/K6
      K=K+1
      M(K)=,5*(4,*C1+C2+C3+2.*S + 4, * S + 4 * C4 + C5)
      IF (ABS(M(K)-M(K-1)).LE.0.001) GO TO 50
      TO TO 10
50    YVAL=S
      RETURN
      END
```

APPENDIX 5

Table A5.1: Results of Heuristic Calculation for equilibrium constants using program SK22.
$H = (10^{-1})$ $S = (10^{-2})$

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^0	10^{-1}	10^2	10^{-2}	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-10}	1.110
10^0	10^{-1}	10^2	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-10}	1.101
10^0	10^{01}	10^2	10^{-1}	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-9}	1.114
10^0	10^{-1}	10^2	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-4}	1.101
10^0	10^{-1}	10^2	10^0	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-8}	1.150
10^0	10^{-1}	10^2	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-10}	1.101
10^0	10^{-1}	10^2	10^1	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-7}	1.510
10^0	10^{-1}	10^2	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-9}	1.105
10^0	10^{-1}	10^2	10^2	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-8}	1.141
10^0	10^{-1}	10^1	10^{-2}	10^{-6}	10^0	1	10^5	10^5	10^3	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-10}	1.110

Table A5.1: Continued

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^{0}	10^{-1}	10^{1}	10^{-2}	10^{-5}	10^{-2}	1	10^{4}	10^{5}	10^{2}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-12}	1.101
10^{0}	10^{-1}	10^{1}	10^{-1}	10^{-6}	10^{0}	1	10^{5}	10^{4}	10^{3}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-9}	1.114
10^{0}	10^{-1}	10^{1}	10^{-1}	10^{-5}	10^{-2}	1	10^{4}	10^{5}	10^{2}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-11}	1.101
10^{0}	10^{-1}	10^{1}	10^{0}	10^{-6}	10^{0}	1	10^{5}	10^{4}	10^{3}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-8}	1.150
10^{0}	10^{-1}	10^{1}	10^{0}	10^{-5}	10^{-2}	1	10^{4}	10^{5}	10^{2}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-10}	1.101
10^{0}	10^{-1}	10^{1}	10^{1}	10^{-5}	10^{-2}	1	10^{4}	10^{5}	10^{2}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-9}	1.105
10^{0}	10^{-1}	10^{1}	10^{2}	10^{-5}	10^{-2}	1	10^{4}	10^{5}	10^{2}	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-8}	1.141
10^{0}	10^{-2}	10^{2}	10^{-2}	10^{-6}	10^{0}	1	10^{5}	10^{4}	10^{3}	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-9}	1.112
10^{0}	10^{-2}	10^{2}	10^{-2}	10^{-6}	10^{-2}	1	10^{4}	10^{5}	10^{2}	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-11}	1.101
10^{0}	10^{-2}	10^{2}	10^{-1}	10^{-6}	10^{0}	1	10^{5}	10^{4}	10^{3}	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-8}	1.132

Table A5.1: Continued

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^0	10^{-2}	10^2	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-10}	1.101
10^0	10^{-2}	10^{-2}	10^0	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-7}	1.330
10^0	10^{-2}	10^{-2}	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-9}	1.103
10^0	10^{-2}	10^{-2}	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-8}	1.123
10^0	10^{-2}	10^{-2}	10^2	10^{-5}		1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-7}	1.321
10^0	10^{-2}	10^{-1}	10^{-2}	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-9}	1.112
10^0	10^{-2}	10^{-1}	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-11}	1.010
10^0	10^{-2}	10^{-1}	10^{-1}	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-8}	1.132
10^0	10^{-2}	10^{-1}	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-2}	10^{-1}	10^{-4}	10^{-10}	1.101
10^0	10^{-2}	10^{-1}	10^0	10^{-6}	10^0	1	10^5	10^4	10^3	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-7}	1.332

Table A5.1: Continued.

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^0	10^{-2}	10^{-1}	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-9}	1.103
10^0	10^{-2}	10^{-1}	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-8}	1.123
10^0	10^{-2}	10^{-1}	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^2	10^{-2}	10^{-1}	10^{-3}	10^{-4}	10^{-8}	1.323
10^1	10^{-1}	10^2	10^{-2}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-10}	1.200
10^1	10^{-1}	10^2	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-12}	1.110
10^1	10^{-1}	10^2	10^{-1}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-9}	1.204
10^1	10^{-1}	10^2	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-11}	1.110
10^1	10^{-1}	10^2	10^0	10^{-5}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-8}	1.240
10^1	10^{-1}	10^2	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-10}	1.110
10^1	10^{-1}	10^2	10^1	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-7}	1.600

Table A5.1: Continued.

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^1	10^{-1}	10^2	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-9}	1.114
10^1	10^{-1}	10^2	10^2	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-8}	1.150
10^1	10^{-1}	10^1	10^{-2}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-10}	1.200
10^1	10^{-1}	10^1	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-12}	1.110
10^1	10^{-1}	10^1	10^{-1}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-9}	1.204
10^1	10^{-1}	10^1	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-11}	1.110
10^1	10^{-1}	10^1	10^0	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-8}	1.240
10^1	10^{-1}	10^1	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-10}	1.110
10^1	10^{-1}	10^1	10^1	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-7}	1.602
10^1	10^{-1}	10^1	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-9}	1.114

Table A5.1: Continued.

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^1	10^{-1}	10^1	10^2	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-8}	1.150
10^1	10^{-2}	10^2	10^{-2}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-9}	1.202
10^1	10^{-2}	10^2	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-11}	1.110
10^1	10^{-2}	10^2	10^{-1}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-8}	1.222
10^1	10^{-2}	10^2	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-10}	1.110
10^1	10^{-2}	10^2	10^0	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-7}	1.420
10^1	10^{-2}	10^2	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-9}	1.112
10^1	10^{-2}	10^2	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-8}	1.132
10^1	10^{-2}	10^2	10^2	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-7}	1.330
10^1	10^2	10^1	10^{-2}	10	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-9}	1.202

Table A5.1: Continued.

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^1	10^{-2}	10^1	10^{-2}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-11}	1.110
10^1	10^{-2}	10^1	10^{-1}	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-8}	1.222
10^1	10^{-2}	10^1	10^{-1}	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-10}	1.110
10^1	10^{-2}	10^1	10^0	10^{-6}	10^0	1	10^5	10^4	10^4	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-7}	1.422
10^1	10^{-2}	10^1	10^0	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-9}	1.112
10^1	10^{-2}	10^1	10^1	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-8}	1.132
10^1	10^{-2}	10^1	10^2	10^{-5}	10^{-2}	1	10^4	10^5	10^3	10^{-2}	10^{-1}	10^{-4}	10^{-4}	10^{-7}	1.330

Table A5.2: Results of Heuristic calculation for equilibrium constants using program SK22 $H = 10^{-4}$ $S = 10^{-5}$

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^{0}	10^{-1}	10^{-1}	10^{-2}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-18}	1.101
10^{0}	10^{-1}	10^{-1}	10^{-2}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-18}	1.110
10^{0}	10^{-1}	10^{-1}	10^{-2}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-18}	1.100
10^{0}	10^{-1}	10^{-1}	10^{-1}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-17}	1.101
10^{0}	10^{-1}	10^{-1}	10^{-1}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-17}	1.110
10^{0}	10^{-1}	10^{-1}	10^{-1}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-17}	1.100
10^{0}	10^{-1}	10^{-1}	10^{0}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-16}	1.101
10^{0}	10^{-1}	10^{-1}	10^{0}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-16}	1.110
10^{0}	10^{-1}	10^{-1}	10^{0}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-16}	1.100
10^{0}	10^{-1}	10^{-1}	10^{1}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-15}	1.103

Table A5.2: Continued.

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^{0}	10^{-1}	10^{-1}	10^{1}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-15}	1.112
10^{0}	10^{-1}	10^{-1}	10^{1}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-15}	1.102
10^{0}	10^{-1}	10^{-1}	10^{2}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-14}	1.121
10^{0}	10^{-1}	10^{-1}	10^{2}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-14}	1.130
10^{0}	10^{-1}	10^{-1}	10^{2}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-17}	10^{-8}	10^{-14}	1.120
10^{0}	10^{-1}	10^{1}	10^{-2}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-18}	1.101
10^{0}	10^{-1}	10^{1}	10^{-2}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-18}	1.110
10^{0}	10^{-1}	10^{1}	10^{-2}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-18}	1.100
10^{0}	10^{-1}	10^{1}	10^{-1}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-17}	1.101
10^{0}	10^{-1}	10^{1}	10^{-1}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-17}	1.110

Table A5.2: Continued.

K_c	K_{d2}	K_{d1}	K_d	K_2	K_1	A1	A2	A3	A4	B2	B3	B4	A	B	F
10^{0}	10^{-1}	10^{1}	10^{1}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-15}	1.112
10^{0}	10^{-1}	10^{1}	10^{1}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-15}	1.102
10^{0}	10^{-1}	10^{1}	10^{2}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-14}	1.121
10^{0}	10^{-1}	10^{1}	10^{2}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-14}	1.130
10^{0}	10^{-1}	10^{1}	10^{2}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-11}	10^{-16}	10^{-8}	10^{-14}	1.120
10^{0}	10^{-2}	10^{2}	10^{-2}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-10}	10^{-16}	10^{-8}	10^{-18}	1.101
10^{0}	10^{-2}	10^{2}	10^{-2}	10^{-5}	10^{-2}	10^{0}	10^{1}	10^{-1}	10^{-7}	10^{-8}	10^{-10}	10^{-16}	10^{-8}	10^{-18}	1.110
10^{0}	10^{-2}	10^{2}	10^{-2}	10^{-5}	10^{0}	10^{0}	10^{1}	10^{-3}	10^{-7}	10^{-8}	10^{-10}	10^{-16}	10^{-8}	10^{-18}	1.100
10^{0}	10^{-2}	10^{2}	10^{-1}	10^{-5}	10^{-1}	10^{0}	10^{1}	10^{-2}	10^{-7}	10^{-8}	10^{-10}	10^{-16}	10^{-8}	10^{-17}	1.101

APPENDIX 6

Equation 7.18 section 7.3.4.1 gives,

$$B = \frac{-(1 + \frac{K_2}{H}) + \sqrt{(1 + \frac{K_2}{H})^2 + 8K_dC_T}}{4K_d} \qquad .....7.18$$

If the square root term is expanded by the binomial,

$$\text{Square root term} = ((1 + \frac{K_2}{H})^2 + 8K_dC_T)^{\frac{1}{2}}$$

$$= (1 + \frac{K_2}{H}) + (\tfrac{1}{2})\, 8K_dC_T\, (1 + \frac{K_2}{H})^{-\frac{1}{2}} + (-\tfrac{1}{2})(\tfrac{1}{2})(\tfrac{1}{2})\, (1 + \frac{K_2}{H})^{-3/2}\, (8K_dC_T)^2$$

assuming $8K_dC_T \ll 1$, the third term and consequent terms can be neglected.

Take the equilibrium,

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

with,

$$K_d = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2}$$

assume the fraction of $[Cr_2O_7^{2-}] = \frac{1}{2}\alpha\, C_T$

and the fraction $[HCrO_4^-] = (1 - \alpha)C_T$

$$\therefore \qquad K_d = \frac{\alpha\, C_T/\, 2}{(1 - \alpha)^2 C_T^{\,2}}$$

$$2K_dC_T = \frac{\alpha}{(1 - \alpha)^2}$$

and

$$8K_dC_T = \frac{4\alpha}{(1-\alpha)^2}$$

now $$0 < 8K_dC_T < 1 \qquad \text{......A6.1}$$

$$\therefore \qquad 0 < \frac{4\alpha}{(1-\alpha)^2} < 1 \qquad \text{......A6.2}$$

Take the L.H.S. of the inequality A6.2

$$0 < \frac{4\,\alpha}{(1-\alpha)^2} \implies \alpha > 0$$

for the R.H.S. of the inequality

$$\frac{4\alpha}{(1-\alpha)^2} < 1$$

i.e. $$4\,\alpha < (1-\alpha)^2$$

i.e. $$4\,\alpha < 1 - 2\,\alpha + \alpha^2$$

i.e. $$0 < 1 - 6\,\alpha + \alpha^2 \qquad \text{......A6.3}$$

consider this case,

$$\alpha^2 - 6\alpha + 1 = 0 \qquad \text{......A6.4}$$

$$\alpha = \frac{6 \pm \sqrt{36-4}}{2} = 3 \pm \tfrac{1}{2}\sqrt{32}$$

$$= 3 \pm 2\sqrt{2}$$

as $\alpha < 1$

$\therefore \alpha^2 - 6\alpha + 1 > 0$ is equivalent to

$\alpha - [3 - 2\sqrt{2}] > 0$

$\therefore \alpha < 3 - 2\sqrt{2} = 0.1716$ A6.5

$\therefore$ for $0 < 8K_dC_T < 1$

this constraint on α applies

$0 < \alpha < 0.1716$ A6.6

This is a very severe constraint for the expansion and consequent truncation to be valid.

APPENDIX 7

SK6

```
C       PROGRAM TO CALCULATE THE EQUILIBRIUM CONSTANT
C       FOR THE DIMERISATION REACTION USING AN
C       ITERITIVE PROCEDURE.
        DIMENSION K (100), FE (100), C (20), R (20), ALPHA (20), Y (20)
        DIMENSION G (20), F (20), EPS (20)
        REAL K, KD, N
        READ (11, -) JN, K(1), K (2)
        READ (11, -) (C(J), J=1, JN)
        1 = 1
      5  READ (11, -) LAMDA
         READ (11, -) (Y(J), J = 1, JN)
         L = 1
     10  SGA = 0.0
         SGY = 0.0
         SG = 0.0
         SAS = 0.0
         SY = 0.0
         SA = 0.0
         SAY = 0.0
         SFE = 0.0
```

```
      DO 100 J = 1, JN
      R (J) = 4. * C (J) * K (L)
      ALPHA (J) = 1. + 1./R (J) - (1./R (J) * SQRT (1.+2.* R (J)
      G (J) = (1.+R (J))/(SQRT (1.+2. * R (J))) - 1.) /R (J)
      SAY = SAY + ALPHA (J) * Y (J)
      SA = SA + ALPHA (J)
      SY = SY + Y (J)
      SAS = SAS + ALPHA (J) * ALPHA (J)
      SG = SG + G (J)
      SGY = SGY + G (J) * Y (J)
      SGA = SGA + G (J) * ALPHA (J)
  100 CONTINUE
      N = FLOAT (JN)
      AM = (N * SAY - SA * SY) / (N * SAS - SA * SA)
      D = (SY - AM * SA) / N
      B = (N * SGY - SG * SY) / (N * SAY - SA * SY) - 2. * ((N * SGA - SG * SA) / (N * SAS - SA * SA))
      E = AM * (B * SA + SG) / N
      DO 110  J = 1, JN
      F (J) = E - AM * (G(J) + B * ALPHA (J))
      EPS (J) = Y (J) - AM * ALPHA (J) - D
      SFE = SFE + F (J) * EPS (J)
  110 CONTINUE
      FE (L) = SFE
```

```
      L = L + 1
      IF (L.LE.2) GO TO 10
      K (L) = (K (1) * FE (L - 1) - K (L - 1) * FE (1)) / (FE (L - 1) - FE (1))
      IF (ABS (K (L) - K (L -1)). LE.0.1) GO TO 200
      GO TO 10
  200 KD = K (L)
      WRITE (12, 210) LAMDA, KD
  210 FORMAT (' FOR WAVELENGTH', 18,'THE CALCULATED VALUE OF KD = ', F10.2)
      I = I + 1
      IF (I.LE.12) GO TO 5
      STOP
      END
EOF..
EOT..
```

```
LI SK7
C     PROGRAM TO CALCULATE THE COEFFICIENTS OF MOLAR
C     ABSORBTIVITY FOR (CR207)
      DIMENSION CT (10), E (10)
      REAL K
      READ (11, -) K, N
      READ (11, -) (CT (I), I = 1, N)
   10 READ (11, -) (E (I), I = 1, N)
      READ (11, -) EB, LAMDA
      SEC = 0.0
      DO 20 I = 1, N
      R = 2. * K * CT (I)
      A = (2. * R + 1. - (SORT (4. * R + 1.))) / (2. * R)
      EC = 2. * (((E (I) - EB ) /A ) + EB)
      SEC = SEC + EC
   20 CONTINUE
      AN = FLOAT (N)
      ECL = SEC / AN
      WRITE (12, 40) LAMDA, ECL
   40 FORMAT (' FOR LAMDA', 15',        EC = ', F8.4)
      GO TO 10
      END
EOF..
EOT..
```

APPENDIX 8

Determination of the experimental error in $\bar{e}_\lambda$

The experimental procedure was to weigh out accurately approximately 2g of potassium chromate and make up a solution in 1 dm^3 volumetric flask.

The samples for the absorptions were prepared by pipetting 4 - 40 mls of solution into 0.1 dm^3 volumetric flasks. From the absorption measurements the overall molar absorptivity was determined.

$$\bar{e}_\lambda = \frac{A_\lambda}{C_T}$$

let
M = wt of K_2CrO_4
V = Volume in 1 dm^3 volumetric flask.
v_1 = Volume pipetted.
v_2 = Volume in 0.1 dm^3 volumetric flask.

$$\therefore \quad C_T = \frac{M}{V} \cdot \frac{v_1}{v_2} \qquad \text{......A8.1}$$

but

$$\bar{e}_\lambda = \frac{A_\lambda}{C_T} = A_\lambda \, Vv_2 / Mv_1 \qquad \text{......A8.2}$$

and

$$\frac{\Delta e_\lambda}{e_\lambda}^2 = \left(\frac{\Delta A_\lambda}{A}\right)^2 + \left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta v_2}{v_2}\right)^2 + \left(\frac{\Delta M}{M}\right)^2 + \left(\frac{\Delta v_1}{v_1}\right)^2 \qquad \text{......A8.3}$$

Now,

the accuracy of the absorption readings,

$$\frac{\Delta A_\lambda}{A_\lambda} = \pm \ 0.01 \text{ (section 4.12)},$$

the accuracy of the amount pipeted,

$$\Delta v_1 = \frac{0.01}{v_1},$$

the accuracy of the 1 dm^3 volumetric flask,

$$\frac{\Delta V}{V} = \pm 0.001 ,$$

the accuracy of the 0.1 dm^3 volumetric flasks,

$$\frac{\Delta v_2}{v_2} = \pm 0.001 ,$$

and the accuracy in the weighing,

$$\frac{\Delta M}{M} = \pm 0.0001 .$$

When the sample pipetted was 4 mls, substituting into A8.3;

$$\left(\frac{\Delta \bar{e}_\lambda}{\bar{e}_\lambda}\right)^2 = 1 \times 10^{-4} + 1 \times 10^{-6} + 1 \times 10^{-6} + 1 \times 10^{-8} + 2.5 \times 10^{-6}$$

$$= 1.05 \times 10^{-4}$$

and $\frac{\Delta \bar{e}_\lambda}{\bar{e}_\lambda} = 0.0102 = 1.02\%$,

and when sample pipetted was 40 mls

$$\left(\frac{\Delta \bar{e}_\lambda}{\bar{e}_\lambda}\right)^2 = 1 \times 10^{-4}$$

$$\therefore \quad \frac{\Delta \bar{e}_\lambda}{\bar{e}_\lambda} = 0.01 = 1.0\% .$$

From this it can be seen that the accuracy of $\bar{e}_\lambda$ is dependent only on the absorption readings and is ± 1%.

Appendix 9

Table A9.1: pH measurements of solutions **of varying Cr^{6} concentration and added nitric acid:**

Added Acid Concentration x 10^4 M	Concentration of Cr^{+6} x 10^4 M									
	4	6	8	10	15	20	25	30	35	40
0.1	7.35	-	-	-	-	-	-	-	-	-
0.2	7.21	-	-	-	-	-	-	-	-	-
0.4	7.07	-	-	-	-	-	-	-	-	-
0.6	6.94	-	-	-	-	-	-	-	-	-
1.0	6.78	7.14	7.25	7.35	7.44	-	-	-	-	-
1.5	6.65	-	-	-	-	-	-	-	-	-
2.0	6.45	6.80	6.91	7.04	7.15	-	-	-	-	-
3.0	6.05	6.55	6.71	6.85	7.00	7.10	7.18	-	-	-
3.5	5.70	6.46	6.60	6.75	6.90	7.00	7.12	-	-	-
4.0	5.10	6.35	6.51	6.65	6.85	6.95	7.06	-	-	-
4.5	4.45	-	-	-	-	-	-	-	-	-
5.0	4.13	5.91	6.30	6.50	6.75	6.80	6.95	7.05	7.13	7.19
6.0	3.84	5.02	6.10	6.36	6.65	6.72	6.85	6.95	-	7.10

Table A9.1: Continued

Added Acid Concentration x 10^4 M	Concentration of Cr^{+6} x 10^4 M									
	4	6	8	10	15	20	25	30	35	40
7.0	3.65	4.20	5.71	6.17	6.53	6.62	6.78	6.82	-	7.00
8.0	3.50	3.86	4.85	5.96	6.99	6.57	6.71	6.82	-	6.95
9.0	-	3.65	4.20	5.66	6.51	-	-	-	-	-
10.0	3.35	3.52	3.83	4.72	6.19	6.43	6.56	6.65	6.85	6.87
15.0	3.10	3.20	3.30	3.46	4.78	6.00	6.30	6.40	6.49	6.65
20.0	3.04	3.06	3.07	3.18	3.33	4.42	5.50	6.16	6.23	6.40
25.0	2.91	2.94	2.96	3.00	3.01	3.50	4.55	5.79	5.86	6.24
30.0	2.81	-	-	-	2.83	3.17	3.44	4.23	5.26	5.99
40.0	2.69	2.67	2.67	2.71	2.75	2.90	2.97	3.17	-	4.26
50	2.59	-	-	-	-	-	-	-	-	-
60	2.50	2.50	2.46	2.51	2.59	2.62	2.65	2.71	-	2.89
80	2.37	2.37	2.31	2.37	2.41	2.43	2.43	2.44	-	2.66
100	2.26	2.27	2.23	2.28	2.30	2.31	2.31	2.34	-	2.43

Table A9.1: Continued

Added Acid Concentration x 10^4 M	Concentration of Cr^{+6} x 10^4 M									
	4	6	8	10	15	20	25	30	35	40
150	2.10	2.08	2.10	2.10	2.12	2.12	2.12	-	-	2.18
200	-	1.95	1.94	1.95	1.96	1.99	1.99	1.99	-	2.02
300	-	1.77	1.77	1.77	1.78	1.80	1.80	1.80	-	1.82
400	-	-	-	1.64	-	1.68	-	1.68	-	-

APPENDIX 10:

Table A10.1: Values of $e_{\lambda D} = \frac{A_{\lambda}}{C_T l}$ measured at 20°C and pH = 9.5

Wavelength	Concentration of $Cr^{+6} \times 10^4$ M				$\bar{e}_{\lambda D}$
nm	1	5	10	15	
295	176.0	164.0	175.0	167.4	170.6
300	97.1	93.0	98.0	91.5	95.0
305	59.7	50.0	46.9	54.7	53.3
310	24.3	27.5	27.3	27.7	26.7
315	25.5	22.5	23.4	31.2	25.6
320	26.7	27.5	31.3	31.0	29.2
325	46.1	42.5	49.7	46.9	46.3
330	65.5	67.5	70.0	70.2	68.3
335	105.6	105.0	110.8	99.8	105.3
340	145.6	150.0	155.9	148.5	150.0

Table A10.1 Continued

Wavelength nm	Concentration of $Cr^{+6} \times 10^4$ M				$\bar{e}_{\lambda D}$
	1	5	10	15	
345	207.5	210.0	217.0	203.1	209.4
350	269.4	277.5	283.3	273.9	275.9
355	347.1	355.0	358.2	347.7	352.0
360	424.8	435.0	424.5	414.1	424.6
365	478.2	481.8	500.0	480.0	485.0
370	531.6	545.6	532.9	519.5	532.5
375	528.0	536.3	546.8	527.3	534.6
380	524.3	530.9	527.3	503.9	521.6
385	462.2	461.4	468.8	449.2	460.4
390	400.4	389.5	398.4	378.9	391.8

Table A10.1: Continued

Wavelength	Concentration of Cr^{+6} x 10^4 M				$\bar{e}_{\lambda D}$
nm	1	5	10	15	
395	319.0	309.8	308.6	293.0	307.6
400	237.9	234.5	234.4	218.8	231.4
405	178.4	165.8	171.9	167.5	170.9
410	118.9	111.0	117.2	111.7	114.7
415	86.7	85.9	87.5	81.1	85.3
420	65.5	67.5	60.9	61.7	63.9

Table A10.2: Values of $e_{\lambda D} = \frac{A}{C_{Tl}}$ measured at 40°C and pH 9.0

Wavelength	Concentration of $Cr^{+6} \times 10^{4}$ M					$\bar{e}_{\lambda D}$
nm	1	5	10	15	20	
295	176.0	180.0	180.0	167.0	168.0	174.0
300	104.0	110.0	106.0	96.0	96.0	102.0
305	59.0	65.0	60.0	53.0	47.0	57.0
310	41.0	45.0	40.0	37.0	27.0	38.0
315	40.0	38.0	33.0	37.0	23.0	34.0
320	42.0	45.0	42.0	40.0	29.0	40.0
325	60.0	55.0	57.0	58.0	55.0	57.0
330	80.0	80.0	80.0	79.0	70.0	78.0
335	110.0	102.0	115.0	112.0	105.0	109.0
340	156.0	148.0	160.0	159.0	154.0	155.0

Table A10.2 Continued

Wavelength	Concentration of Cr^{+6} x 10^4 M					$\bar{e}_{\lambda D}$
nm	1	5	10	15	20	
345	214.0	200.0	220.0	221.0	215.0	214.0
350	282.0	270.0	290.0	287.0	283.0	282.0
355	352.0	342.0	360.0	363.0	357.0	355.0
360	422.0	410.0	430.0	437.0	439.0	428,0
365	487.0	480.0	495.0	506.0	503.0	494.0
370	524.0	528.0	528.0	547.0	560.0	537.0
375	532.0	536.0	535.0	555.0	571.0	546.0
380	511.0	516.0	515.0	533.0	555.0	526.0
385	452.0	470.0	460.0	467.0	482.0	466.0
390	392.0	397.0	390.0	387.0	406.0	394.4

Table A10.2: Continued

Wavelength nm	Concentration of $Cr^{+6} \times 10^4$ M					$\bar{e}_{\lambda D}$
	1	5	10	15	20	
395	300.0	300.0	305.0	310.0	320.0	307.0
400	230.0	224.0	225.0	235.0	236.0	230.0
405	170.0	165.0	162.0	168.0	171.0	167.0
410	115.0	113.0	111.0	117.0	118.0	114.8
415	89.0	81.0	84.0	82.0	88.0	85.0
420	64.0	62.0	65.0	67.0	66.0	65.0

Table A10.3: Values of $e_{\lambda D} = \frac{A}{lC_T}$ measured at 60°C and pH = 9.5

Wavelength	Concentration of $Cr^{+6} \times 10^4$ M				$\bar{e}_{\lambda D}$
nm	1	5	10	15	
295	173.0	172.0	170.0	174.0	172.0
300	108.0	99.0	100.0	104.0	103.0
305	60.0	50.0	53.0	60.0	56.0
310	41.0	31.0	33.0	38.0	36.0
315	36.0	29.0	28.0	30.0	31.0
320	38.0	32.0	33.0	37.0	35.0
325	52.0	49.0	50.0	52.0	51.0
330	79.0	72.0	72.0	76.0	75.0
335	110.0	115.0	105.0	107.0	109.0

Table A10.3 Continued

Wavelength nm	Concentration of $Cr^{+6} \times 10^4$ M				$\bar{e}_{\lambda D}$
	1	5	10	15	
340	154.0	165.0	147.0	162.0	157.0
345	210.0	231.0	217.0	225.0	221.0
350	277.0	295.0	287.0	300.0	290.0
355	360.0	380.0	367.0	376.0	371.0
360	438.0	463.0	443.0	457.0	450.0
365	496.0	523.0	517.0	520.0	514.0
370	545.0	570.0	553.0	569.0	559.0
375	558.0	575.0	567.0	563.0	568.0
380	530.0	552.0	550.0	541.0	543.0

Table A10.3: Continued

Wavelength nm	Concentration of $Cr^{+6} \times 10^4$ M				$\bar{e}_{\lambda D}$
	1	5	10	15	
385	465.0	490.0	486.0	482.0	481.0
390	390.0	410.0	407.0	398.0	401.0
395	308.0	313.0	313.0	310.0	311.0
400	232.0	243.0	233.0	239.0	237.0
405	170.0	179.0	170.0	174.0	173.0
410	120.0	122.0	120.0	121.0	121.0
415	88.0	90.0	90.0	88.0	89.0
420	72.0	72.0	70.0	70.0	71.0

Table A10.4: Values of $\bar{e}_\lambda = \frac{A_\lambda}{lC_T}$ measured at 20°C, pH = 5.52 and ionic strength μ = 0.25

Wavelength	Concentration of Cr^{+6} x 10^4 M									
nm	4	6	8	10	15	20	25	30	35	40
295	124.7	128.3	120.6	125.0	113.0	126.8	132.0	130.0	120.3	-
300	99.1	90.8	95.3	99.0	98.0	99.8	103.0	103.0	103.9	-
305	78.5	72.1	75.3	78.8	77.5	77.6	82.5	80.5	81.2	-
310	64.6	60.4	64.4	67.0	64.8	65.5	69.2	67.5	68.0	-
315	62.7	57.5	61.3	63.0	62.0	62.3	65.6	64.3	64.1	-
320	68.9	65.4	68.4	70.0	69.0	68.5	70.8	69.8	70.3	-
325	83.7	81.7	83.8	84.5	84.0	83.5	84.4	83.7	85.4	-
330	102.7	95.8	102.5	103.5	103.3	102.8	103.4	103.3	103.6	-
335	125.3	124.2	125.0	125.5	125.3	124.5	125.6	125.0	125.0	-
340	145.6	145.8	145.6	146.5	146.7	144.5	145.6	145.8	145.4	-
345	165.0	165.8	164.1	165.5	166,0	162.8	164.4	165.0	163.7	-
350	179.2	180.0	178.1	178.5	179.3	176.0	177.6	179.2	177.9	-

Table A10.4: Continued

Wavelength	Concentration of Cr^{+6} x 10^4 M									
nm	4	6	8	10	15	20	25	30	35	40
355	189.2	190.0	188.1	188.0	189.3	185.8	185.8	188.7	187.1	-
360	193.5	195.0	191.3	191.5	193.3	189.3	190.0	193.7	191.3	-
365	194.2	195.8	192.2	192.0	193.7	189.8	191.0	193.7	191.7	-
370	187.8	189.9	185.0	185.0	187.3	183.8	183.6	189.2	187.9	-
375	178.5	180.0	175.0	175.0	178.3	174.5	175.0	180.8	179.7	-
380	161.3	161.7	156.9	157.5	161.3	157.8	159.2	165.8	165.0	-
385	141.6	140.8	137.5	138.0	141.7	139.0	140.4	146.3	147.1	-
390	118.0	115.0	112.5	114.0	116.7	115.0	116.4	121.7	122.1	-
395	94.7	92.5	89.4	91.0	93.3	92.8	94.0	98.3	99.3	-
400	73.0	70.8	68.8	69.0	72.7	72.0	72.2	75.8	76.9	-
405	55.5	53.3	51.9	52.5	58.3	53.8	55.2	57.5	58.6	-

Table A10.5: Values of $\bar{e}_{\lambda} = \frac{A_{\lambda}}{lC_T}$, measured at 40°C, pH = 5.45 and ionic strength = 0.25

Wavelength	Concentration of $Cr^{+6} \times 10^4$ M									
nm	4	6	8	10	15	20	25	30	35	40
295	121.1	107.0	123.8	122.8	120.3	125.0	128.0	115.8	130.0	-
300	96.7	75.0	98.8	97.8	95.5	99.6	100.1	100.9	194.4	-
305	75.0	50.0	77.8	77.5	74.3	78.0	79.2	79.3	81.6	-
310	64.1	46.3	67.2	65.3	63.2	65.9	66.2	66.7	68.9	-
315	60.7	45.8	63.1	62.0	60.3	62.6	62.8	62.9	64.6	-
320	66.6	55.4	68.1	67.8	66.2	68.1	68.0	68.0	69.7	-
325	81.4	73.3	81.9	82.8	81.0	82.1	82.2	82.2	83.4	-
330	100.9	95.4	101.9	102.0	100.7	100.8	100.7	100.7	100.9	-
335	122.2	120.8	123.1	120.2	121.7	122.0	125.6	121.3	122.9	-
340	142.2	141.7	142.5	143.8	133.7	142.0	147.0	142.2	142.9	-
345	161.8	160.4	161.2	162.0	161.3	161.2	166.0	161.7	160.7	-

Table A10.5 Continued

Wavelength	Concentration of Cr^{+6} x 10^4 M									
nm	4	6	8	10	15	20	25	30	35	40
350	174.9	172.5	175.3	175.0	174.0	174.5	180.0	174.2	174.3	-
355	185.3	181.7	185.6	185.0	184.3	184.5	191.0	184.2	185.4	-
360	188.2	184.2	188.8	187.8	187.7	188.0	193.0	188.3	187.4	-
365	188.9	184.2	189.1	188.0	188.7	189.5	195.0	189.5	188.4	-
370	182.3	176.7	182.5	181.0	183.0	182.8	188.4	183.3	182.6	-
375	173.2	165.8	173.4	172.0	173.7	174.8	180.0	175.0	174.6	-
380	156.9	148.3	156.3	154.5	157.3	157.5	163.0	159.2	159.7	-
385	137.8	129.2	137.5	135.0	139.0	139.5	144.0	141.7	142.1	-
390	114.8	107.5	115.0	113.0	116.0	116.0	120.0	116.7	119.3	-
395	91.6	85.0	90.6	89.0	91.7	92.5	97.0	95.0	96.9	-
400	71.5	65.8	71.3	70.0	71.0	72.5	76.0	75.0	75.0	-
405	54.2	50.0	54.7	52.5	54.3	55.0	58.0	56.6	57.1	-

Table A10.6: Values $\bar{e}_{\lambda} = \frac{A_{\lambda}}{lC_T}$, measured at 60°C, pH = 5.62 and ionic strength μ = 0.25

Wavelength	Concentration of $Cr^{+6} \times 10^4$ M									
nm	4	6	8	10	15	20	25	30	35	40
295	118.0	116.0	110.0	112.5	114.0	113.0	122.4	119.0	118.9	120.0
300	91.0	89.0	81.0	86.5	85.7	85.8	94.8	94.5	96.0	97.0
305	70.0	69.2	61.9	65.5	64.0	65.0	72.4	72.0	73.8	74.0
310	57.0	58.3	51.0	53.3	52.5	53.0	58.5	59.5	61.0	61.0
315	54.0	55.8	48.8	51.5	51.0	51.0	55.6	56.3	56.9	55.4
320	63.0	60.0	58.0	59.0	60.0	59.0	63.0	64.0	64.0	64.0
325	78.0	81.0	76.0	76.0	78.0	76.0	79.0	80.0	79.0	79.0
330	99.0	102.0	97.0	97.0	100.0	97.0	99.0	100.0	99.0	100.0
335	122.0	125.0	121.0	123.0	123.0	120.0	123.0	123.0	122.0	123.0
340	144.0	148.0	143.0	144.0	146.0	141.0	145.0	145.0	144.0	143.0
345	164.0	168.0	164.0	165.0	166.0	161.0	166.0	165.0	163.0	163.0

Table A10.6 continued

Wavelength	Concentration of Cr^{+6} x 10^4 M									
nm	4	6	8	10	15	20	25	30	35	40
350	179.0	181.0	179.0	180.0	180.0	175.0	180.0	180.0	177.0	178.0
355	190.0	192.0	188.0	193.0	192.0	186.0	191.0	192.0	189.0	189.0
360	195.0	195.0	195.0	198.0	196.0	190.0	195.0	196.0	194.0	194.0
365	197.0	196.0	197.0	201.0	198.0	192.0	196.0	198.0	196.0	197.0
370	191.0	189.0	191.0	196.0	192.0	186.0	191.0	193.0	191.0	193.0
375	183.0	180.0	183.0	187.0	183.0	178.0	182.0	184.0	184.0	186.0
380	165.0	163.0	162.0	169.0	163.0	161.0	165.0	168.0	168.0	170.0
385	147.0	143.0	147.0	149.0	147.0	145.0	146.0	149.0	148.0	150.0
390	123.0	120.0	123.0	125.0	123.0	119.0	122.0	125.0	125.0	125.0
395	98.0	97.0	97.0	100.0	98.0	95.0	98.0	100.0	100.0	100.0
400	77.0	76.0	77.0	78.0	76.0	75.0	77.0	78.0	79.0	81.0
405	58.0	58.0	58.0	59.0	57.0	56.0	59.0	60.0	60.0	62.0

Table A10.7: Values $\bar{e}_{\lambda} = \frac{A_{\lambda}}{1C_T}$, measured at 20°C, pH = 4.94 and ionic strength μ = 0.25

Wavelength nm	Concentration of Cr^{+6} x 19^{4} M									
	4	6	8	10	15	20	25	30	35	40
295	121.2	123.0	124.4	125.8	128.6	135.0	135.0	136.0	139.0	141.2
300	101.4	102.4	104.4	105.0	106.4	110.8	108.8	110.8	113.2	116.2
305	84.0	85.6	86.5	89.6	89.2	90.6	90.8	90.9	93.8	95.0
310	73.0	73.4	73.8	76.0	76.0	77.5	77.8	78.1	79.2	81.0
315	70.0	70.8	71.6	72.6	73.1	73.2	73.4	73.5	73.5	73.6
320	77.0	77.3	77.5	77.8	78.0	78.2	78.3	78.3	78.4	78.4
325	91.2	91.6	91.8	92.2	92.6	93.0	93.0	93.0	93.1	93.1
330	110.4	111.0	109.8	110.0	109.8	109.6	109.8	109.6	109.8	109.8
335	131.2	131.0	129.4	131.0	129.2	121.0	129.2	130.0	129.2	130.8
340	147.0	148.0	148.8	147.4	147.6	147.5	147.6	147.0	147.5	147.2
345	159.6	158.4	159.8	160.4	160.0	160.2	160.8	161.2	161.3	161.3

Table A10.7 Continued

Wavelength	Concentration of $Cr^{+6} \times 10^4$ M									
nm	4	6	8	10	15	20	25	30	35	40
350	184.6	184.2	185.2	186.0	187.0	187.3	187.6	188.0	188.4	188.9
355	164.6	166.2	168.8	170.0	171.6	172.6	173.4	174.1	174.8	175.2
360	158.0	160.8	163.0	165.0	167.2	168.8	169.6	170.8	172.2	175.0
365	148.8	151.2	153.8	156.4	159.6	163.6	165.4	167.0	170.2	173.0
370	138.0	141.0	143.2	146.6	148.6	152.6	152.0	155.0	159.0	162.4
375	126.0	130.0	131.8	134.6	137.4	142.8	142.0	144.4	149.0	152.8
380	109.0	112.0	113.8	116.8	121.0	125.0	126.4	129.8	134.0	137.4
385	92.0	94.0	98.8	103.6	116.4	112.6	113.4	117.8	122.8	127.8
390	72.0	74.4	80.0	84.0	87.0	92.0	94.0	97.2	104.4	108.6
395	59.0	61.2	63.8	67.6	71.0	76.0	77.0	79.0	84.4	88.6
400	47.0	48.6	50.0	53.0	55.6	60.6	61.6	63.6	66.4	69.0
405	35.0	37.0	38.2	41.4	42.6	46.6	47.6	49.6	52.0	54.4

Table A10.8: Values $\bar{e}_\lambda = \frac{A_\lambda}{lC_T}$ measured at 40°C, pH = 4.85 and ionic strength $\mu = 0.25$

Wavelength	Concentration of $Cr^{+\%} \times 10^4$ M									
nm	4	6	8	10	15	20	25	30	35	40
295	101.5	106.5	107.0	110.8	118.0	126.5	133.0	-	139.3	142.0
300	82.0	85.5	87.4	90.9	95.9	102.4	108.4	-	113.0	117.5
305	63.0	65.0	66.3	71.0	76.6	85.5	91.0	-	94.5	96.5
310	53.0	55.0	56.0	60.0	64.3	72.0	77.6	-	80.5	82.6
315	50.0	53.5	56.3	58.0	61.3	65.3	68.4	-	70.0	71.3
320	63.0	64.0	66.0	67.0	68.7	60.0	76.0	-	74.6	75.0
325	83.0	83.5	84.0	84.2	84.7	84.9	85.5	-	86.1	86.5
330	105.0	105.5	106.0	106.5	106.7	106.9	107.0	-	107.2	107.3
335	123.3	124.0	125.0	125.1	125.2	125.0	125.6	-	125.6	125.7
340	140.5	141.0	141.3	141.2	141.3	142.0	142.5	-	143.0	143.5
345	156.7	156.7	155.9	155.5	156.0	155.8	157.0	-	156.7	157.2

Table A10.8 Continued

Wavelength	Concentration of Cr^{+6} x 10^{4} M									
nm	4	6	8	10	15	20	25	30	35	40
350	165.6	165.6	165.7	165.8	165.4	165.0	165.3	-	165.5	165.0
355	165.0	165.1	165.2	165.0	165.0	166.2	166.6	-	167.9	168.4
360	156.0	156.6	157.6	158.5	159.3	160.3	162.0	-	164.0	165.0
365	149.0	150.0	151.2	153.0	153.8	145.5	156.0	-	158.9	160.0
370	133.0	134.0	135.6	140.5	140.0	144.0	147.5	-	150.5	153.8
375	122.0	124.2	123.8	128.0	129.3	132.5	134.0	-	137.9	140.4
380	107.0	108.0	110.6	112.5	113.3	117.2	119.9	-	122.8	125.2
385	91.0	92.5	93.9	97.5	98.3	102.3	104.4	-	107.9	110.0
390	74.0	75.0	76.3	79.5	81.7	84.5	87.0	-	90.8	92.9
395	57.0	58.0	61.0	64.0	65.0	67.8	71.0	-	74.7	77.6
400	45.5	46.3	47.5	50.0	51.7	54.5	55.8	-	58.7	61.6
405	35.0	35.5	36.4	39.0	40.5	41.3	43.0	-	46.1	47.5

Table A10.9: Values of $\bar{e}_{\lambda} = \frac{A_{\lambda}}{lC_T}$ measured at 60°C, pH = 4.94 and ionic strength $\mu = 0.25$

Wavelength nm	Concentration of $Cr^{+6} \times 10^{4}$ M									
	4	6	8	10	15	20	25	30	35	40
295	101.0	104.0	108.5	112.5	117.7	123.0	128.4	133.1	138.0	141.8
300	90.0	91.0	92.5	94.0	98.0	103.5	105.4	107.8	109.5	112.5
305	73.0	74.0	75.0	75.5	78.7	83.0	86.4	88.7	90.7	92.9
310	63.0	64.0	65.0	66.5	67.7	71.0	74.4	75.4	76.3	77.8
315	60.0	60.5	61.3	61.6	63.3	66.8	68.2	69.2	70.0	70.8
320	65.0	65.7	67.5	70.0	70.0	73.3	74.6	75.2	76.0	77.0
325	82.0	82.1	82.5	84.0	84.3	86.0	88.4	88.7	88.9	90.1
330	102.0	101.9	101.9	103.0	104.3	105.0	105.4	105.8	106.4	107.5
335	125.0	125.0	124.9	125.5	126.0	126.5	126.0	126.0	125.7	127.0
340	142.5	143.3	142.0	142.5	143	144.0	143.0	142.7	142.9	142.9
345	156.3	155.8	155.1	156.0	156.5	156.5	156.0	156.0	156.1	156.6

Table A10.9:Continued

Wavenlength nm	Concentration of $Cr^{+6} \times 10^{4}$ M									
	4	6	8	10	15	20	25	30	35	40
350	160.0	161.7	160.5	161.5	162.0	162.5	163.0	163.5	163.7	163.9
355	161.3	162.5	163.5	164.0	166.0	168.0	168.5	168.7	168.9	169.5
360	155.0	156.0	157.2	158.5	160.8	164.0	164.8	165.3	165.7	165.9
365	147.5	148.5	145.8	150.8	153.3	156.5	157.0	157.8	158.6	159.8
370	132.5	134.5	136.5	138.3	141.2	144.6	146.0	149.5	151.7	153.6
375	118.8	121.3	123.1	125.6	130.2	133.7	135.5	140.5	144.2	145.2
380	103.8	106.0	108.3	109.6	113.5	115.8	116.8	120.0	122.9	125.5
385	88.8	91.7	93.1	95.0	98.6	102.5	103.7	107.1	109.8	112.5
390	72.0	75.0	77.5	78.5	81.6	84.8	86.5	91.0	93.0	94.5
395	58.8	60.6	60.6	62.5	65.3	67.5	68.7	70.0	72.6	74.1
400	46.3	48.3	48.8	50.5	52.7	54.0	54.5	55.8	57.9	60.3
405	39.7	39.7	40.4	41.5	42.5	44.3	45.0	46.2	47.2	48.2

Table A10.10: Calculation of K_2, Temperature 20°C
Ionic Strength = 0.25 with $\frac{1}{H_1}$ = 331131.0 and $\frac{1}{H_2}$ = 83176.0

Wavelength	$\bar{e}_{\lambda 1}$	$\bar{e}_{\lambda 2}$	$e_{\lambda D} K_2$ x 10^5	e_D	K_2 x 10^7
295	124.7	121.0	1.5	170.6	0.9
300	99.1	101.5	1.0	95.0	1.0
305	78.5	84.0	2.2	53.3	4.2
310	64.6	73.0	3.4	26.7	12.7
315	62.7	70.0	2.9	25.6	11.5
320	68.9	77.0	3.3	29.5	11.1
325	83.7	91.0	2.9	46.3	6.4
330	101.2	109.0	2.7	68.3	4.0
335	125.3	130.0	1.9	105.0	1.8
340	145.6	147.0	0.6	159.0	0.4
345	165.0	160.0	2.0	209.0	1.0
350	179.2	164.0	6.1	275.9	2.2
355	189.2	165.0	9.8	352.0	2.8
360	193.5	160.0	13.5	424.0	3.2
365	194.2	152.0	17.0	483.0	3.5
370	182.8	138.0	20.4	532.0	3.8
375	178.5	127.0	21.0	534.6	3.9
380	161.3	109.0	21.0	521.0	4.0

Table A10.10 Continued

Wavelength	$\bar{e}_{\lambda 1}$	$\bar{e}_{\lambda 2}$	$e_{\lambda D}K_2$ x 10^5	e_D	K_2 x 10^7
385	141.6	92.0	20.0	460.4	4.3
390	118.0	72.0	18.6	391.8	4.7
395	94.7	57.0	15.2	307.6	4.9
400	73.0	47.0	10.5	231.4	4.5
405	55.5	35.0	18.3	170.9	4.8

APPENDIX 11

The equation for the equilibrium between the $HCrO_4^-$ ion and CrO_4^{2-} given in chapter 6 leads to:-

$$\frac{A}{lC_T} = e_B + (e_D K_2) \cdot \frac{1}{H} \qquad \text{...11.1}$$

This is an equation of a straight line,

$$\text{with} \quad Y = \frac{A}{lC_T}$$

$$X = \frac{1}{H}$$

slope $M = e_D K_2$

$$\text{since, } M = \frac{Y_1 - Y_1}{X_1 - X_2} \qquad \text{...11.2}$$

By the theory of the combination of random errors, the error in M is given by

$$(\Delta M)^2 = \Delta (e_D K_2)^2 = \left(\frac{\partial M}{\partial Y_1}\right)^2 \cdot (\Delta Y_1)^2 + \left(\frac{\partial M}{\partial Y_2}\right)^2 \cdot (\Delta Y_2)^2 + \left(\frac{\partial M}{\partial X_1}\right)^2$$

$$\cdot (\Delta X_1)^2 + \left(\frac{\partial M}{\partial X_2}\right)^2 \cdot (\Delta X_2)^2 \qquad \text{...11.3}$$

Assuming that the error in the pH reading is

$$\Delta pH = \pm 0.02$$

$$\therefore \quad \frac{\Delta H}{H} = \pm 0.05$$

$$\therefore \quad \Delta H = \pm \frac{0.05}{X} = \Delta X$$

$$\Delta Y^2 = \left(\frac{\partial Y}{\partial A}\right)^2 \Delta A^2 + \left(\frac{\partial Y}{\partial l}\right)^2 \Delta l^2 + \left(\frac{\partial Y}{\partial C_T}\right)^2 \Delta C_T^2 \qquad \text{...11.4}$$

as l does not change $\Delta l \rightarrow 0$

$$\Delta A = 0.002 = \cancel{0.002}$$

?

$$\frac{\Delta C_T}{C_T} = 0.001$$

$$\Delta C_T^2 = (0.001)^2 C_T^2$$

$$\therefore \quad \Delta Y^2 = \left(\frac{1}{lC_T}\right)^2 (0.002)^2 + \left(\frac{A}{lC_T^2}\right)^2 (0.001)^2 C_T^2 \qquad \text{...11.5}$$

$$\frac{\partial M}{\partial Y_1} = \frac{1}{X_1 - X_2} = \frac{\partial M}{\partial Y_2} \qquad \text{...11.6}$$

$$\frac{\partial M}{\partial X_1} = (Y_1 - Y_2)(X_1 - X_1)^{-2} \qquad \text{...11.7}$$

$$\frac{\partial M}{\partial X_2} = (Y_2 - Y_1)(X_1 - X_2)^{-2} \qquad \text{...11.8}$$

$$\therefore \Delta M^2 = \left(\frac{1}{X_1 - X_2}\right)^2 \left[\left(\frac{0.002}{lC_T}\right)^2 + \left(\frac{0.001A_1}{lC_T}\right)^2\right]$$

$$+ \left(\frac{1}{X_1 - X_2}\right)^2 \left[\left(\frac{0.002}{lC_T}\right)^2 + \left(\frac{0.001A_2}{lC_T}\right)^2\right]$$

$$+ \left(\frac{Y_1 - Y_2}{(X_1 - X_2)^2}\right)^2 \left(\frac{0.05}{X_1}\right)^2 + \left(\frac{Y_1 - Y_2}{(X_1 - X_2)^2}\right)^2 \left(\frac{0.05}{X_2}\right)^2 \qquad \text{...11.9}$$

But,
$(X_1 - X_2) >> (Y_1 - Y_2)$.

therefore the two last terms in equation All.9 tend to zero, and equation All.9 becomes,

$$\Delta M^2 \cong \left(\frac{1}{X_1 - X_2} \right)^2 \left[\left(\frac{0.002}{lC_T} \right)^2 + (A_1^2 + A_2^2) \left(\frac{0.001}{lC_T} \right)^2 \right]$$

A_1 and A_2 have a maximum value of 0.1 for the concentration of $Cr^{+6} = 4 \times 10^{-4}$ M.

$$\therefore \quad \Delta M^2 = 2 \left(\frac{1}{X_1 - X_2} \right)^2 \left(\frac{0.002}{lC_T} \right)^2$$

$C_T = 0.0004$

and $l = 2$ mm

$$\therefore \Delta M \simeq \pm \frac{5}{X_1 - X_2}$$

$\therefore$ the error in the slope, $(e_D\ K_2)$, $= \pm 5 \left(\frac{H_1\ H_2}{H_1 - H_2} \right)$ ...All.10

APPENDIX 12

Calculation of K_d from Absorption Data

Assuming the only equilibrium in the solution is the dimerisation reaction.

$$2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad \text{A12.1}$$

the equilibrium constant is given by

$$K_d = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2}$$

Assuming $(1 - \alpha)\,C_T$ to be the fraction of $HCrO_4^-$ in the solution and $\frac{1}{2}\,\alpha\,C_T$ the fraction of $Cr_2O_7^{2-}$, then at any concentration, i :

$$2\,K_d\,C_{Ti} = \frac{\alpha i}{(1 - \alpha_i)^2}$$

and hence

$$\alpha_i = 1 + \frac{1}{4K_dC_{Ti}} - \frac{1}{4K_dC_{Ti}}\sqrt{(1 + 8K_dC_{Ti})} \qquad \text{A12.2}$$

As shown by Lukkari and Tong et al. the overall coefficient of molar absorptivity can be expressed at any one wavelength as:-

$$\bar{e}_i = m\,\alpha_i + d$$

$$\text{where } m = \left(\frac{e_{20}}{2} + e_{11}\right)$$

and $d = e_{11}$ where e_{11} and e_{20} are the coefficients of molar absorptivity of $HCrO_4^-$ and $Cr_2O_7^{2-}$ respectively.

Due to experimental errors:-

$$\bar{e}_i = m\,\alpha_i + d + \Delta\varepsilon_i \qquad \text{A12.3}$$

where $\Delta\varepsilon_i$ is the error in $\bar{e}_i$ let $K_d = K_{do}$ when $\Sigma(\Delta\varepsilon_i)^2$ is a minimum. Consider what happens to $\Sigma(\Delta\varepsilon_i)^2$ by changing $K = K_{do}(1+\delta)$ where $\delta \ll 1$ from A12.2.

$$\alpha_i = 1 + \frac{1}{4K_{do}C_{Ti}(1+\delta)} - \frac{1}{4K_{do}C_{Ti}(1+\delta)}\sqrt{(1 + 8K_{do}C_{Ti}(1+\delta))}$$

and using the binomial expansion

$$\alpha_i = 1 + \frac{1}{4K_{do}C_{Ti}} - \frac{(1+\ K_{do}C_{Ti})^{\frac{1}{2}}}{4K_{do}\,C_{Ti}} +$$

$$\frac{1+4K_{do}\,C_{Ti}}{(1+8K_{do}\,C_{Ti})^{\frac{1}{2}}} - 1 \quad \frac{\delta}{4K_{do}C_{Ti}}$$

$$\text{or}\quad \alpha_i = \alpha_{io} + a_i\delta \qquad \text{.....A12.4}$$

where α_{io} is α_i at $K_d = K_{do}$ and,

$$a_i = \frac{\dfrac{1+4K_{do}C_{Ti}}{(1+8K_{do}C_{Ti})^{\frac{1}{2}}} - 1}{4K_{do}C_{Ti}} \qquad \text{.....A12.5}$$

The normal equations for solving α_{io} and a_i are

$$\Sigma\alpha_i^{\ 2} = \Sigma\alpha_{io}^{\ 2} + 2\,\delta\,\Sigma\alpha_{io}a_i + 0(\delta^2) \qquad \text{.....A12.6}$$

$$\Sigma\alpha_i = \Sigma\alpha_{io} + \delta\,\Sigma a_i$$

and

$$(\Sigma\alpha_i)^2 = (\Sigma\alpha_{io})^2 + 2\,\delta(\Sigma\alpha_{io})(\Sigma a_i) + 0(\delta^2)\text{.....A12.7}$$

$$\Sigma\alpha_i^{\,2} = \Sigma\alpha_{io}^{\,2} + 2\delta\,\Sigma_{io}a_i + 0(\delta^2) \qquad ..\text{A12.6}$$

$$\Sigma\alpha_i = \Sigma\alpha_{io} + \Sigma a_i$$

and

$$(\Sigma\alpha_i)^2 = (\Sigma\alpha_{io})^2 + 2\delta(\Sigma a_i) + 0(\delta^2) \qquad ..\text{A12.7}$$

$$\Sigma\alpha_i y_i = \Sigma\alpha_{io}y_i + \delta\,\Sigma\alpha_i y_i \qquad ..\text{A12.8}$$

$$\Sigma\alpha_i\,\Sigma y_i = \Sigma\alpha_{io}\,\Sigma y_i + \delta\,\Sigma a_i\,\Sigma y_i\,. \qquad ..\text{A12.9}$$

Now the slope

$$= \frac{n\,\Sigma\alpha_i y_i - \Sigma\alpha_i\,\Sigma y_i}{n\,\Sigma\alpha_i^2 - (\Sigma\alpha_i)^2}$$

$$= m_o\left(1 + \delta\left\{\frac{n\,\Sigma a_i y_i - \Sigma a_i\,\Sigma y_i}{n\,\Sigma\alpha_{io}y_i - \Sigma\alpha_{io}\Sigma y_i} - \frac{2n\,\Sigma\alpha_{io}a_i - \Sigma\alpha_{io}\Sigma_{ai}}{n\,\Sigma\alpha_{io}^2 - (\Sigma\alpha_{io})^2}\right\}\right)$$

Therefore $= m_o\,(1 + b\delta\,)$ $\qquad ..\text{A12.10}$

$$\text{where} \quad b = \frac{n\,\Sigma a_i y_i - \Sigma a_i\,\Sigma y_i}{n\,\Sigma\alpha_{io}y_i - \Sigma\alpha_{io}\,\Sigma y_i} - \frac{2n\,\Sigma\alpha_{io}a_i - \Sigma\alpha_{io}\,\Sigma a_i}{n\,\Sigma\alpha_{io}^{\,2} - (\Sigma\alpha_{io})^2} \qquad ..\text{A12.11}$$

$$\text{now} \quad d = \frac{1}{n}\,(\Sigma y_i - \Sigma\alpha_i)$$

$$d = \frac{1}{n}\,\Sigma y_i - \frac{m_o}{n}\,(1 + b\delta)\,(\Sigma\alpha_{io} + \delta\,\Sigma a_i)$$

$$d = \frac{1}{n}\,\Sigma y_i - \frac{m_o}{n}\,\Sigma\alpha_{io} - \frac{M_o}{n}\delta\,(b\Sigma\alpha_{io} + \Sigma a_i)$$

$$d = d_o - \frac{m_o}{n}\,(b\,\Sigma\alpha_{io} + \Sigma a_i)\,,$$

therefore $d = d - g\delta$

where $g = \frac{m_o}{n}(b\,\Sigma\alpha_{io} + \Sigma a_i)$

now $\Delta\varepsilon_{io} = y_i - m_o\alpha_{io} - d_o$

and $\Delta\varepsilon_i = y_i - m\alpha_i - d = y_i - m_o(1 + b\delta)(\alpha_{io} + a_i\delta) - d_o + g$

$$= y_i - m_o(\alpha_{io} + \delta[a_i + b\alpha_{io}]) - d_o + g\,d$$

$$\Delta\varepsilon_i = y_i - m_o\alpha_{io} - d_o + \delta(g - m_o(a_i + b\alpha_{io})),$$

therefore $\Delta\varepsilon_i = \Delta\varepsilon_{io} + \delta f_i$, ..A12.14

where $f_i = g - m_o(a_i + b\alpha_{io})$ ..A12.15

$$\Sigma\Delta\varepsilon_i^2 = \Sigma(\Delta\varepsilon_{io} + \delta f_i)^2$$

$$= \Sigma(\Delta\varepsilon_{io}^2 + 2\delta f_i\Delta\varepsilon_{io} + 0(\delta^2))$$

$$= \Sigma\Delta\varepsilon_{io}^2 + 2\delta\,\Sigma f_i\Delta\varepsilon_{io} + 0(\delta^2). \quad ..A12.16$$

The miniumum occurs when

$$\Sigma f_i\Delta\varepsilon_{io} = 0 .$$

Therefore the condition for $\Sigma\Delta\varepsilon_i^2$ to be a minimum is:-

$$F(Kd_o) = \Sigma f_i\Delta\varepsilon_i = 0 . \quad ..A12.17$$

By choosing values of Kd and solving numerically by the Reguli Falsi iteration method the actual value of Kd can be determined.

APPENDIX 13

Model for calculating $[CrO_4^{2-}]$ concentration

In section 5.3.2 it was shown that in acidic solutions of barium chromate, the total Cr^{+6} species can be accounted for by the ions,

$$[HCrO_4^-],\ [CrO_4^{2-}],\ [Cr_2O_7^{2-}],\ [CrO_3Cl^-] \text{ and } [HCr_2O_7^-].$$

Neglecting $[HCr_2O_7^-]$ as it is relatively small, a mass balance on the total concentration of Cr^{+6} gives:

$$C_T = [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] + [CrO_4^{2-}] + [CrO_3Cl^-]$$

$$= B + 2C + D + E. \qquad \text{....A13.1}$$

Assuming the $[Cl^-]$ concentration = the $[H^+]$ concentration, and rearranging equations A3.9, A3.10 and A3.13 in terms of D and substituting into equation A13.1

$$C_T = \frac{HD}{K_2} + \frac{2K_d\,H^2D^2}{K_2^2} + D + \frac{K_c\,H^3D}{K_2},$$

$$\therefore \quad C_T = \frac{2K_d\,H^2}{K_2^2}\,D^2 + \left(1 + \frac{H}{K_2} + \frac{K_c\,H^3}{K_2}\right) D. \qquad \text{....A13.2}$$

This is a quadratic equation in D, the solution of which is

$$D = \frac{-\left(1 + \frac{H}{K_2} + \frac{K_c\,H^3}{K_2}\right) + \left(\left(1 + \frac{H}{K_2} + \frac{K_c\,H^3}{K_2}\right)^2 + \frac{8K_dH^2C_T}{K_2^2}\right)^{\frac{1}{2}}}{4K_d\,H^2 / K_2^2} \qquad \text{....A13.3}$$

This is a general equation for the calculation of the concentration of $[CrO_4^{2-}]$, using programme SK10.

SK10

```
C          PROGRAM TO CALCULATE THE CONCENTRATION OF THE
C          CHROMATE ION FROM THE SOLUBILITY DATA........
           DIMENSION MU (15)
           REAL MU,KD,K2,KC
           READ (11,-)R1,R2,R3
           WRITE (12,60)
       5   READ (11,-)SE,H
           I = 1
           MU(1) = 0.0
      10   A1 = 7.0605 + 1.542 * (MU(I) ** (.5))/(1. + 1.324 * (MU(I) ** (.5)))
           A2 = 1.276 + 028 * (MU(I) ** (.5))/1. + 1.324 * (MU(I) ** (.5)))
           A3 = 0.9445 + 0.514 * (MU(I) ** (.5))/(1. + 0.993 * (MU(I) ** (.5)))
           K2 = 10. ** (A1)
           KD = 10. ** (A2)
           KC = 10. ** (A3)
           WRITE (12,30) K2,KD,KC
      30   FORMAT (' K2 = ', F10.8, 2X', KD = ', F5.2, 2X,' KC = ', F5.2, /)
           R = 1. + K2/H+ (H**2)* KC
```

```
      W = 4. * KD
      B = (-R + SQRT (R*R + 2.* W * SE))/(W)
      WRITE (12,33) R,W
33    FORMAT ('R = ', F10.7,' W = ', F10.7,/)
      D = B * K2/H
      C = B * B * KD
      E = B * H * H * KC
      I = I + 1
      MU (I) = 0.5 * (b + E + 2. * H + 4. * (D + C))
      WRITE (12,40) MU(I)
40    FORMAT (' MU = ', F10.6, /)
      IF (ABS((MU(I) - MU (I - 1))/MU(I).LE.0.01) GO TO 50
      GO TO 10
60    FORMAT (15X,' SE', 15X,'B', 15X, 'C', 15X, 'D', 15X, 'E')
50    WRITE (12,70)SE,B,C,D,E,
70    FORMAT (4F20.11)
      GO TO 5
      END
```

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