THE ESTIMATION OF LATTICE ENERGIES OF IONIC CRYSTALS: A CRITICAL EXAMINATION OF THE METHOD OF DETERMINATION AND USE OF LYOTROPIC NUMBERS

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ABSTRACT

The estimation of lattice energies for crystals for which structural parameters are unavailable depends on the use of (a) wholly- or semi-empirical equations, such as the Kapustinskii equation, or (b) correlations between solution thermodynamic quantities, especially hydration enthalpies and lyotropic numbers. Approach (b) depends on the experimental measurement of lyotropic numbers; previous measurements of this kind are limited in number and are experimentally ill-defined. In the present work lyotropic number determinations have been carried out for selected anions using reproducible gelatin indicator and with photometric end-point determination using a commercial turbidimeter. The shape of the graphs obtained is discussed and from them the lyotropic numbers of the anions have been evaluated. The influence of changes of conditions, involving variations in temperature, pH, ionic strength and indicator concentration, has been investigated and the effects assessed. Lyotropic number is related to ion hydration enthalpy and, where sufficient data exist, combined ion hydration enthalpy values have been used to estimate the lattice enthalpies of Group I and Group II salts. Some values from the present work are compared to existing values; for several ionic crystals the lattice enthalpy values now found are new. The application of lyotropic methods to the estimation of lattice energies is discussed.

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CONTENTS

INTRODUCTION

(a) Calculation of lattice energy when structural parameters are known

The lattice energy of an ionic crystal may be defined as "the change in potential energy of the system at 0 K when gaseous ions separated by an infinite distance are brought to their equilibrium positions in the crystal lattice." Figure 1 shows a graph of potential energy versus distance of separation of ions, r_0 being the equilibrium separation and U_0 being the lattice energy.

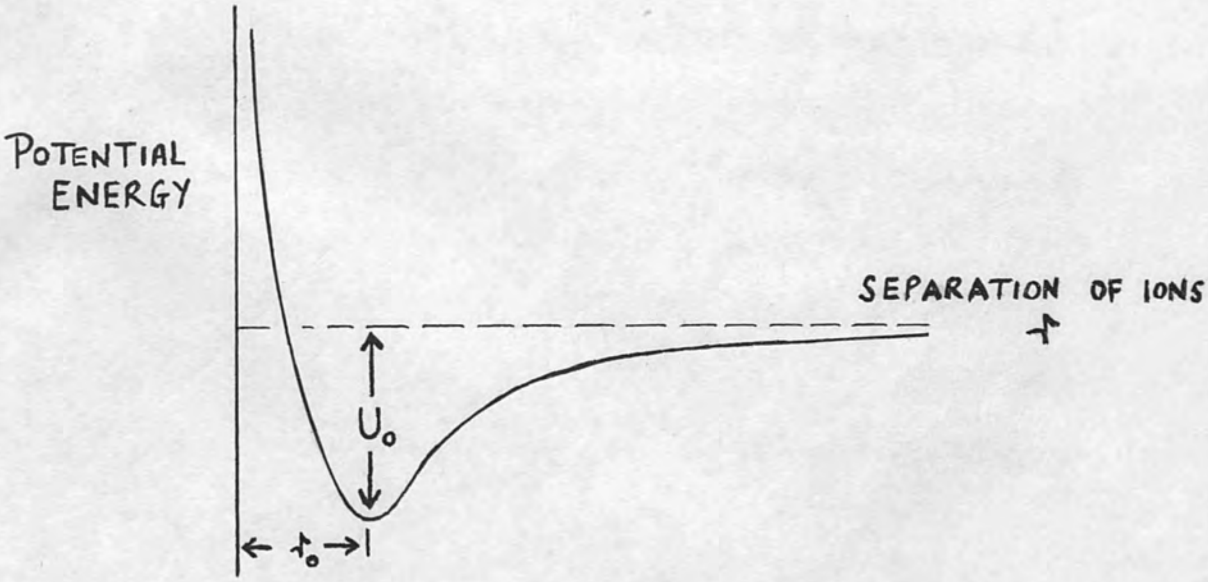

Fig. 1

The difference between the values of lattice energy at 0 K and ambient temperatures is small and is very often ignored. The lattice energy at T K, U_T, is related to the lattice energy at 0 K, U_0, by the expression

$$U_T = U_0 + \int_0^T \left[C_p(M^+) + C_p(X^-) - C_p(MX) \right] dT - 2RT$$

It is usually assumed that the specific heat capacities $C_p(M^+)$, $C_p(X^-)$ are $\frac{5}{2}R$ cal mol^{-1} so that

$$U_T = U_0 + \int_0^T [\,3R - C_p(MX)\,]\,.\,dT$$

The integral has a value of approximately 1 kcal mol^{-1} if T = 298 K.*

The lattice energy, correctly defined as a change in internal energy, is often approximated by an enthalpy term $\Delta H_L(298\ \text{K})$. The two are related by the expression

$$\Delta H_L = U + 2RT$$

for 1:1 salts. The approximate contribution of 2RT is 1 kcal mol^{-1}.

Since ions are electrically charged they attract or repel one another, according to their sign. Both these effects are governed by Coulomb's Law. There are other forces of attraction and repulsion between one ion and the others, and the evaluation of lattice energy involves the summation of all the forces on a single ion. Summation for all ions gives the total energy of the crystal.

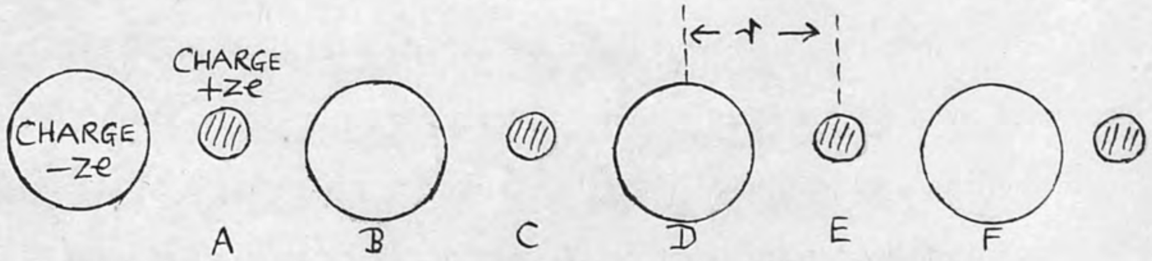

Fig. 2

Consider the linear arrangement of ions in Fig. 2. Ion D is attracted by its immediate neighbours C and E and the potential energy due to this is $2 \times \left(-\frac{z^2 e^2}{r}\right)$. The repulsive energy of the interaction

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* cal = 4.184 J in this thesis

of D with B and F is 2 x $\left(+\frac{z^2e^2}{2r}\right)$. The total Coulombic energy of interaction of ion D with all ions in the line is

$$u_c = 2\left\{\frac{-z^2e^2}{r} + \frac{z^2e^2}{2r} \quad - \frac{z^2e^2}{3r} + \ldots\ldots\ldots\right\}$$

$$= \frac{-2z^2e^2}{r}\left\{1 - \tfrac{1}{2} + \tfrac{1}{3} - \ldots\ldots\ldots \right\}$$

Summation to infinity gives

$$u_c = \frac{-2z^2e^2}{r} \ln 2$$

For an actual crystal the principle is the same. In the sodium chloride lattice any one ion is surrounded by six ions of opposite sign at a distance r, twelve ions of the same charge at a distance $r\sqrt{2}$, eight of opposite sign at a distance $r\sqrt{3}$, six of the same charge at 2r etc. The Coulombic energy for one ion is therefore

$$u_c = \frac{-e^2}{r}\left\{\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \ldots\ldots\ldots\right\}$$

$$u_c = \frac{-Me^2}{r} \qquad \text{EQUATION 1}$$

The series within the bracket does not converge rapidly and considerable computation is necessary for summation and hence evaluation of M, Madelung's constant. For sodium chloride this constant has the approximate value 1.7476 [1]. It is characteristic of a particular geometrical arrangement of ions and consequently the crystal structure must be known in detail before the Coulombic energy can be evaluated. Values for other crystal types are given in Table 1.

TABLE 1

Some values of the Madelung constant[2]

Crystal type	Madelung constant, M, to 5 significant figures
Cs Cl	1.7627
CaF_2	5.0388
Cu_2O	4.4425
wurtzite	1.6413

The total coulombic energy (given by equation 1) for one ion is therefore related to the coulombic attractive energy for ion-pairs by the factor M. In general the coulombic energy for one ion is given by

$$u_c = \frac{M z_1 z_2 e^2}{r}$$ where z_1 and z_2 are the valences of the ions. EQUATION 2

In addition to coulombic forces there are also repulsive forces due to the interpenetration of the electron clouds of the ions. Born and Landé[3] represented these forces as varying inversely as the n th power of the distance. Summation for the repulsive energy in sodium chloride gives

$$u_i = \frac{\lambda}{r^n}\left\{ \frac{6}{(\sqrt{1})^n} + \frac{12}{(\sqrt{2})^n} + \frac{8}{(\sqrt{3})^n} + \dots\dots\dots\dots \right\}$$

where λ and n are constants.

This series converges very rapidly. Denoting the summation by A and writing $B = \lambda A$ we have

$$u_i = B/r^n$$ EQUATION 3

Combination of equations 2 and 3 gives the total energy for one ion as

$$u(r) = \frac{-M\,z_1z_2e^2}{r} + \frac{B}{r^n} \qquad \text{EQUATION 4}$$

When the ions are in their equilibrium positions the net force acting on them is zero. Applying the condition $\left(\frac{\partial u}{\partial r}\right)_{r=r_0} = 0$ eliminates B and gives

$$u(r_0) = \frac{-Mz_1z_2e^2}{r_0}\left(1 - \frac{1}{n}\right)$$

$$\text{or} \quad U_0 = \frac{NMz_1z_2e^2}{r_0}\left(1 - \frac{1}{n}\right) \quad \text{for 1 mole of crystal.} \qquad \text{EQUATION 5}$$

where N = Avogadro number

r_0 = equilibrium separation of ions .

(Born-Landé expression)

n can be evaluated with a knowledge of the compressibility of the crystal and r_0 by X-ray techniques which also lead to M.

With the development of wave mechanics came the realization that the outermost shell electron density falls off exponentially with distance. Pauling[4] pointed out that application of wave mechanics results in a term for the repulsive energy which is exponential. Born and Mayer[5] gave the following expression for the repulsive energy:

$u_r = a \exp(-r/\rho)$ where a, ρ are constants and r is the separation distance of the ions.

a and ρ replace B and n of equation 4 and are evaluated by a treatment similar to that in the Born-Landé approach. This gives the lattice energy per mole as

$$U_o = \frac{N M z_1 z_2 e^2}{r_o} \left(1 - \frac{\rho}{r_o} \right) \qquad \text{EQUATION 6}$$

(Born-Mayer expression)

Both the Born-Landé and Born-Mayer expressions are applicable only when the structure of the crystal is known(e.g. using X-ray techniques).

Subsequent attempts at evaluating lattice energy have centred round a more accurate assessment of the non-coulombic forces, and "term-by-term" calculations have been used. The lattice energy is expressed in the form

$$U(r_o) = -U_C + U_R - U_D + U_Z \qquad \text{EQUATION 7}$$

where the terms on the right hand side of the equation represent the coulombic, repulsion, dispersion and zero-point energies respectively. The nature of the forces involved in the first two terms have already been mentioned. U_D is the dispersion energy, so-called because the electronic oscillations producing the attractive forces are also responsible for the dispersion of light by the particles. London[6] has shown that there are attractive forces between all molecules or ions. This arises because at any one instant the nuclei and electrons in the particle are arranged in such a way that a dipole moment exists. These dipoles induce dipoles in other molecules and produce attractive forces. Mayer[7] has indicated that a term representing induced dipole - induced quadrupole interactions should be included.

The zero-point energy term, U_z, is the energy retained by the crystal at the absolute zero and is given by the Debye theory as

$U_z = N \frac{9}{4} h \nu_{MAX}$ where N is the Avogadro number,

h is Planck's constant,

ν_{MAX} is the Debye maximum frequency.

Extended calculations of this type have been carried out by Huggins[8,9], using the concept of "basic radii", and by Ladd and Lee[10] who derived the expression

$$U_o = \frac{N M z_1 z_2 e^2}{r_o}\left(1 - \frac{\rho}{r_o}\right) - \frac{N C}{r_o^6}\left(1 - \frac{6\rho}{r_o}\right) - \frac{N D}{r_o^8}\left(1 - \frac{8\rho}{r_o}\right) + \frac{9}{4} N h \nu_{MAX}$$

EQUATION 8

C and D are constants and the other symbols have their previous meanings. On the right hand side the first term gives the coulombic and repulsive energy, terms two and three the dispersion energy (dipole-dipole and dipole-quadrupole respectively), and term four the zero-point energy.

Evaluation of lattice energies by these extended calculations is subject to the same limitation as the Born-Landé and Born-Mayer methods, namely that structural parameters must be known. In addition, the concept of "basic radii" is limited. Ladd and Lee have shown[11] that a consistent set of basic radii can be deduced only where a number of isostructural compounds of similar degree of ionic character is available, for example the alkali metal halides[8], and the alkaline earth metal chalcides[12].

The term-by-term calculations of the type referred to above applies only to an arrangement of spherical ions. If non-spherical ions are present then the calculation must be modified since in evaluating the coulombic energy it is assumed that a charged ion may be replaced by a point charge at its centre. This is not true for a non-spherical ion such as azide ($\overset{-}{N_3}$). This difficulty can be overcome if the charge distribution on the ion is known or can be calculated. In this case the charge on the ion can be represented as a point charge together with a permanent electrical multipole. The electrostatic energy term now becomes two terms, one a simple Madelung term for the point charges and the other the multipole energy, This latter term itself consists of two terms, the first being the multipole-multipole interaction energy and the second the energy of interaction of the multipole with the surrounding point charges. Waddington[2,13] has done this for azide; the charge distribution for an isolated azide ion[14] and the equivalent point charge and quadrupole are shown below:

$$\begin{array}{ccccc} N & - & N & - & N \\ -0.83e & & +0.66e & & -0.83e \end{array}\ \underbrace{\begin{array}{ccccc} N & - & N & - & N \\ 0 & & -e & & 0 \end{array}\ \begin{array}{ccccc} N & - & N & - & N \\ -0.83e & & +1.66e & & -0.83e \end{array}}_{\text{point charge} \qquad\qquad\qquad \text{quadrupole}}$$

Waddington's equation for the term-by-term calculation was therefore

$$U_o = U_M + U_Q - U_R + U_L - U_z \qquad \text{EQUATION 9}$$

where U_Q is the quadrupole term and the other terms have their previous meanings.

Values of the lattice energies calculated in this way are given in Table 2 below.

TABLE 2
Term-by-term calculations for azides

Azide	Lattice Energy(298 K) / kcal mol^{-1}
K N_3	157
Rb N_3	150
Cs N_3	143

(b) The Kapustinskii Method

So far the methods for calculating lattice energy require a knowledge of the structure of the crystal. Kapustinskii[15] developed a method for the evaluation of lattice energy without this knowledge in order to extend the calculations. The Born-Mayer expression for lattice energy is

$$U_o = \frac{N\,M\,z_1 z_2 e^2}{r_o}\left(1 - \frac{\rho}{r_o}\right) \quad .$$

If the number of ions per "molecule" is n then the number in a mole is N n and the above equation can be re-written as

$$U_o = \left(\frac{N\,n}{2}\right)\left(\frac{\alpha\, z_1 z_2 e^2}{r_o}\right)\left(1 - \frac{\rho}{r_o}\right) \qquad \text{where } \alpha = M/\left(\frac{n}{2}\right)$$

α is not the same for different lattice types but Kapustinskii found that on changing the lattice type the change in α is proportional to the change in the interionic distance. Any crystal can therefore be theoretically reformed, in an "iso-energetic" way, into a rock-salt lattice by using the value of α (1.745) for a rock-salt lattice and replacing r_o by the sum of the Goldschmidt radii $(T_A + T_C)$. The Born-Mayer expression now becomes

$$U_o = \left(\frac{Nn}{2}\right)\left[\frac{1.745\ z_1 z_2 e^2}{(T_C + T_A)}\right]\left[1 - \frac{\rho}{(T_C + T_A)}\right]$$

or

$$U_o = \frac{287.2\ n\ z_1 z_2}{(T_C + T_A)}\left[1 - \frac{0.345}{(T_C + T_A)}\right] \quad \text{kcal mol}^{-1}$$

EQUATION 10

which is the Kapustinskii equation.

This method will not produce values of lattice energy as exact as those from the extended term-by-term calculation. Three disadvantages may be mentioned. Firstly, the equation only takes into account the Madelung term and the repulsive energy term, other terms being ignored. Secondly, there is the difficulty of assigning a radius to either a non-spherical ion or to a complex ion. Thirdly, the sum of the Goldschmidt radii of anion and cation may be only a poor approximation to the interionic distance (there are salts in which the unlike ions are not touching).

The problem of complex ion radii was overcome by using the concept of "thermochemical radius". If the Born-Haber cycle is applied to two compounds M_1X and M_2X then

$$\Delta H_L(M_1X) - \Delta H_L(M_2X) = \Delta H_f^o(M_1^+,g) - \Delta H_f^o(M_2^+,g) - \Delta H_f^o(M_1X,c) + \Delta H_f^o(M_2X,c)$$

Using equation 10,

$$\Delta H_L(M_1X) - \Delta H_L(M_2X) = K\left\{\frac{1}{(T_{M_1^+} + T_{X^-})}\left[1 - \frac{0.345}{(T_{M_1^+} + T_{X^-})}\right] - \frac{1}{(T_{M_2^+} + T_{X^-})}\left[1 - \frac{0.345}{(T_{M_2^+} + T_{X^-})}\right]\right\}$$

In both equations ΔH_L is the lattice enthalpy. From the equations T_{X^-} may be found, assuming that values of $\Delta H_f^o(M_1X,c)$, $\Delta H_f^o(M_2X,c)$, $\Delta H_f^o(M_1^+,g)$ and $\Delta H_f^o(M_2^+,g)$ are known, as well as the Goldschmidt radii of M_1^+ and M_2^+. Some values of thermochemical radii, calculated by Kapustinskii and Yatsimirskii[15,16] are given in Table 3. Substitution of these values in the Kapustinskii equation then yield the required lattice

TABLE 3
Thermochemical Radii

Ion	Radius/10^{-8}cm	Ion	Radius/10^{-8}cm
ClO_4^-	2.36	$CO_3^=$	1.85
MnO_4^-	2.40	NO_3^-	1.89
BF_4^-	2.28	ClO_3^-	2.00
$SO_4^=$	2.30	NO_2^-	1.55
$CrO_4^=$	2.40	CN^-	1.82
$MoO_4^=$	2.54	OH^-	1.40

energies.

Kapustinskii and Yatsimirskii have modified equation 10 [15,16] to take into account the dependence of ρ on the sum $(T_C + T_A)$ and have put forward the equations

$$U(r_o) = \frac{287.2\, n\, z_1\, z_2}{(T_C + T_A)}\left[1 - \frac{0.345}{(T_C + T_A)} + 0.00435\,(T_C + T_A)\right] \text{kcal mol}^{-1}$$

$$U(r_o) = \frac{287.2\, n\, z_1\, z_2}{(T_C + T_A)}\left[1 - \frac{0.345}{(T_C + T_A)} + 0.0087\,(T_C + T_A)\right] \text{kcal mol}^{-1}$$

The effect of these changes is to increase the lattice energies of all 1:1 compounds by 2.6 and 5.0 kcal mol^{-1} respectively.

(c) Application of the Born-Haber Cycle

"Experimental" values for lattice energy may be found from the Born-Haber cycle for a metal halide, shown below:

$$\begin{tikzcd}
MX(\text{cryst}) \arrow[r, "-\Delta H_L"] & M^+(\text{gas}) \arrow[d, "-I"] & + & X^-(\text{gas}) \arrow[d, "+E"] \\
& M\ (\text{gas}) \arrow[d, "-S"] & & X\ (\text{gas}) \arrow[d, "-\frac{1}{2} D"] \\
& M(\text{solid}) \arrow[uul, "\Delta H_f^o"] & & \frac{1}{2} X_2(\text{gas})
\end{tikzcd}$$

The changes are taken to occur at standard pressure and 25°C. Using Hess's Law we obtain

$$\Delta H_L^o = \Delta H_f^o - I + E - S - \tfrac{1}{2}D$$

where ΔH_f^o = enthalpy of formation of MX(cryst),
I = ionization potential of alkali metal M,
E = electron affinity of halogen X,
S = enthalpy of sublimation of metal M,
D = dissociation enthalpy of halogen,
ΔH_L^o = lattice enthalpy.

ΔH_f^o, S, D, and I can be found experimentally by standard methods. Experimental values of E are now quite good for the halogens and oxygen; otherwise the determination of E, both theoretically and experimentally, is difficult[17]. For example theoretical methods are unreliable when the negative ion is not spherically symmetrical, and experimental determination is limited to the reaction $X + e \longrightarrow X^-$. In consequence it is more usual to use values of lattice energy to find electron affinities or ΔH_f^o (X^-,g) when considering complex anions.

(d) The use of Hydration Enthalpies

Lattice energy values may also be found using ion hydration enthalpies, provided that also available are values of the standard enthalpy of solution. The thermodynamic cycle under consideration is as follows:

$$\begin{tikzcd}
MX(\text{cryst}) \arrow[rr, "\Delta H_L^\circ"] & & M^+(\text{gas}) + X^-(\text{gas}) \arrow[dl, "H"] \\
& M^+(\text{aq}) + X^-(\text{aq}) \arrow[ul, "-\Delta H_s^\circ"] &
\end{tikzcd}$$

where ΔH_L° = lattice enthalpy at 25°C,

H = standard enthalpy of hydration of the two ions,

ΔH_s° = standard enthalpy of solution of MX(cryst).

Using Hess's law,

$$\Delta H_L^\circ + H - \Delta H_s^\circ = 0 \qquad \text{EQUATION 11}$$

This method is especially applicable to compounds containing polyatomic ions and in cases where structural parameters are unknown. Two methods have been used for evaluating H. The first method involves the relationship between the hydration enthalpy and anion radius, the second the relationship between ion hydration enthalpy and lyotropic number. Since the lattice enthalpies of the alkali halides have been accurately calculated and the enthalpies of solution of these compounds are known, H is known for them. Before discussing the determination and use of lyotropic numbers, the problem of dividing up the combined ion hydration enthalpy, H, into the values for anion and cation will be considered. Various methods have been used. Randles[18] measured the potential difference, ψ, between potassium chloride solution in equilibrium with $Hg_2Cl_2(s)/Hg_1$ and mercury at zero potential (the latter forming an axial jet in a tube down the internal wall of which the potassium chloride solution was allowed to flow). The two relevant cells giving rise to ψ and E^o_{KCl} respectively were

$$\boxed{Q} \text{ — } Hg_1(\text{jet}) / N_2 / KCl_{aq} / Hg_2Cl_2\,(s) / Hg_1 \text{ — } \boxed{P}$$

where Q = quadrant electrometer acting as null-point indicator

P = potentiometer

and $K / Hg_1 / Hg_2Cl_2(s) / KCl_{aq} / K$

With the known mercury photoelectric limit W (i.e. the lowest free energy necessary to evict an electron from the uncharged metal), the following sequence gives the absolute hydration free energy of K^+ provided that (i) represents correctly the reaction in the first cell.

(i) $\frac{1}{2} Hg_2Cl_2(s) + e_{Hg} \longrightarrow Hg_1 + Cl^-aq$ $\quad -F.\psi$

(ii) $e_{Hg} \longrightarrow e_g$ $\quad W$

(iii) $K_s + \frac{1}{2} Hg_2Cl_2(s) \longrightarrow K^+aq + Cl^-aq + Hg_1$ $\quad F.E^o_{KCl}$

(iv) $K_s \longrightarrow K^+(g) + e_g$ $\quad \Delta G_{sub} + \Delta G_I$

(v) $K^+(g) \longrightarrow K^+aq$ $\quad \Delta G_h\,(K^+)$

Since, for the free energy changes indicated,

$$(v) = \Delta G_h(K^+) = -(i) + (ii) + (iii) - (iv)$$

substitution of the known free energies gives $\Delta G_h(K^+) = -80.6$ kcal mol^{-1}.

Blandamer and Symons[19] divided the combined hydration enthalpy of rubidium chloride by two, assuming that since Rb^+ and Cl^- ions have approximately the same size their ionic hydration enthalpies are equal. However, it is generally believed that such hydration enthalpies are not equal (see ref. 20 and 21).

Latimer et al.[20] used the Born expression

$$-\Delta G = \frac{q^2}{2r_e}\left(1 - \frac{1}{D}\right) \qquad \text{EQUATION 12}$$

to evaluate the hydration free energy of a monovalent ionic species; q is the ion charge, r_e the effective ion radius, D the dielectric constant of water. The difference between the hydration free energies of anion and iodide ion is plotted against the reciprocal of the Pauling crystal radius of the anion; a straight line is obtained. When a similar procedure is carried out for the cations (related to Cs^+) a curve is obtained. Addition of 0.1 A to the anion radii and 0.85 A to the cation radii gives the best fit to the Born expression (Fig. 3):

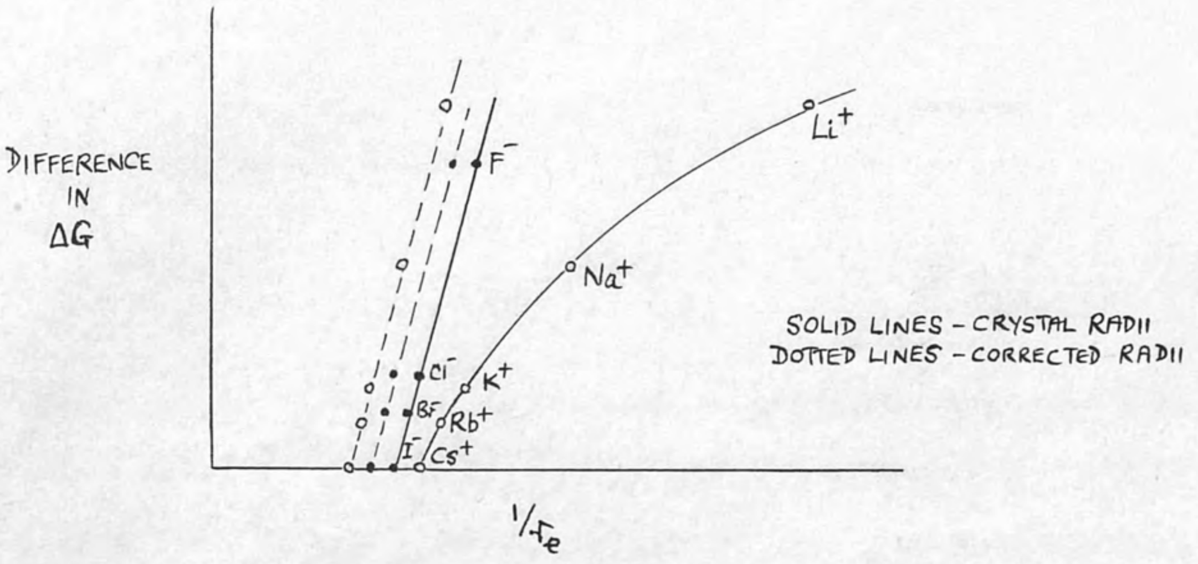


Fig. 3

The sum of the hydration free energies, of say caesium and iodide ions, is then divided up so that both positive and negative ions fall on the same line. This line is now that given by the Born equation (Fig. 4).

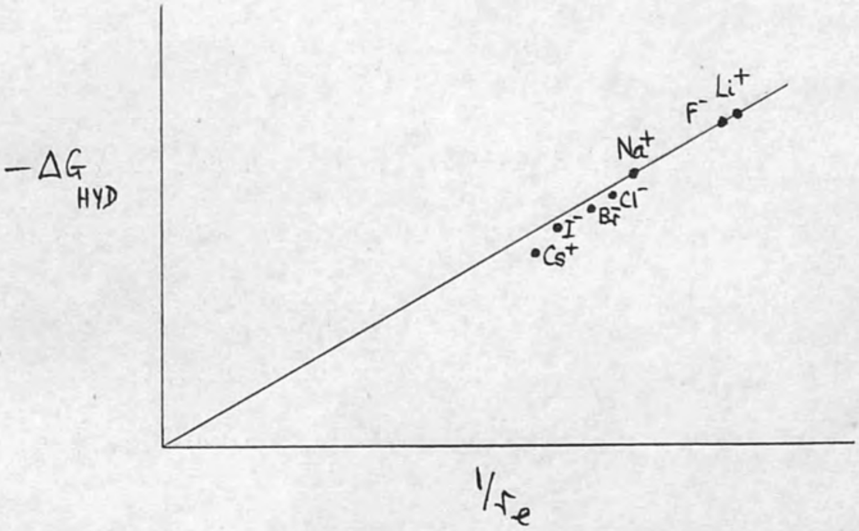


Fig. 4

This procedure was also carried out for the temperature coefficient of the free energy, i.e. the entropy of hydration of gaseous ions. The theoretical expression becomes

$$\Delta S = -\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \frac{q^2}{2r_e . T . D}\left(\frac{\partial \ln D}{\partial \ln T}\right)_P \qquad \text{EQUATION 13}$$

The division of ΔS between cation and anion to give coincidence (as before) results in a straight line. In this treatment the water in the neighbourhood of the ion is assumed to have the bulk dielectric constant.

Noyes[22] uses the relationship

$$\Delta G^o_{HYD} = \Delta G^o_{NEUT} + \Delta G^o_{el} \qquad \text{EQUATION 14}$$

Here the ion is discharged, the neutral species hydrated, and the particle re-charged. By finding ΔG^o_{el} (given by the Born equation) Noyes shows that, using crystal radii, the dielectric constant is much reduced in the neighbourhood of the ion. The energy changes involved are defined by the following equations:

$$M\ (ss) + z\,H^+(aq) \longrightarrow M^{z+}(aq) + \frac{z}{2} H_2\ (g) \qquad \Delta G^o_{aq}\ \text{CATION}$$

$$X\ (ss) + \frac{z}{2} H_2(g) \longrightarrow X^{z-}(aq) + z\,H^+(aq) \qquad \Delta G^o_{aq}\ \text{ANION}$$

$$M\ (ss) \longrightarrow M^{z+}(g) + ze\ (g) \qquad \Delta G^o_{ION}\ \text{CATION}$$

$$X\ (ss) + ze\ (g) \longrightarrow X^{z-}(g) \qquad \Delta G^o_{ION}\ \text{ANION}$$

$$\tfrac{1}{2} H_2\ (g) \longrightarrow H^+(aq) + e\ (g) \qquad \Delta G^o_H$$

ss refers to standard states.

Zero free energy and enthalpy are assigned to electrons at one atmosphere fugacity.

The changes may be connected by the following cycles

$$\begin{tikzcd}
& M^{z+}(g) + z\,e\,(g) + z\,H^{+}(aq) \arrow[d, "(\Delta G^{o}_{HYD} - z\,\Delta G^{o}_{H})"] \\
M\,(ss) + z\,H^{+}(aq) \arrow[ur, "\Delta G^{\circ}_{ION}"] & \\
& M^{z+}(aq) + \frac{z}{2}H_2\,(g) \arrow[uul, "-\Delta G^{\circ}_{aq}"]
\end{tikzcd}$$

Therefore $\Delta G^{o}_{HYD} = \Delta G^{o}_{aq} - \Delta G^{o}_{ION} + z\ \Delta G^{o}_{H}$ CATION

Similarly $\Delta G^{o}_{HYD} = \Delta G^{o}_{aq} - \Delta G^{o}_{ION} - z\ \Delta G^{o}_{H}$ ANION

The quantities ΔG^{o}_{aq} and ΔG^{o}_{ION} are measurable and the conventional free energy of hydration is the difference between them:

$$\Delta G^{o}_{CON} = \Delta G^{o}_{aq} - \Delta G^{o}_{ION} \qquad \text{(ANION or CATION)}$$

and $$\Delta G^{o}_{HYD} = \Delta G^{o}_{CON} + z\,\Delta G^{o}_{H} \qquad \text{(CATION)} \qquad \text{EQUATION 15}$$

$$\Delta G^{o}_{HYD} = \Delta G^{o}_{CON} - z\,\Delta G^{o}_{H} \qquad \text{(ANION)} \qquad \text{EQUATION 16}$$

Estimation of ΔG^{o}_{H} therefore gives ΔG^{o}_{HYD}.

ΔG^{o}_{NEUT} is best estimated using the zero energy assumption, i.e. that there is no internal energy change when 1 mole of a neutral species at 1 atmosphere fugacity dissolves in water to an ideal 1 molal solution under a pressure of 1 atmosphere. The enthalpy and entropy changes are just those calculable from the change in volume associated with the change of state. At 25° C the volume change is 24.47 litres and

$\Delta S^\circ_{NEUT} = - R \ln 24.47 = - 6.35$ cal mol^{-1} deg^{-1}

$\Delta H^\circ_{NEUT} = - 23.47$ litre-atm mol^{-1} $= - 0.568$ kcal mol^{-1}

$\Delta G^\circ_{NEUT} = 1.325$ kcal mol^{-1} .

Using equations 12 and 13 and considering singly-charged ions dissolved in water at 25°C (for which $D = 78.3$ and $\left(\frac{\partial \ln D}{\partial \ln T}\right)_P = -1.357$) the equations give

$$\Delta G^\circ_{el} = - \frac{163.89}{r} \text{ kcal mol}^{-1}$$

$$\Delta S^\circ_{el} = - \frac{9.649}{r} \text{ cal mol}^{-1} \text{ deg}^{-1}$$

(r is the effective radius of the ion in A)

These equations are valid for the hydration of spheres that are large enough for the macroscopic dielectric constant of water to be applicable. For smaller spheres Noyes modified these equations, giving the free energy changes as

$$\Delta G^\circ_{el} = - \frac{163.89}{r} + \frac{B}{r^2} \qquad \text{(CATION)}$$

$$\Delta G^\circ_{el} = - \frac{163.89}{r} + \frac{C}{r^2} \qquad \text{(ANION)}$$

Combining these with equations 14, 15, and 16 we have

$$\Delta G^\circ_{H} + \frac{163.89}{r} - \frac{B}{r^2} = - \Delta G^\circ_{CON} + \Delta G^\circ_{NEUT} \qquad \text{(CATION)}$$

and $$\Delta G^\circ_{H} - \frac{163.89}{r} + \frac{C}{r^2} = \Delta G^\circ_{CON} - \Delta G^\circ_{NEUT} \qquad \text{(ANION)}$$

Plots of the right hand side against 1/r give the curves of Fig. 5 :

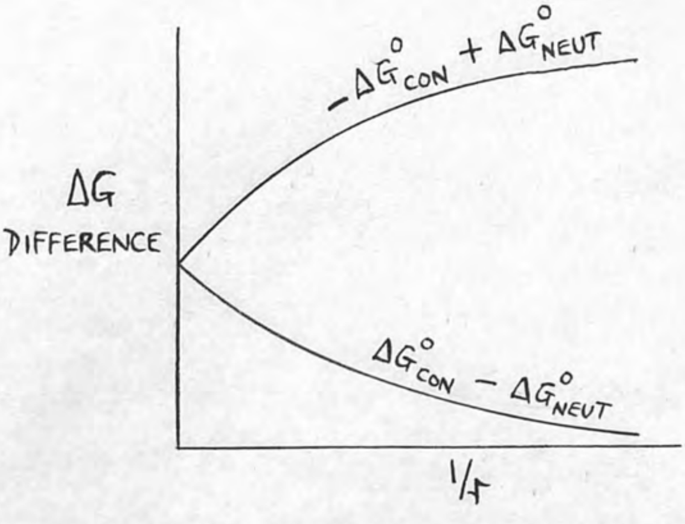


Fig. 5

The slopes of the curves are 163.89 kcal-A mol^{-1}. A three-parameter least squares technique gives the values of the parameters as

$$\Delta G^{o}_{H} = 104.81 \text{ kcal mol}^{-1}$$
$$B = 78.05 \text{ kcal A}^{2} \text{ mol}^{-1}$$
$$C = 57.22 \text{ kcal A}^{2} \text{ mol}^{-1} .$$

It is therefore possible to establish the free energy of hydration of cations (and therefore anions) using equation 15.

By means of equation 14 Noyes found ΔG^{o}_{el} and it was invariably less than that predicted by the Born equation. The discrepancy can be eliminated by either (a) using the macroscopic dielectric constant and assigning the ion an effective radius greater than the crystal radius, or (b) using the crystal radius and assigning to the solvent an effective dielectric constant less than the macroscopic value. Since it is not possible to assign radii such that ΔG^{o}_{el} and ΔS^{o}_{el} both agree with the Born equation Noyes assigns crystal radii and finds the effect on the dielectric properties of the solvent. He finds that D = 78.3 for

$r > 2.86$ A and $D = \dfrac{1}{0.6009 + \dfrac{0.1163}{r}}$ for $r < 2.86$ A, r being the ion radius.

Halliwell and Nyburg[21] have used the difference between the conventional hydration enthalpies of cation and anion to find the absolute hydration enthalpies of ions (W). These quantities are related by the following equations

$$\Delta H^o\text{CONV.HYD. } M^{z+}(g) = W_{M^{z+}} - z\,W_{H^+} \qquad \text{EQUATION 17}$$

$$\Delta H^o\text{CONV.HYD. } X^{z-}(g) = W_{X^{z-}} + z\,W_{H^+} \qquad \text{EQUATION 18}$$

where W_{H^+} is the absolute hydration enthalpy of the proton. Values of $\Delta H^o\text{CONV.HYD. } M^+(g)$ can be determined using the equation

$$\Delta H^o_{298}\text{CONV.HYD. } M^+(g) = \Delta H^o_f\text{ CON. } M^+(aq) - L - I - \frac{5}{2}RT + \Delta H^o_f\, H^+(g) \qquad \text{EQUATION 19}$$

where ΔH^o_f CON. $M^+(aq)$ = conventional enthalpy of formation $M^+(aq)$

L = enthalpy of sublimation of M

I = enthalpy change in the process $M(g) \rightarrow M^+(g)$

$\Delta H^o_f\, H^+(g)$ = standard enthalpy of formation of gaseous H^+.

All the quantities on the right hand side are experimentally determinable.

For univalent anions the equation is

$$\Delta H^o_{298}\text{CONV.HYD. } X^-(g) = (W_{M^+} + W_{X^-}) - \Delta H^o_{298}\text{CONV.HYD. } M^+(g) \qquad \text{EQUATION 20}$$

Knowledge of the lattice enthalpy will give (W_{M^+} + W_{X^-}) so that these values for X^- are secondary.

Halliwell and Nyburg express half the difference between conventional hydration enthalpies of cation and anion as

$$\tfrac{1}{2}\left[\Delta H^{\circ}\text{CONV.HYD. } M^{+}(g) \;-\; \Delta H^{\circ}\text{CONV.HYD. } X^{-}(g)\right] = \tfrac{1}{2}\Delta\left[\Delta H^{\circ}\text{CONV.HYD.}\right]$$

$$= \tfrac{1}{2}\sum_{i=3}^{j} \frac{c_i}{(R + a)^{i}} - \Delta H^{\circ}\text{ABS.HYD } H^{+}(g)$$

The values of R used were cation radii due to Ahrens[23] and anion radii due to Pauling. 'a' is the radius of the water molecule (as for ice). The left hand side is known from equations 19 and 20 and if the leading term of the summation has i=3 then a plot of the left hand side against $(R + a)^{-3}$ will be linear at large (R + a) and will cut the ordinate axis at $-\ \Delta H^{\circ}$ABS.HYD. $H^{+}(g)$.

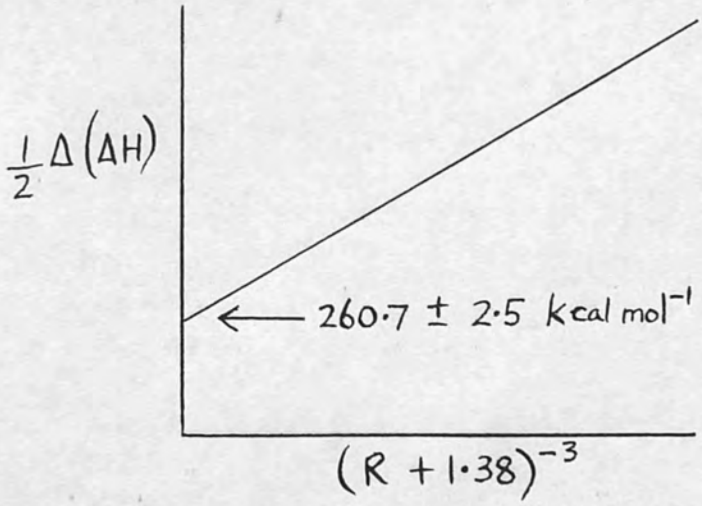


Fig. 6

Morris[24] has recalculated W_{H^+} using radii from electron density distributions and finds the value to be 263.7 ± 3.0 kcal mol^{-1}. Another method used by Morris (and similar to Noyes) uses the enthalpy of hydration as

$$W = W_{el} + W_{NEUT}$$

where W_{NEUT} is given by $W_{NEUT} = -0.2\,R^4$ kcal mol^{-1}.

Therefore

$$(W_{M^+} + W_{X^-})_{el} = (W_{M^+} + W_{X^-}) - (W_{M^+} + W_{X^-})_{NEUT}$$

The left hand side is plotted against cation radii for series' of salts of common anion and against anion radii for series' of salts of common cation (Fig. 7).

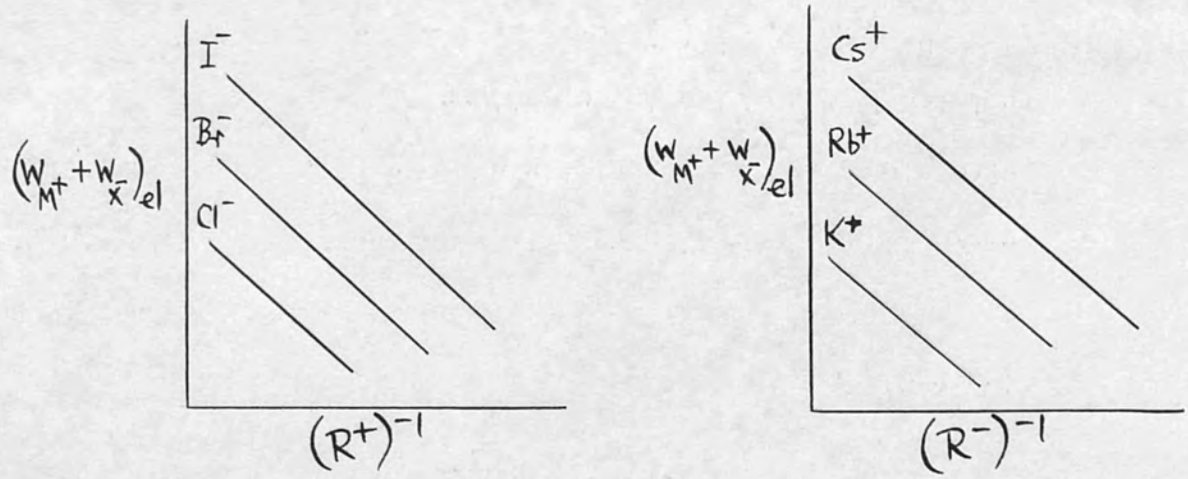


Fig. 7

Extrapolation of $(R^+)^{-1}$ and $(R^-)^{-1}$ to zero gives two values for the absolute hydration enthalpies of ions. Some values of absolute hydration enthalpies obtained by various workers are given in Table 4:

TABLE 4
Absolute hydration enthalpies of ions (kcal mol^{-1})

	Latimer et al. $-\Delta H$	Halliwell and Nyburg $-\Delta H$	Noyes $-\Delta H$	Morris $-\Delta H$		
				I	II	III
Na^+	94.6	97.0	104.1	99.7	97.5	99.2
K^+	75.8	77.0	83.9	79.6	77.5	79.0
Rb^+	69.2	71.9	78.1	73.3	71.1	72.7
Cs^+	62.0	66.1	70.2	69.1	66.9	68.5
F^-	122.6	120.8	98.4	120.0	122.3	120.5
Cl^-	88.7	86.8	80.9	87.5	89.6	88.1
Br^-	81.4	80.3	72.8	80.0	82.1	80.6
I^-	72.1	70.5	62.4	70.2	72.4	70.7

Morris values: I using conventional hydration values and the Halliwell and Nyburg method

II using cation radii

III using anion radii

Two relationships involving hydration enthalpy have been observed. The first is between combined ion hydration enthalpy and anion radius; the second is between combined ion hydration enthalpy and lyotropic number. In both cases the relationship is approximately linear[13,25].

(e) Lyotropy; lyotropic numbers and their application

Lyophilic colloids require large concentrations (e.g. 2 mol dm^{-3}) of electrolytes for precipitation (or flocculation - both, in this thesis, refer to the appearance of turbidity in a colloidal system). Hofmeister was the first person to carry out systematic experiments on the flocculation of such colloids (albumen used) by different salts, and he arranged them in a series, the Hofmeister series, according to diminishing power of flocculation: citrate, tartrate, sulphate, acetate, chloride, nitrate, chlorate. It was found impossible for some salts, such as bromide and iodide, even using saturated solutions, to cause flocculation.

Buchner and Kleijn[26], using agar, worked with mixtures of salts in order to extend the series. Also they deduced that flocculating power was additive in nature. Each salt was mixed with sodium sulphate, in varying proportions, and the mixture added to an agar sol. For each mixture the salt concentration could be adjusted slightly so that the sol was just flocculated. It was found that a certain quantity of sodium sulphate could be replaced by another corresponding quantity of, for example, sodium tartrate. As the flocculating power of the second salt decreases, a greater concentration of this salt is required to replace a definite quantity of sodium sulphate. With iodide, more sodium sulphate is required in the presence of iodide than in its absence. The iodide therefore counteracts the sulphate, i.e. it is anti-flocculating. The same was found for bromide, chlorate, nitrate, dichromate, perchlorate and nitrite (though not all these are anti-flocculating in other sols).

To summarise, for any one colloid there is a flocculating group of anions and an anti-flocculating group and flocculating power is additive in character. The following lines are typical of those of Buchner and Kleijn:

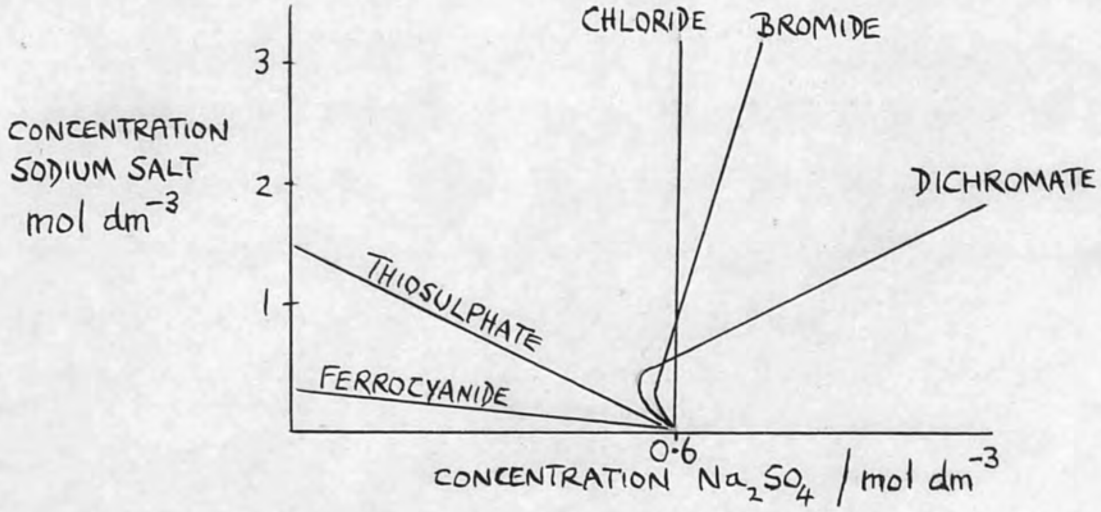


Fig. 8

Buchner, Voet and Bruins[27,28,29] put lyotropy on to a quantitative basis by showing how a number, the lyotropic number N, can be assigned to an ion. This number is given by the equation

$$N = a \cot\phi + b$$

where ϕ is the angle between the linear portion of the graph and the sulphate axis, and 'a' and 'b' are constants.

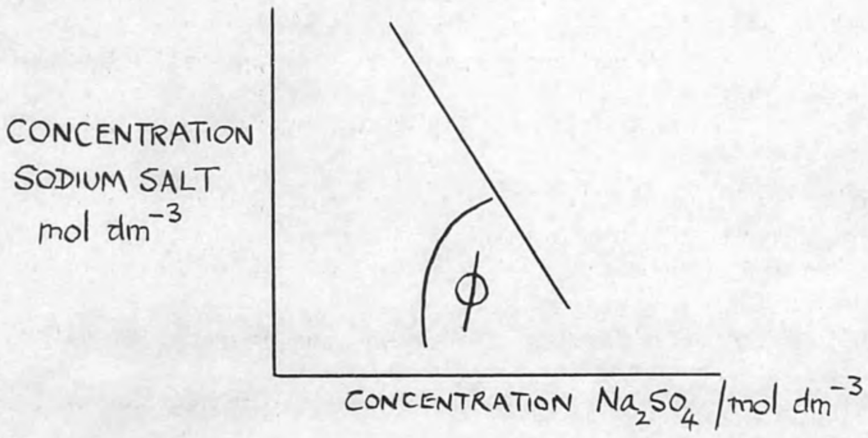


Fig. 9

The constants are evaluated by fixing the lyotropic numbers of two ions, N = 2 for sulphate and N = 10 for chloride. This means that the lower the lyotropic number the greater the flocculating power of the anion, and at some point this number will become negative.

Buchner's values[29,30] for the lyotropic numbers of some anions are given in Table 5.

TABLE 5

Lyotropic number, N

Anion	N	Anion	N
F^-	4.8	IO_3^-	6.25
Cl^-	10.0	ClO_4^-	11.8
Br^-	11.3	NO_3^-	11.6
I^-	12.5	NO_2^-	10.2
ClO_3^-	10.65	SCN^-	13.25
BrO_3^-	9.55	N_3^-	11.5

Lyotropic numbers have been related to various other properties[28,29]. If the increase in weight of gelatin swollen in different solutions of sodium salts of the same concentration is plotted against lyotropic number, linear relations occur. The rate of saponification of esters, as influenced by different salts, also shows a linear relation with lyotropic number, as does the viscosity of salt solutions (Fig. 10).

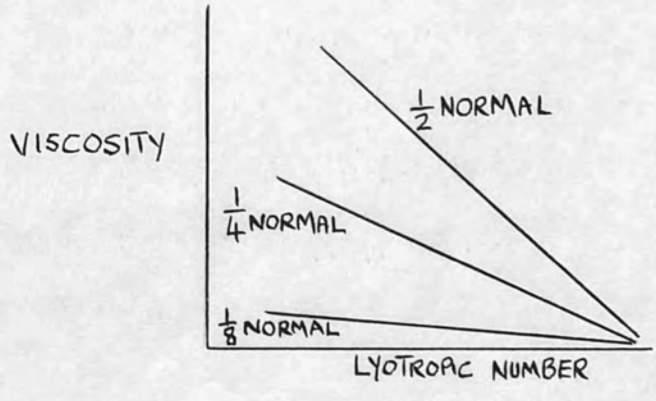


Fig. 10

Voet[29] expresses the view that lyotropic effects are caused by the different electric field strengths of the ions; this is supported by the fact that the energies of ionisation of the alkali metals are in linear relation with their lyotropic numbers. Support for the view is also provided by the linear relation between the combined ion hydration enthalpy and anion lyotropic number (or between anion hydration enthalpy and anion lyotropic number). Morris[25] has used the data from Latimer et al. for combined ion hydration enthalpy, H, and Buchner's lyotropic numbers. His graphs of H against lyotropic number are given in Fig. 11.

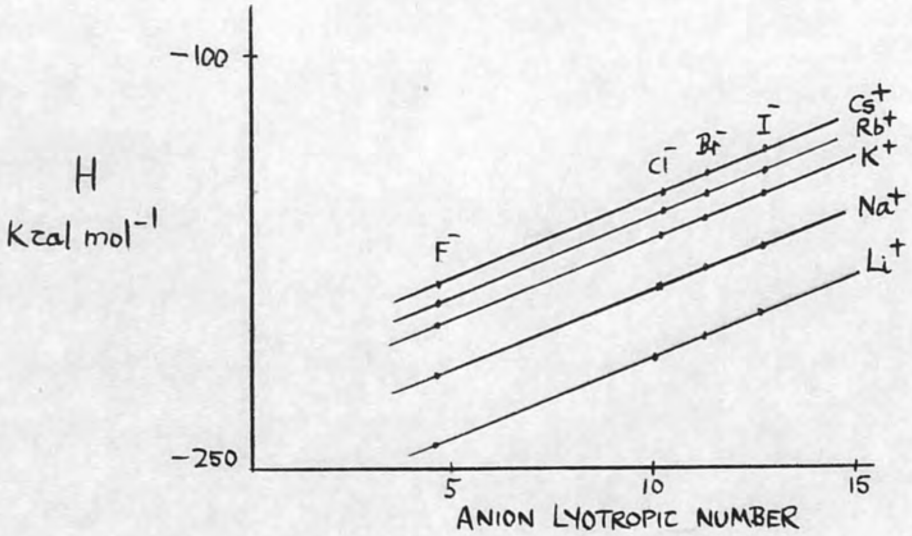


Fig. 11

By interpolation Morris found the combined ion hydration enthalpies for the nitrates, chlorates, perchlorates and thiocyanates of the alkali metals. With the corresponding enthalpies of solution[35] the lattice energies were evaluated (Table 6) using equation 11.

TABLE 6

Hydration enthalpies (H), enthalpies of solution (ΔH^o_s) and lattice enthalpies (ΔH^o_L). Data in kcal mol^{-1} (298K).

Compound	-H	ΔH^o_s	ΔH^o_L
lithium nitrate	199.4	-0.647	198.8
sodium nitrate	172.7	4.899	177.6
potassium nitrate	154.2	8.348	162.5
rubidium nitrate	147.1	8.74	155.8
caesium nitrate	140.2	9.51	149.7
sodium chlorate	178.8	4.95	183.8
potassium chlorate	160.4	9.96	170.4
rubidium chlorate	153.5	11.4	164.9
sodium perchlorate	171.4	3.49	174.9
potassium perchlorate	152.9	12.15	165.1
rubidium perchlorate	145.9	13.57	159.5
caesium perchlorate	138.9	13.26	152.2
sodium thiocyanate	161.8	1.63	163.4
potassium thiocyanate	142.9	5.82	148.7
rubidium thiocyanate	136.4	12.30	148.7

A similar procedure has been used by Gray and Waddington[13] for the alkali metal azides.

The view that a lyotropic number is a quantitative measure of the power of an anion to bind water to itself at the expense of hydrated colloid particles is supported by the work of Meyerstein and Treinin[33]. They have shown that the absorption spectrum of I^- in solution is very sensitive to environmental effects. For all the added electrolytes studied the onset of the absorption band of I^- was shifted to the ultraviolet. Fig. 12 shows the variation of $\Delta\nu$ (the shift) with lyotropic number:

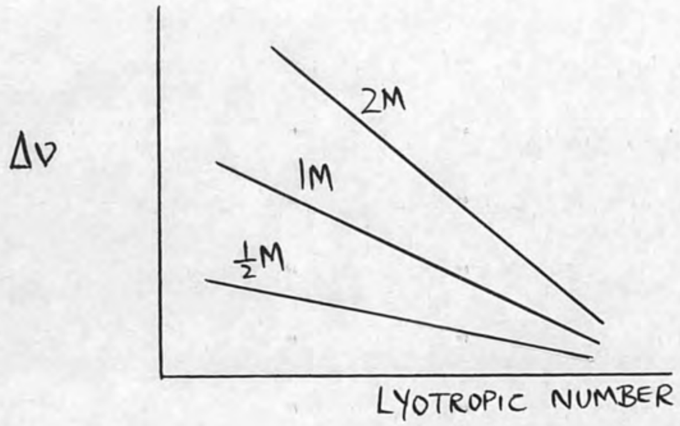


Fig.12

Thus the more flocculating the ion the greater the shift produced. The results indicate a close relation between the state of solvation of the light absorbing ion and the energy of the transition involved, and it would seem that the more flocculating ions are capable of desolvating I^- to a greater extent and therefore have a greater influence on the energy of transition. Meyerstein and Treinin divided the anions into two groups: (a) the halides - their effect is small and the order is $F^- > Cl^- > Br^- > I^-$. OH^- may be placed between F^- and Cl^-; (b) the complex ions - they exert larger effects and the order is citrate > tartrate > phosphate $\gg HPO_4^{=} \gg SO_4^{=} > CN^- >$ acetate > formate $> H_2PO_4^- > ClO_3^- > ClO_4^- > HSO_4^-$.

There has been little work reported on the influence of various factors on lyotropic numbers, i.e. on the gradients of the concentration curves such as those shown in Fig. 8 . Some work has been done on pH[34] but there is only a very brief mention of temperature (see for example ref. 26); there has been no discussion of the influence of ionic strength on the phenomenon of flocculation. In his article on pH Buchner[34] reports that previous work carried out on this topic was of little value. In his own work haemoglobin was used in the early stages but was later rejected. The appearance of the precipitate from alkaline solutions differed from the acid precipitates and the colour of the sol changed from blood red to brown red on adding acid or base. He considered that another colloid, not showing these effects, should be tried. Gelatin was used. The results obtained are shown in Fig. 13 and Fig. 14 .

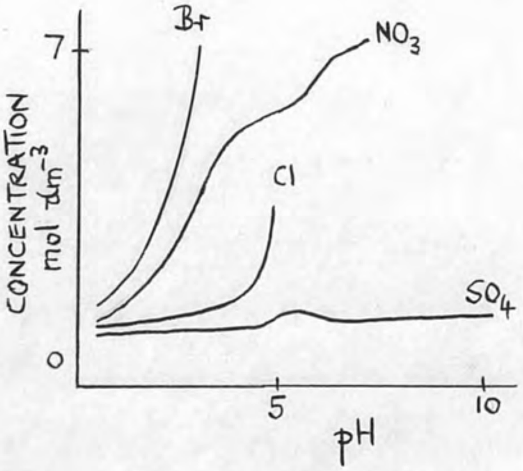


Fig. 13

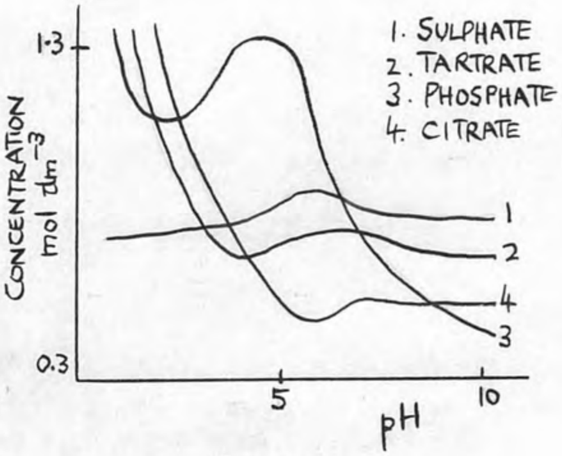


Fig. 14

It may be concluded from these results that some salts have a decreasing flocculating power as pH increases (Fig. 13) whereas others (Fig. 14) show an increasing power. Two other points may be mentioned:

(a) the flocculating power of the sulphate ion changes little with pH;

(b) the greatest change in flocculating power generally occurs for pH < 5.

There are no reports of the effect of pH on flocculation by salt mixtures, i.e. the effect on the concentration curves.

(f) Summary

When the structural parameters of a crystal are unknown its lattice energy can be found by using the anion lyotropic number to find the combined ion hydration enthalpy. Previous work done in this field is open to the following criticisms:

(1) The determinations are limited in number,

(2) There exists a need for the effects of temperature, pH, and ionic strength on the concentration curves, and on lyotropic number, to be investigated.

(3) The experimental procedure is ill-defined. Very little detail is given (see for example ref. 26 and 32); in particular it is not clear how Buchner detected the onset of opalescence in the gelatin and agar sols. This is of paramount importance to the accuracy of the lyotropic lines (concentration curves) and to the investigation of the effect of such factors as temperature on the concentration of electrolyte needed to cause opalescence.

The present work is concerned with (a) the development of a reproducible and hopefully accurate instrumental method for the determination of lyotropic numbers, (b) the calculation of a self-consistent set of such numbers and new lattice energy values. An assessment of the application of lyotropic methods to lattice energy determination (polyatomic ions) will then be possible.

EXPERIMENTAL

SECTION 1: TURBIDIMETER

When solutions of electrolytes are gradually added to sols of lyophilic colloids turbidity appears in the sol when a certain volume of electrolyte has been added. The onset of turbidity was determined photo-electrically using a 'Titrator' supplied by Evans Electroselenium Ltd., Halstead, Essex. The principle of this instrument may be seen by reference to Fig. 15. The liquid under test (gelatin sol-salt solution mixture in this work) is stirred magnetically whilst titrant (sodium sulphate solution) is added from the burette. A beam of light from the lamp passes through the liquid and the photocell response is recorded on a spot galvanometer. The stirrer speed control is adjusted so that the liquid vortex does not intercept the light beam. The galvanometer reading is taken after each titrant addition and a graph may be plotted of galvanometer reading against volume of titrant. This is of the type shown in Fig. 17 .

TURBIDIMETER

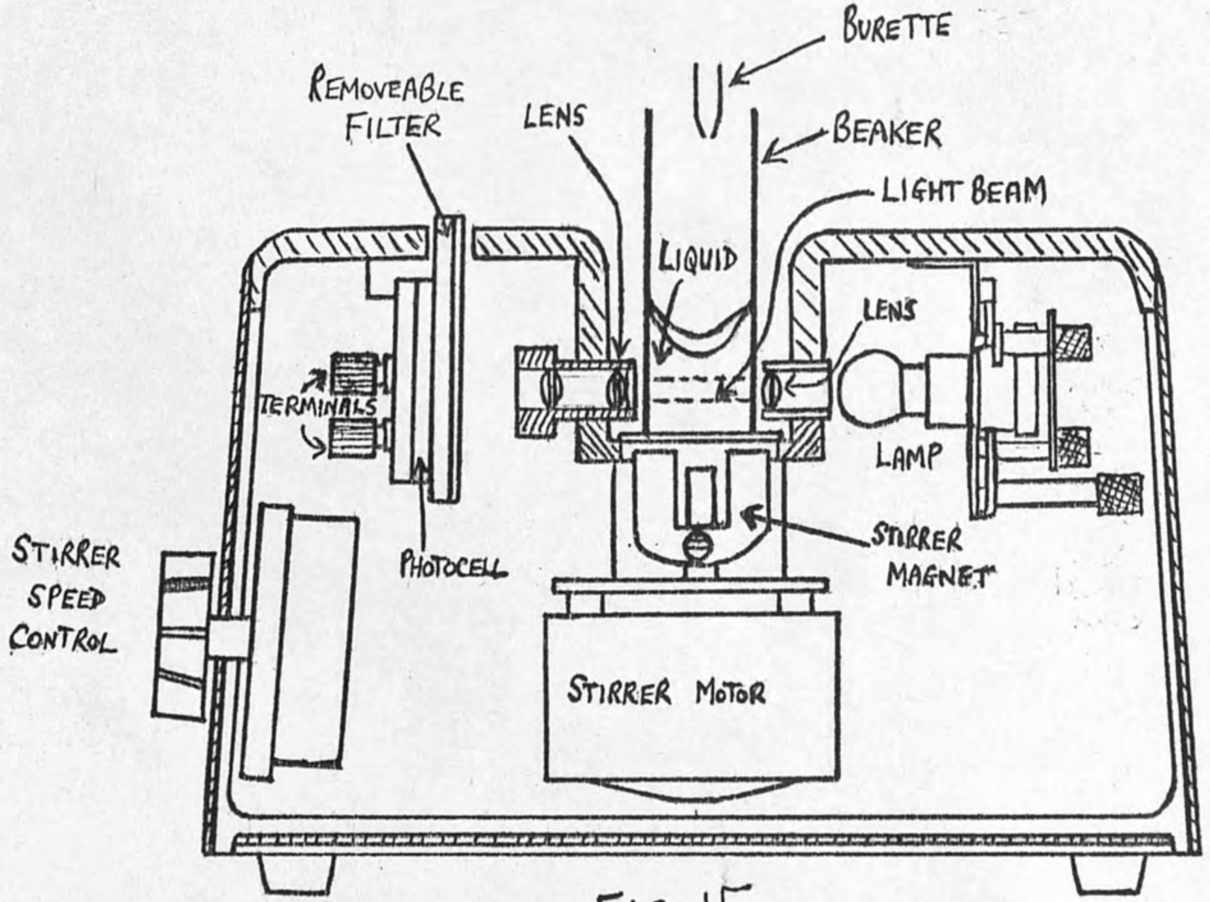


FIG. 15

TURBIDIMETER CIRCUITS

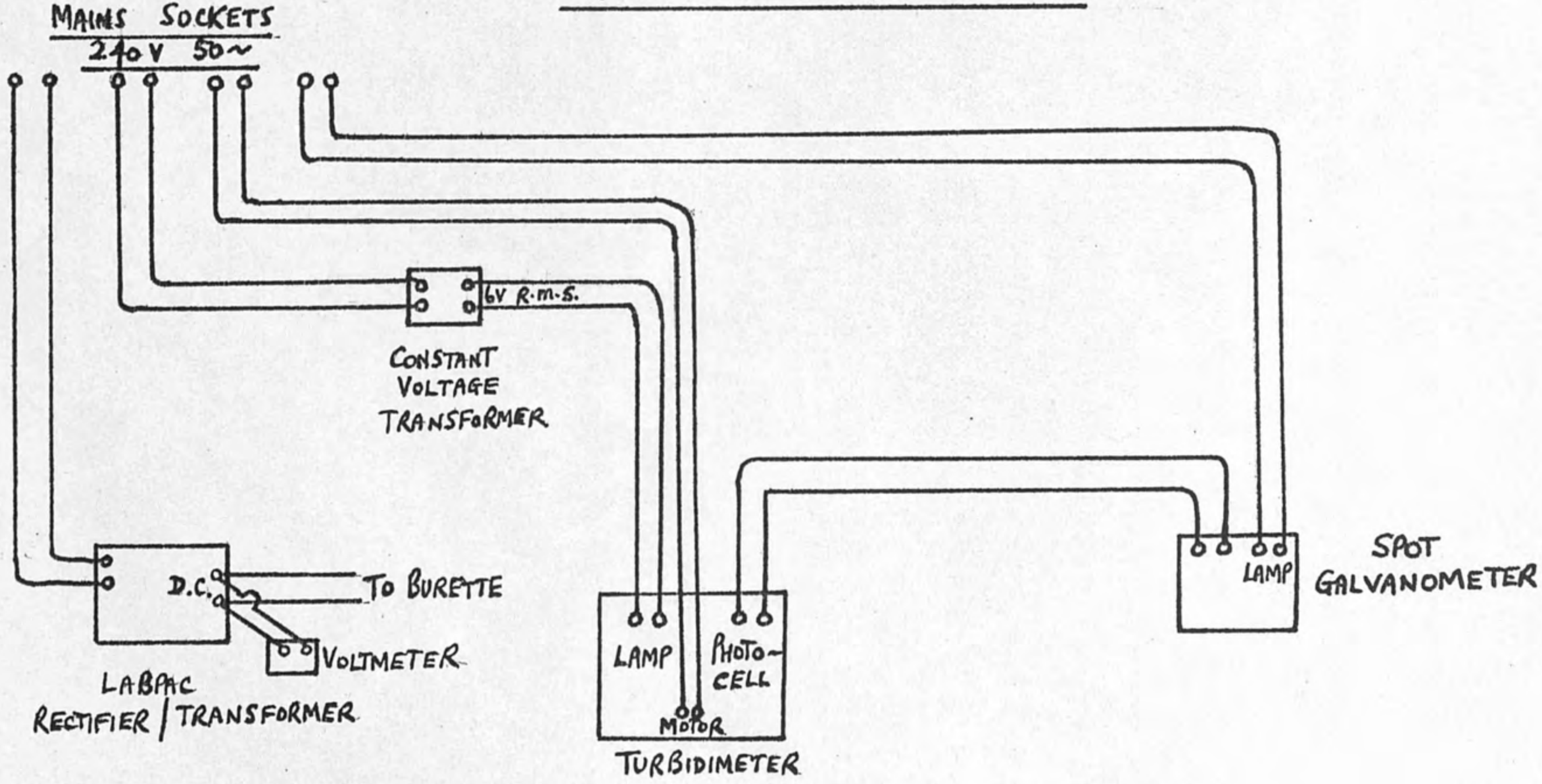


FIG. 16

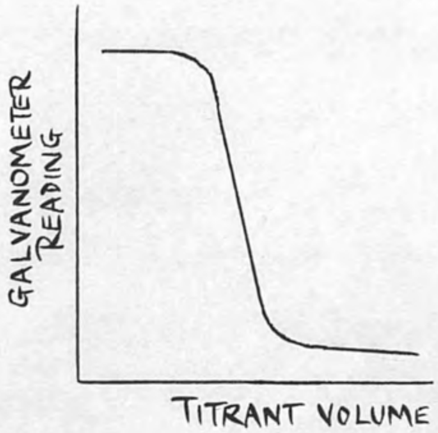


Fig. 17

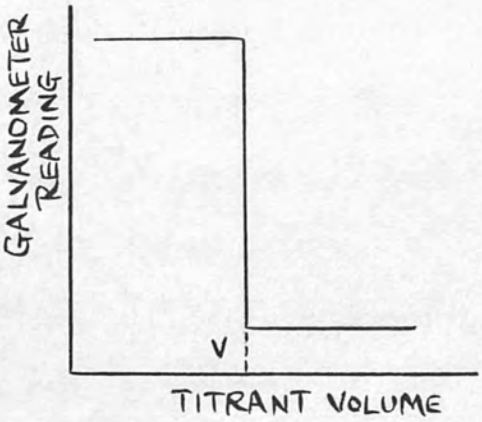


Fig. 18

The aim was to make the graph shape approach as far as possible that shown in Fig. 18, 'v' being the required volume of titrant. Results are not affected by external light.

The complete turbidimeter arrangement is shown in Fig. 16. The constant voltage transformer was model CV 15E and was supplied by Advance Electronics Ltd., Hainault, Essex. It is important that the titrator lamp should provide steady illumination of the solution. The output voltage to the titrator lamp was 6 R.M.S. (variation ± 1% for input voltage variations of ± 15%). The photocell response was measured by the spot galvanometer (Cambridge Instruments Co. Ltd.).

SECTION 2: OTHER APPARATUS AND MATERIALS

The salts used were of highest available purity (mostly Analar standard) and these, together with the gelatin and agar powder (Japanese), were supplied by B.D.H. Chemicals Ltd.

All items of glassware were supplied by Ferris and Co. Ltd., Bristol, and the more important items were as follows:

Burettes: 10 cm^3 (0.02 divisions) to B.S. 846
Graduated pipettes: 10 cm^3 (0.10 divisions) to B.S. 700
Volumetric flasks: 100 (±0.08), 250 (±0.15), 500 (±0.25) cm^3
to B.S. 1792 .

Small masses of substance were measured out on an automatic three-place balance (model R 10, L. Oertling Ltd., Orpington, Kent); larger masses were measured out on a top-pan Sartorius, model 2254 (supplied by Balance Consultancy, Trowbridge, Wilts). Concentrations of solutions, made up using de-ionised water throughout, were therefore accurate to more than one part in 1000.

pH values of solutions were found (to an accuracy of 0.1 unit) using the Griffin pH meter and combination electrode. The instrument was calibrated using the appropriate buffer powder (Electronic Instruments Ltd.) of pH close to that being measured. The buffers give a pH accurate to ± 0.02 pH unit.

SECTION 3: TEMPERATURE CONTROL

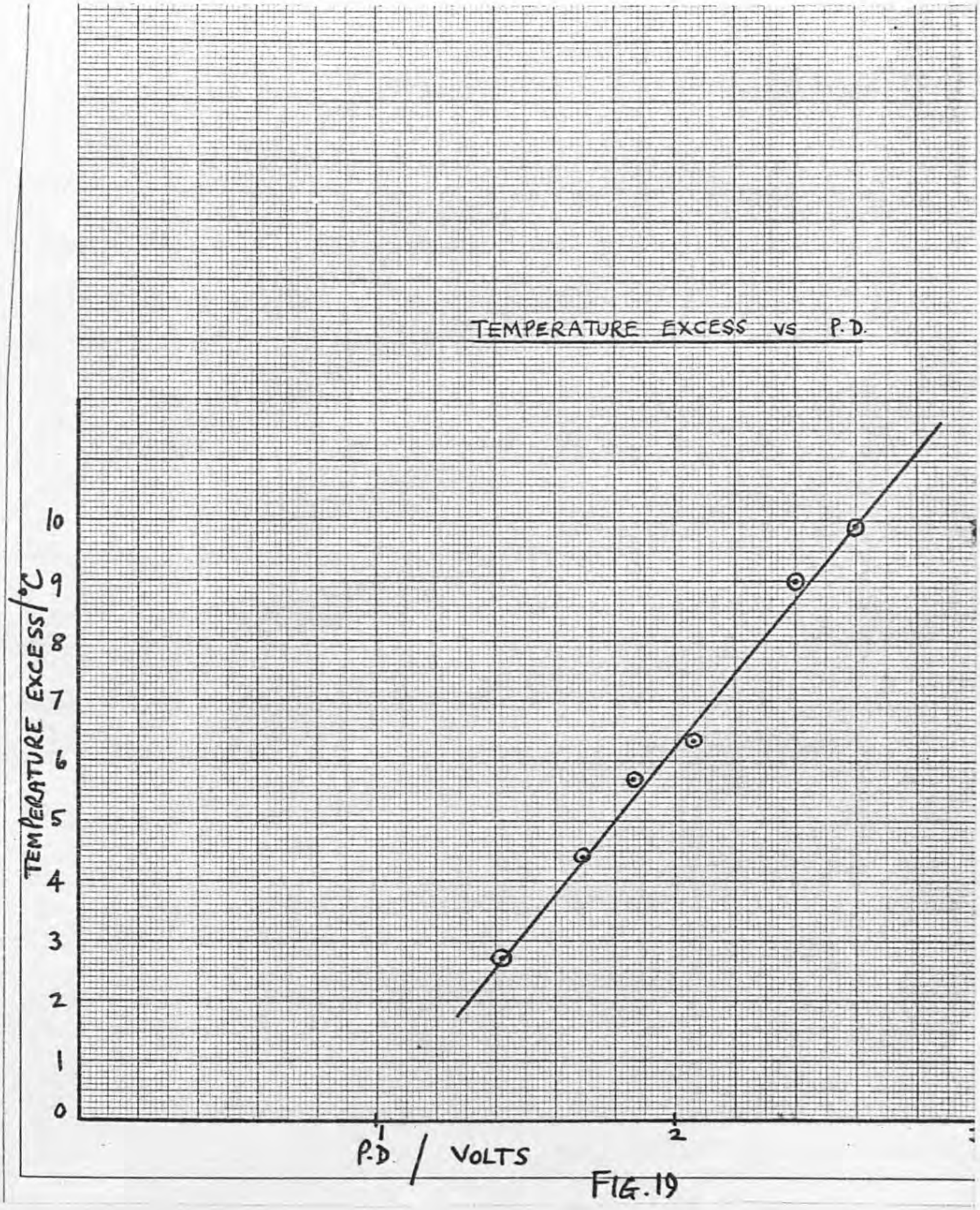
When running sodium sulphate solution from the burette into the beaker containing salt - gelatin mixture, temperature control consists of:

(a) Fixing the beaker temperature before titration

This was accomplished by standing the beaker in a water bath the temperature of which was thermostatically controlled by a 1 kW Techne Tempunit with tubular type helically wound heater and six-bladed stirrer. The temperature control was ± 0.03 °C. The sulphate solution was also allowed to equilibrate in the water bath before being put into the burette.

(b) Maintaining the burette liquid at the required temperature

The 10 cm^3 burette was electrically heated using silk-covered constantan wire (20 S.W.G.) of resistance 727 Ω per 1000 metres. The equilibrium temperature of sodium sulphate solution (concentration 1.80 mol dm^{-3}) within the burette was found for different potential differences applied across the constantan and temperature excess plotted against potential difference - see Fig. 19 . The burette temperature can therefore be suitably adjusted to the working temperature. As previously mentioned the sodium sulphate titrant was previously maintained at this temperature in the water bath. The supply was obtained from a Labpac rectifier/transformer unit (Radford Electronics Ltd., Bristol) and the P.D. was measured using a D.C. Elliot moving coil voltmeter.



TEMPERATURE EXCESS VS P.D.
TEMPERATURE EXCESS/°C
0
1
2
3
4
5
6
7
8
9
10
1
2
P.D / VOLTS

FIG. 19

(c) Minimising Newtonian cooling during titration

The extent of Newtonian cooling of the beaker contents depends on room temperature and the temperature of the liquid. Room temperature was generally within the range 21 - 23 °C and with continuous titration the average amount of cooling was 0.25 °C for a burette and water bath temperature of 25.0 °C. As will be seen later this amount of cooling can be ignored. However, when greater control was sought, as in the temperature investigation, the procedure was to titrate very nearly to the end-point (this having been previously found by continuous titration), to re-thermostat the beaker, and then to complete the titration. In this way the temperature could be kept consistently close to the required temperature, and if the thermostat is set at 0.1 °C above the required temperature then it is possible to restrict cooling to within 0.10 °C of the required temperature (25.0 or 30.0 °C) .

SECTION 4: DETERMINATION OF A LYOTROPIC CURVE (25.0 °C)

The method consists of titrating a mixture of gelatin sol and sodium salt solution with sodium sulphate solution of concentration 1.80 mol dm^{-3}.

A 2% gelatin sol (B.D.H. gelatin) was prepared and a concentrated solution of the salt, e.g. sodium nitrate, close to saturation (the sodium nitrate was of concentration 6.00 mol dm^{-3}). Mixtures of the two were then prepared as in Table 7.

TABLE 7

Mixture number	Volume of sodium nitrate solution/cm^3	Volume de-ionised water/cm^3	Volume 2 % gelatin/cm^3
1	7.00	0.00	2.00
2	6.50	0.50	2.00
3	6.00	1.00	2.00
4	5.50	1.50	2.00
5	5.00	2.00	2.00
6	4.50	2.50	2.00
7	4.00	3.00	2.00
8	3.50	3.50	2.00
9	3.00	4.00	2.00
10	2.50	4.50	2.00
11	2.00	5.00	2.00
12	1.50	5.50	2.00
13	1.00	6.00	2.00
14	0.50	6.50	2.00
15	0.00	7.00	2.00

These mixtures were then allowed to reach equilibrium in the water bath at the required temperature (standard determinations at 25.0 °C). The sodium sulphate solution, having been allowed to reach 25.0 °C in the water bath, was introduced into the burette to which the appropriate P.D. was applied. The sulphate was run into each mixture in turn, 0.05 cm^3 at a time, and the onset of turbidity taken to be when the rate of change of galvanometer readings with titrant volume first changed. The temperature and pH of the solution were taken. Normally the determinations were carried out in triplicate (in the investigations of temperature influence and the effect of variation of gelatin concentration on end-point the determinations were carried out in quintuplicate) and from the titres the end-point concentrations of sodium sulphate and sodium nitrate were evaluated - see Table 8 .

These concentrations when plotted give the graph shown in Fig. 20 . With some salts not all of the mixtures 1 - 15 give results, e.g. for a salt with greater flocculating power than nitrate mixtures 1 - 4 might be turbid on being made up.

The lower part of the lyotropic curve (see Fig. 20) very often has a gradient quite different from that at higher concentrations of NaX (the salt under investigation). As will be seen later this low concentration part of the graph is not used for the calculation of lyotropic number.

TABLE 8

Mixture number	Titre /cm^3	Concentration of $NaNO_3$ /mol dm^{-3}	Concentration of Na_2SO_4 /mol dm^{-3}
1	0.20	4.57	0.039
2	0.67	4.03	0.125
3	1.05	3.58	0.188
4	1.42	3.17	0.245
5	1.75	2.79	0.293
6	2.07	2.44	0.337
7	2.32	2.12	0.369
8	2.58	1.82	0.401
9	2.77	1.53	0.424
10	2.98	1.25	0.448
11	3.17	0.990	0.469
12	3.35	0.730	0.488
13	3.70	0.472	0.524
14	4.30	0.226	0.582
15	5.50	0.000	0.682

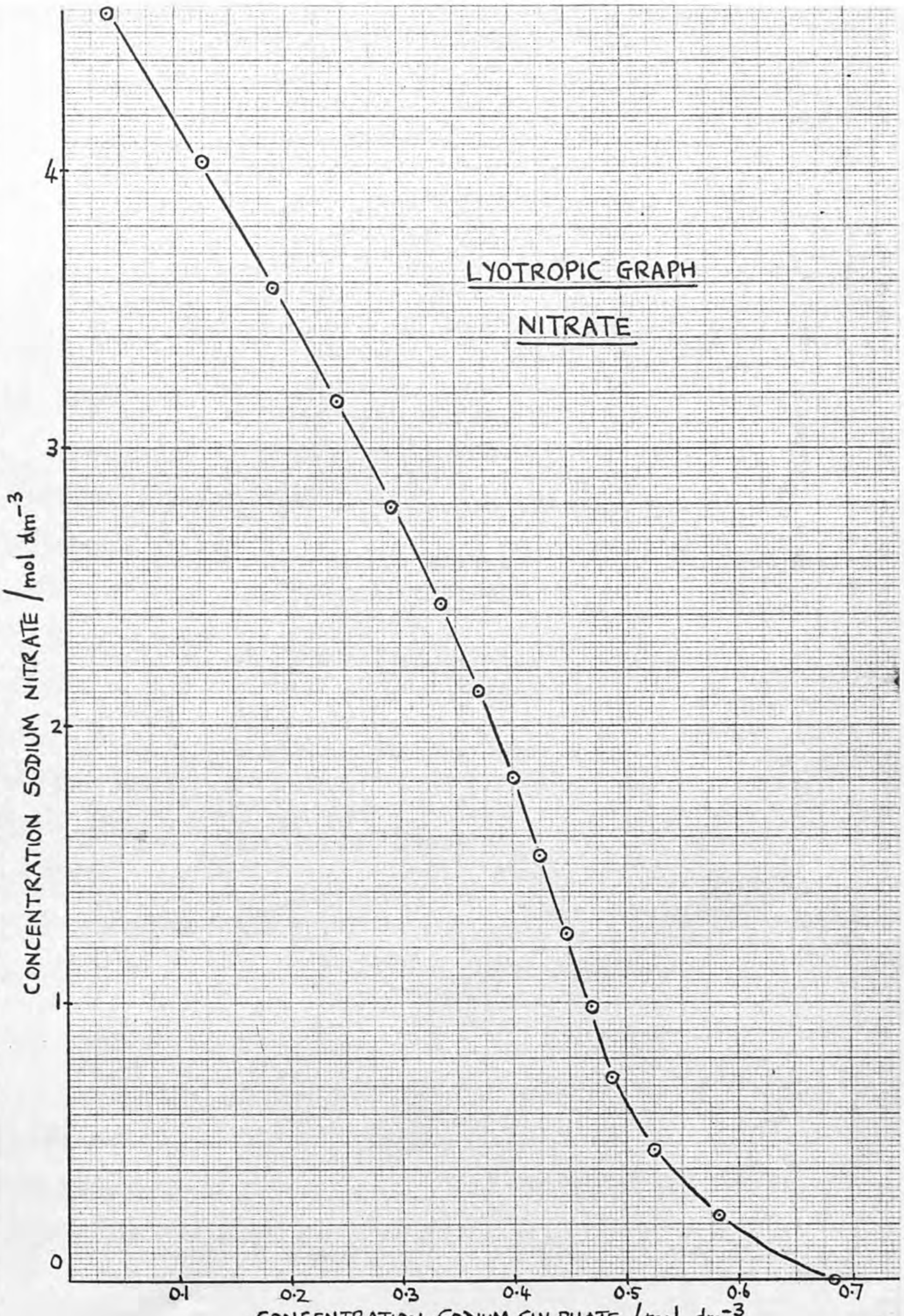

LYOTROPIC GRAPH
NITRATE
CONCENTRATION SODIUM NITRATE /mol dm^{-3}
0
1
2
3
4
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM SULPHATE /mol dm^{-3}

FIG. 20

RESULTS AND DISCUSSION

(a) LYOTROPY

Section 1

(i) Electrolyte concentration and gelatin sample

Different gelatin samples have different solubilities (lyotropic curve displaced) in electrolyte solutions and the gradients of the lines can also change - see Fig. 21 . This is probably a pH effect (see Results and Discussion, Section 1 (iii)), the pH values of 2 % sols of the gelatin samples being: gelatin, Royal Holloway College chemical store, 5.4 ; gelatin, serva entwicklungslabor, Heidelberg, 6.2 ; B.D.H. gelatin, 5.1 . It was therefore necessary to use the same sample throughout the determinations; B.D.H. gelatin was used. This had the smallest solubility and gives more scope with the anti-flocculating ions since longer curves are obtained. This gives greater accuracy in the determination of the lyotropic numbers of these ions.

(ii) The influence of temperature

The lyotropic curves of four ions, chloride, bromide, nitrate and chlorate were determined, using the procedure given in EXPERIMENTAL, at 25 °C and 30°C. Sufficient quantities of solutions were prepared to ensure that exactly the same materials were used at

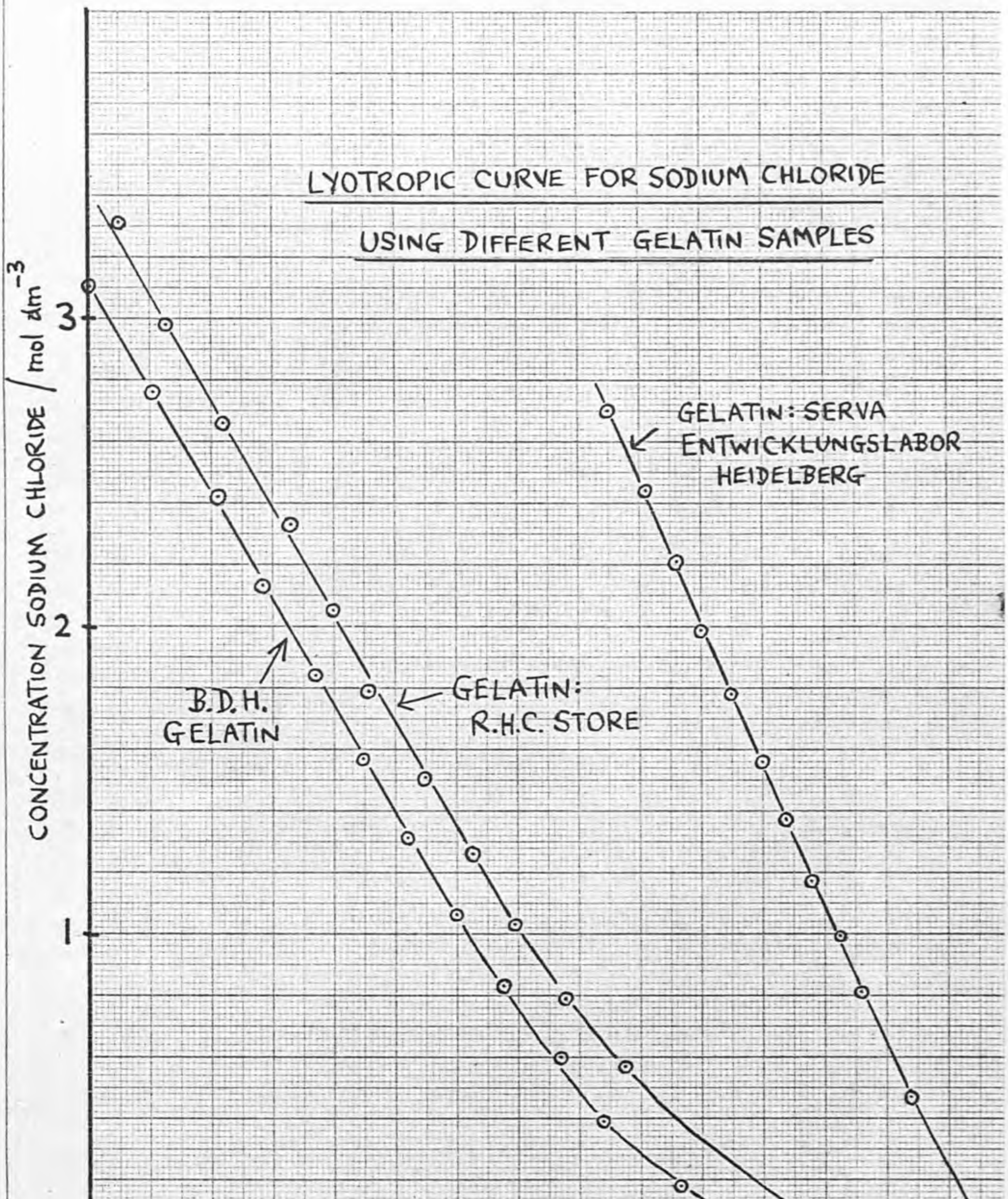

LYOTROPIC CURVE FOR SODIUM CHLORIDE
USING DIFFERENT GELATIN SAMPLES
CONCENTRATION SODIUM CHLORIDE / mol dm⁻³
3
2
1
GELATIN: SERVA ENTWICKLUNGSLABOR HEIDELBERG
B.D.H. GELATIN
GELATIN: R.H.C. STORE
0·2
0·3
0·4
0·5
0·6
0·7
0·8
CONCENTRATION SODIUM SULPHATE / mol dm⁻³

FIG. 21

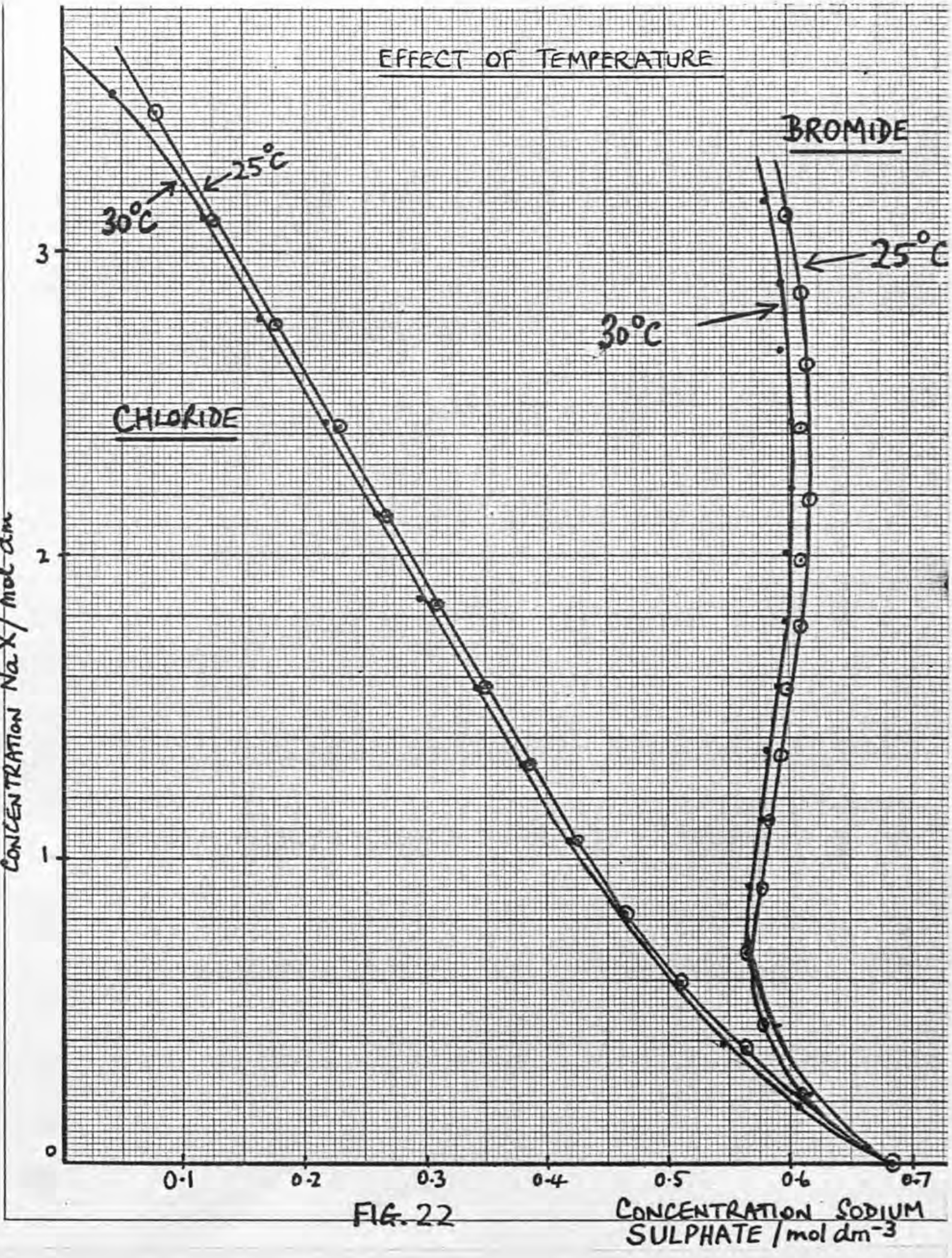

EFFECT OF TEMPERATURE
BROMIDE
CHLORIDE
25°C
30°C
25°C
30°C
CONCENTRATION NaX / mol dm^{-3}
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}
0
1
2
3
0·1
0·2
0·3
0·4
0·5
0·6
0·7

FIG. 22

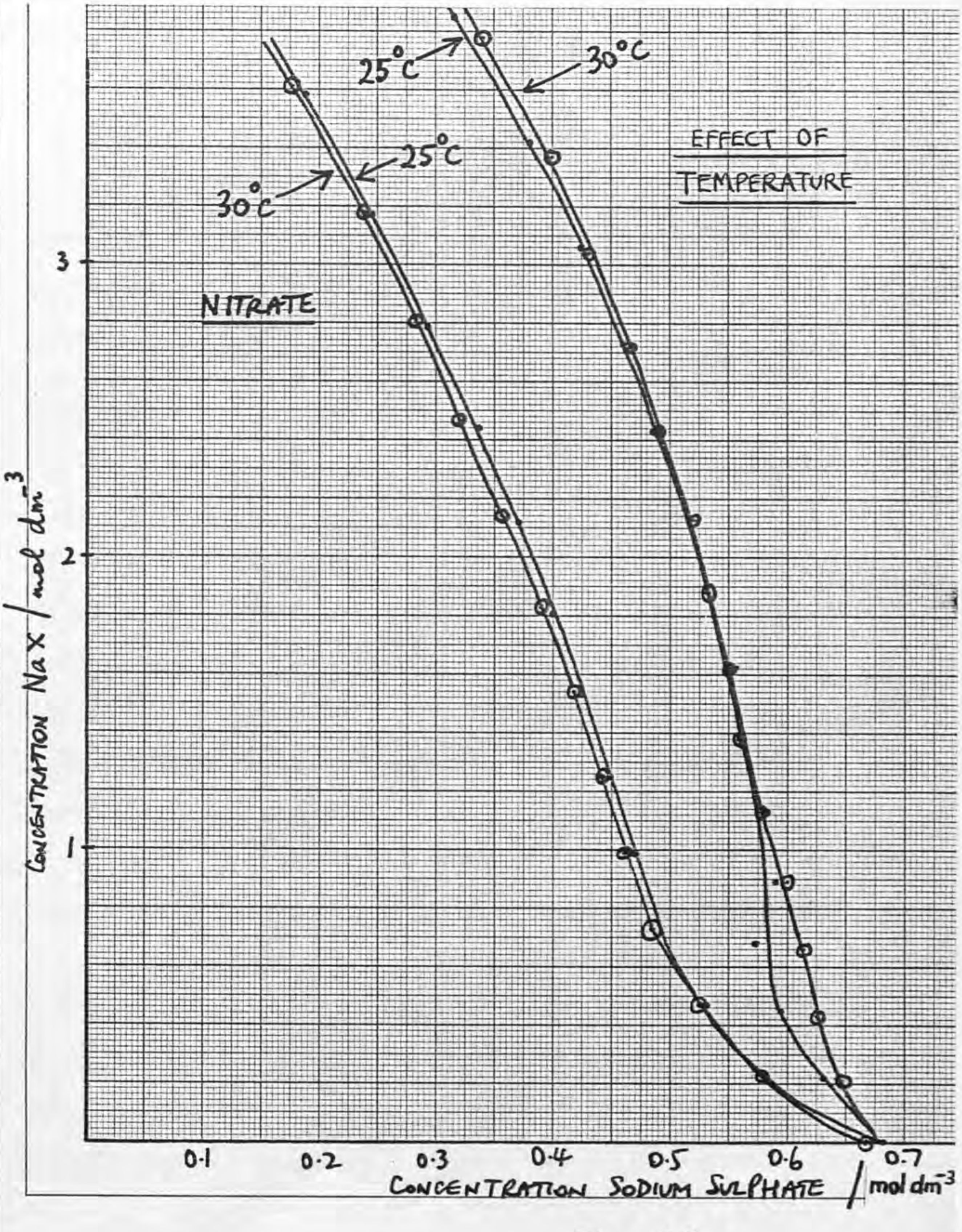

25°C
30°C
30°C
25°C
EFFECT OF TEMPERATURE
NITRATE
3
2
1
CONCENTRATION NaX / mol dm⁻³
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM SULPHATE / mol dm⁻³

FIG. 23

both temperatures. The results are shown in Fig. 22 and Fig. 23 . These show that there is a very small temperature effect on end-point electrolyte concentration and that for the amount of Newtonian cooling encountered in the present determinations ($\ngtr 0.5\ ^{\circ}C$) the effect on the results is negligible.

(iii) The influence of pH

As has been already pointed out there has existed a need for an investigation regarding the effect of pH on the salting-out of gelatin by salt mixtures and hence its effect on lyotropic number, N. In this research four ions were investigated (chloride, bromide, formate, acetate), these being chosen to vary the pH of the salt solution and hence the pH of the gelatin - salt (NaX) - sodium sulphate mixture as turbidity appears. For example, the pH of a normal chloride determination is 5.0, that of a normal acetate determination 7.5 . The gelatin - salt mixtures, previously described in EXPERIMENTAL, were slightly modified to include either sodium hydroxide solution or the acid whose anion is that present in the salt under investigation. For example various concentrations of sodium hydroxide and hydrochloric acid were used in the chloride determinations. The results are shown in Fig. 24 - 27. These indicate that, in the case of strong-acid salts, the POSITION of the

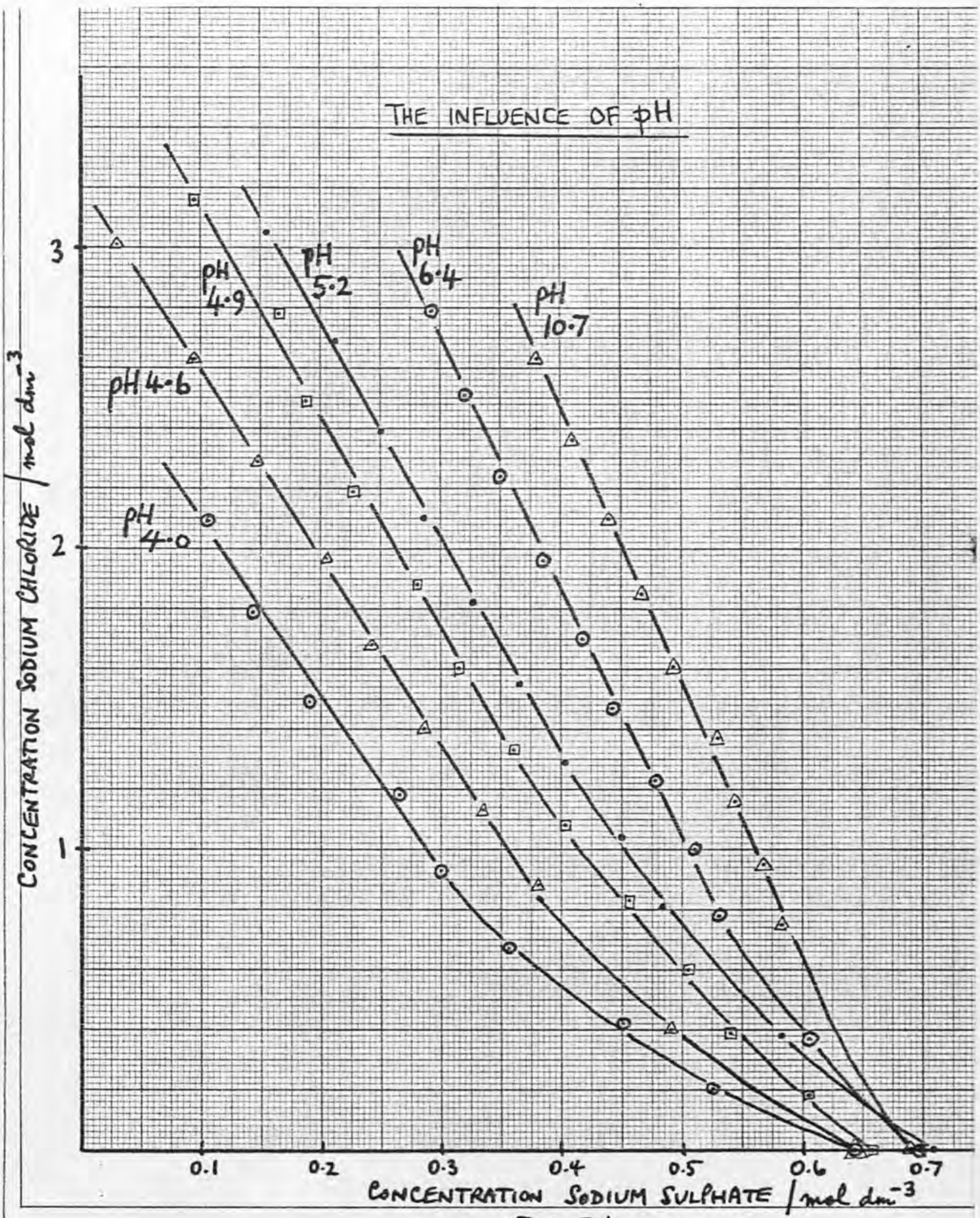

THE INFLUENCE OF pH
pH 4·0
pH 4·6
pH 4·9
pH 5·2
pH 6·4
pH 10·7
3
2
1
0.1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM CHLORIDE / mol dm^{-3}
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}

FIG. 24

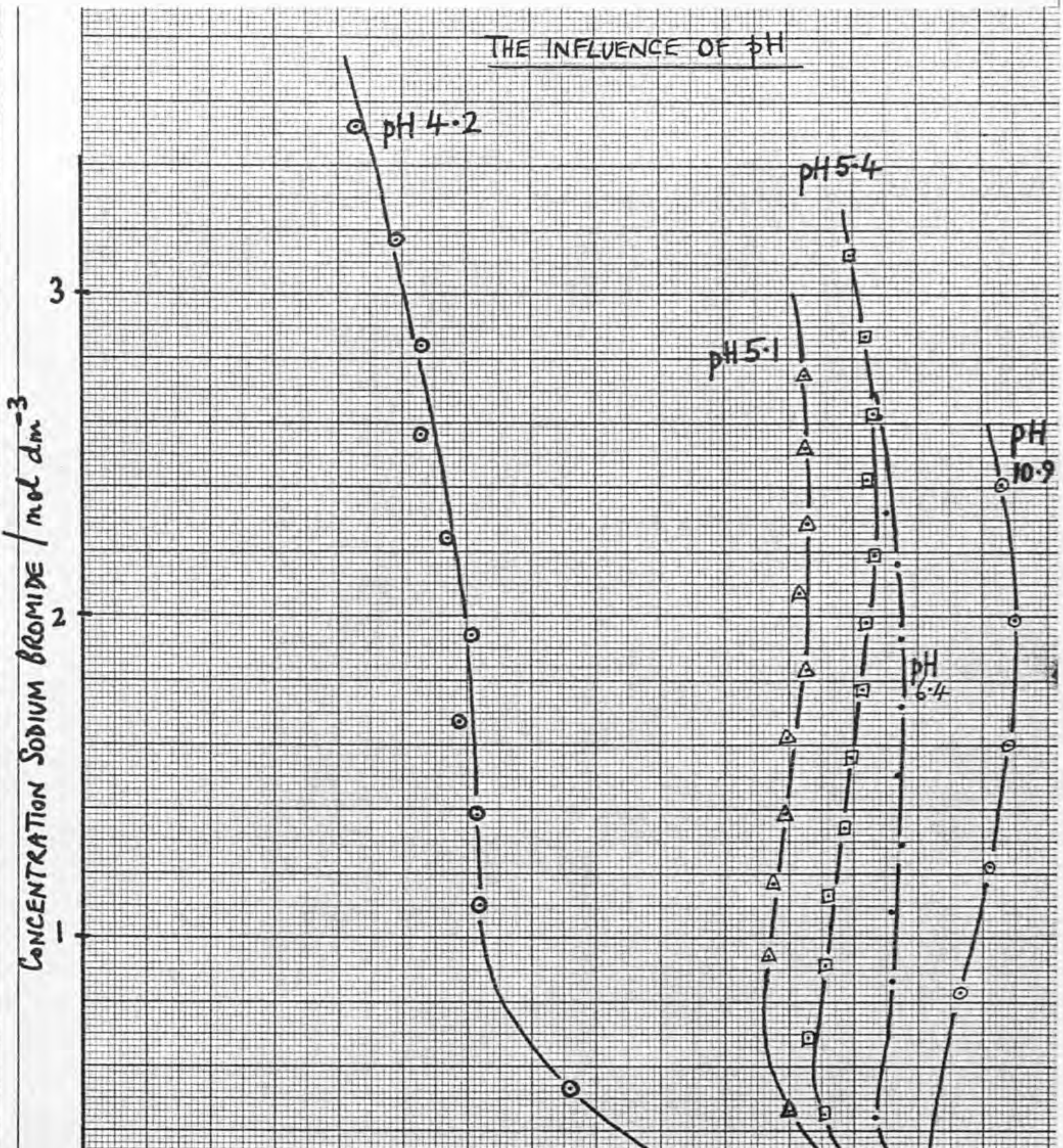

THE INFLUENCE OF pH
pH 4·2
pH 5·4
pH 5·1
pH 6·4
pH 10·9
3
2
1
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM BROMIDE / mol dm^{-3}
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}

FIG. 25

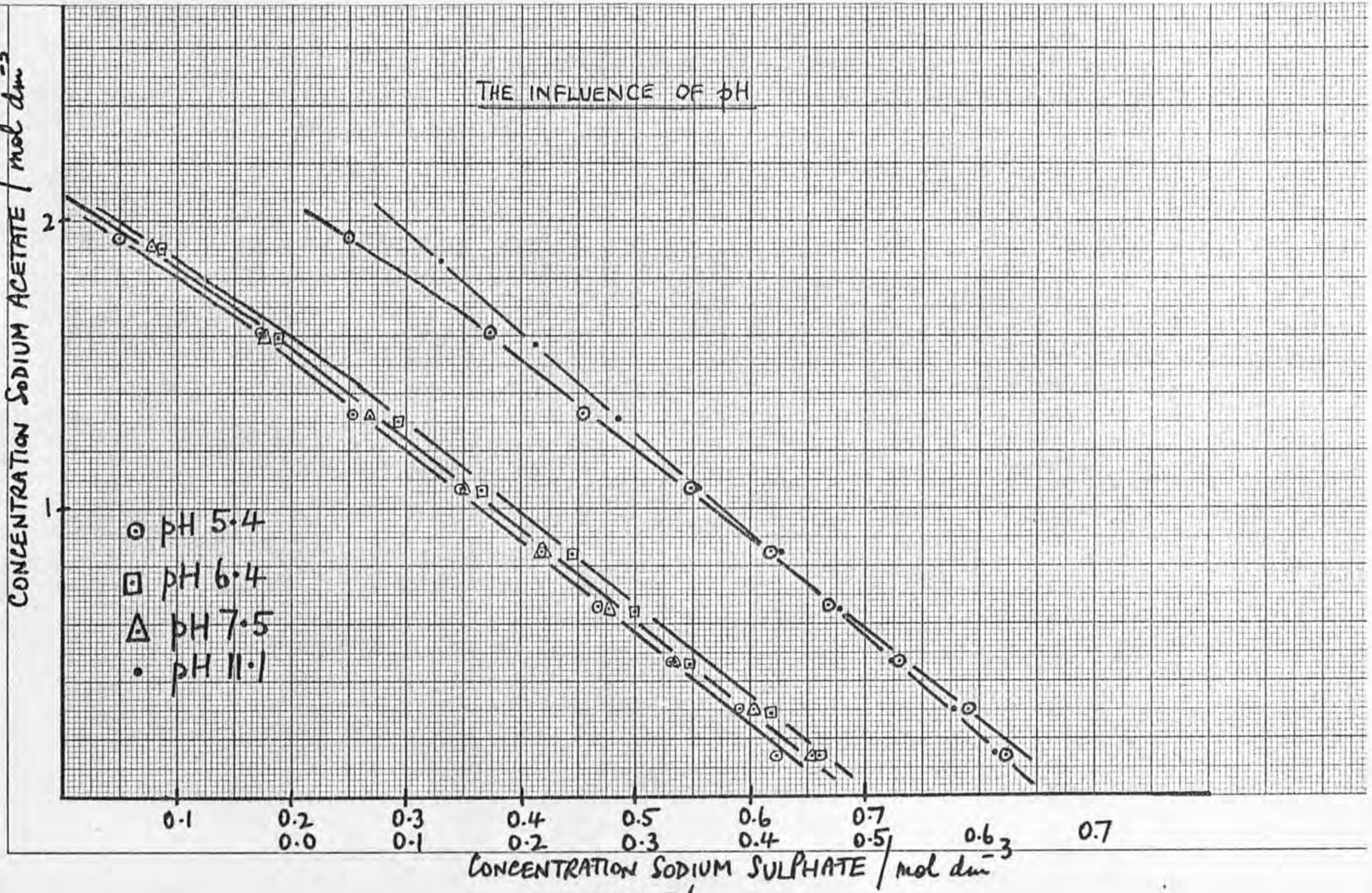

THE INFLUENCE OF pH
○ pH 5·4
□ pH 6·4
△ pH 7·5
• pH 11·1
CONCENTRATION SODIUM ACETATE / mol dm^{-3}
2
1
0·1
0.2
0.0
0·3
0·1
0.4
0·2
0.5
0·3
0·6
0.4
0·7
0·5
0·6
0.7
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}

FIG. 26

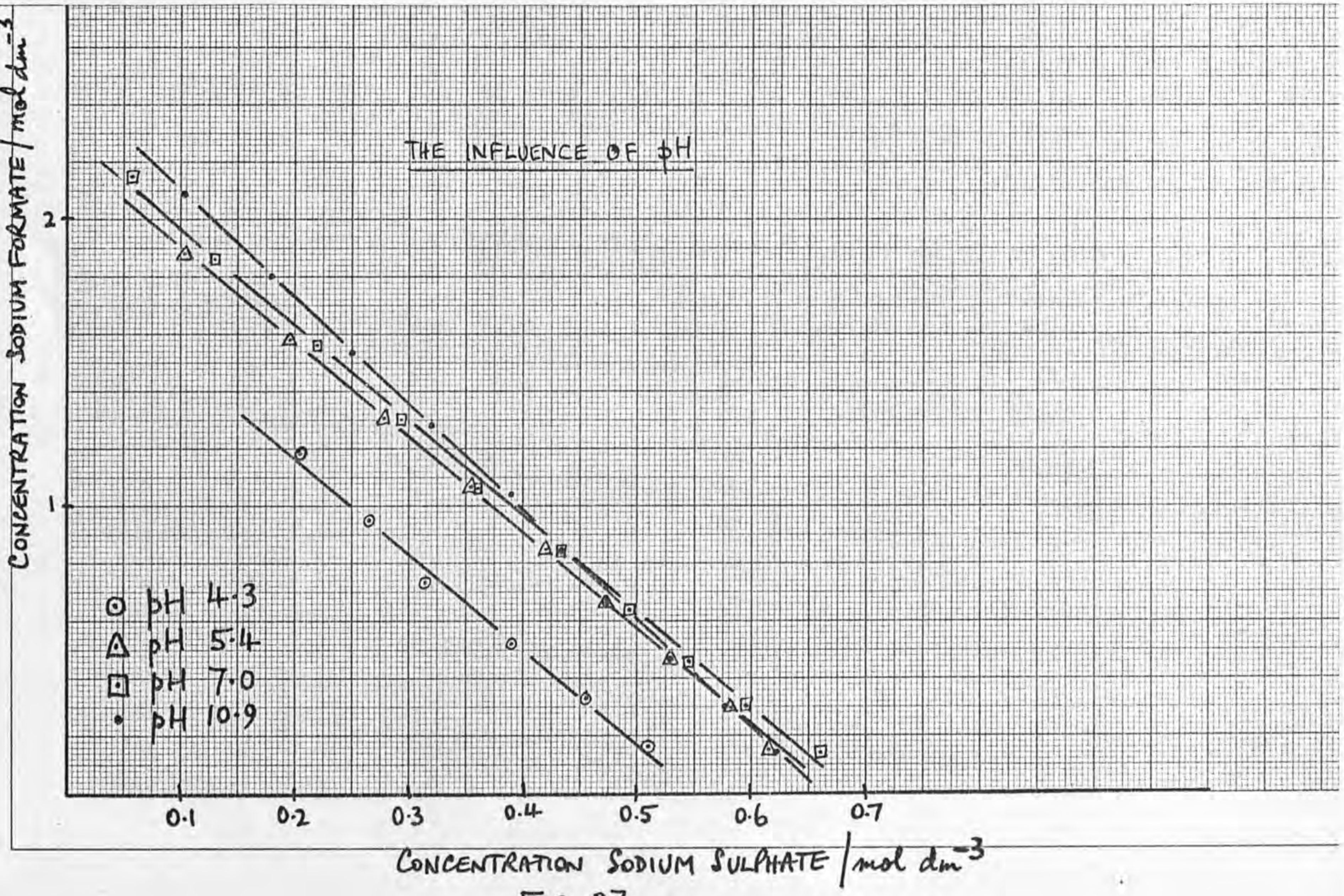

THE INFLUENCE OF pH
⊙ pH 4·3
△ pH 5·4
⊡ pH 7·0
• pH 10·9
CONCENTRATION SODIUM FORMATE / mol dm^{-3}
2
1
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}

FIG. 27

line will vary appreciably with changing pH; with increasing pH a higher concentration of electrolyte is needed to cause turbidity in the gelatin. Sensitivity to pH is greatest near the isoelectric point of gelatin (4.8) and more so below this pH value than above it. However, the GRADIENT of the linear portion of the line is not affected unless the pH of the system departs appreciably from the normal pH, i.e. the pH of the system in the absence of added acid or alkali. There is about a 2 % change in both lyotropic numbers resulting from the change of gradient associated with changing the pH from 5.1 to 6.4 in the case of bromide, and 5.0 to 6.4 in the case of chloride. For sigmoid curves the central linear part is used to determine lyotropic number so that it is the gradient here that must be particularly considered. For weak-acid salts the effect of pH is much smaller. The position of the lyotropic line is changed very little over the range pH 5.5 - 7.5 and the gradient is not changed. At pH 4.3 (formate) the gradient still remains constant but at pH 11.0 there is an appreciable gradient change for both formate and acetate. To summarise, these experiments indicate that small variarions of pH at the normal pH of the system will not change lyotropic numbers.

Since there is thought to be a connection between the hydration enthalpy of an ion and its ability to precipitate a gelatin sol it seems appropriate to find the gradient and lyotropic number at the normal pH of the system. The heat of solution of a sodium salt is found by dissolving the salt in pure water and the pH of the resulting solution will differ from one salt to another. The magnitude of the quantity is not adjusted to some common pH and it therefore seems appropriate to use the lyotropic curve determined at the normal pH of the system.

In view of the fact that sensitivity to pH is greatest at and below the isoelectric point consideration was given to the use of Fibroin, isoelectric point about 2.2, since determinations would be likely to take place well above this pH. Investigation of the properties of this substance, however, led to the abandonment of the idea. In particular, fibroin sols are unstable and are readily precipitated by shaking or stirring[36].

(iv) Gelatin concentration and sharpness of end-point

From the beginning of the research it was evident that the sharpness with which turbidity appears is increased by a reduction in volume at this point. This can be achieved by: (a) using a minimum volume of mixture before titration. This minimum is 9.0 cm^3 as this allows stirring without interference with the light beam; (b) using the strongest solution of sodium sulphate (1.80 mol dm^{-3}) consistent with its solubility at 25.0 °C (see Fig. 28 - this

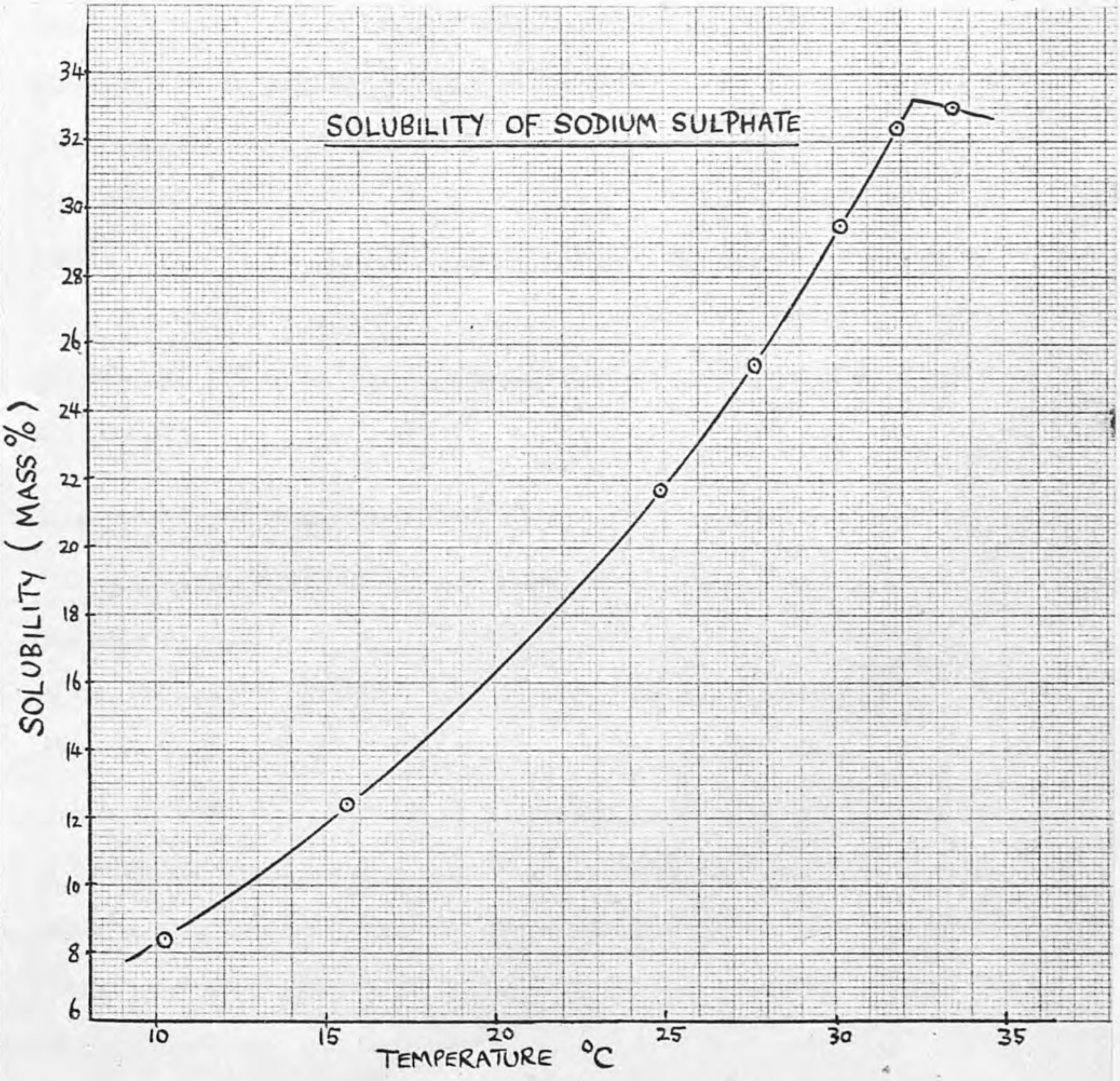
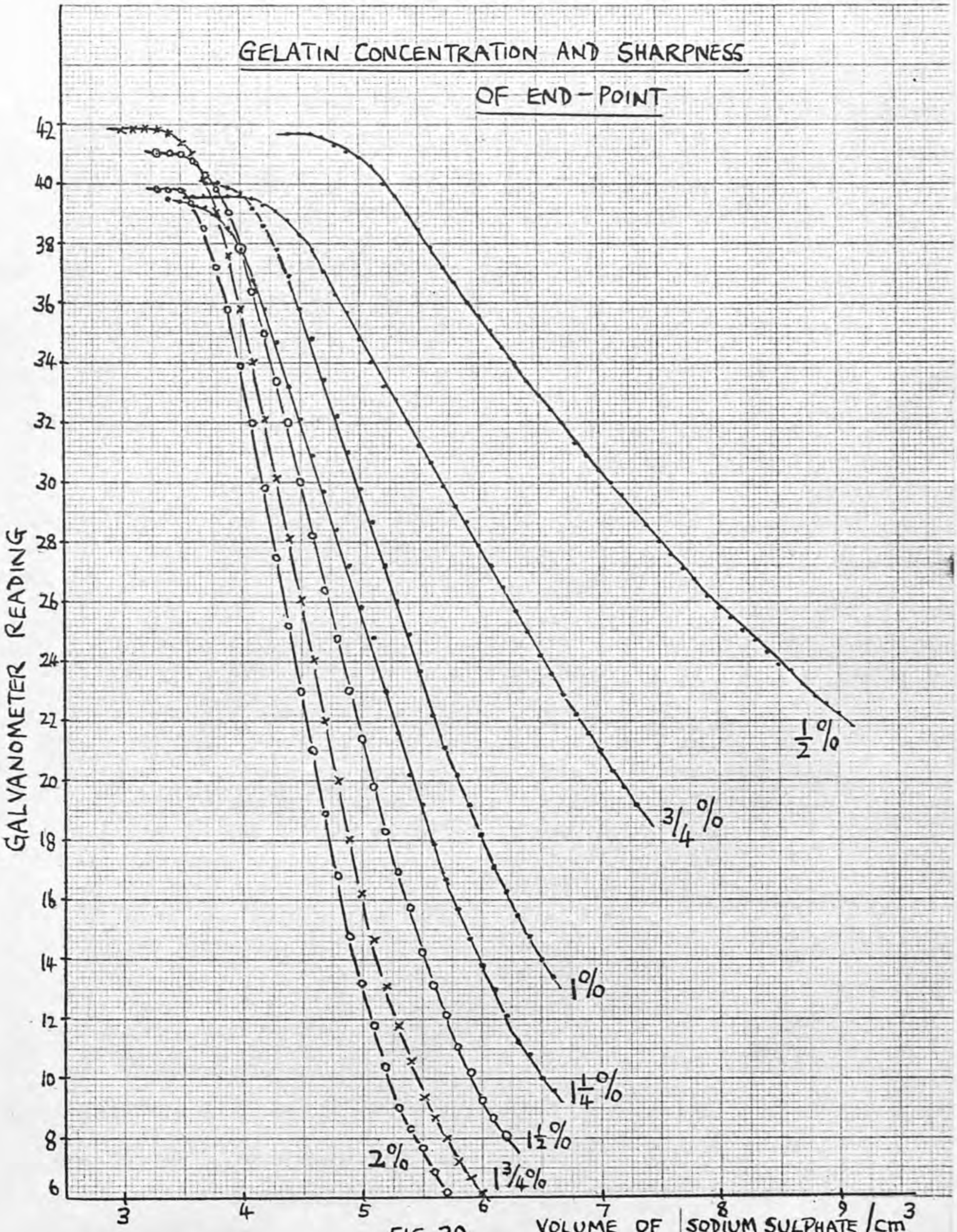

SOLUBILITY OF SODIUM SULPHATE
SOLUBILITY (MASS %)
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
10
15
20
25
30
35
TEMPERATURE °C

FIG. 28

concentration, which is 20.4 mass %, is saturated at a temperature close to 24.0 °C); (c) using the most concentrated gelatin sol consistent with its remaining stable (liquid) for short periods. Investigation of the effect of gelatin concentration on the sharpness of the end-point (2.00 cm^3 gelatin sol, 2.00 cm^3 sodium chloride solution of concentration 5.00 mol dm^{-3}; and 5.00 cm^3 water used) gives the curves shown in Fig. 29 . Titrant (concentration as above) was added in 0.10 cm^3 portions and additions were made at $\frac{1}{2}$ - minute intervals. It is clear from the curves that an optimum gelatin concentration is reached at about 2 %. Also this does not set quickly.

(v) Gelatin concentration and end-point

Also investigated was the possible influence of gelatin concentration on the end-point titrant volume. Three different sodium chloride - gelatin mixtures were titrated with sodium sulphate (1.80 mol dm^{-3}) using 2 %, 3 %, 4 % gelatin sols. The change in gradient due to changing gelatin concentration affects the lyotropic number to the extent of approximately 0.4 %. This can be ignored. Confirmation of this was provided by determining the bromide and nitrate lyotropic curves in such a way that the gelatin end-point concentration was the same for all mixtures, i.e. the various mixtures contained different gelatin concentrations before titration. The



GELATIN CONCENTRATION AND SHARPNESS OF END-POINT

FIG. 29

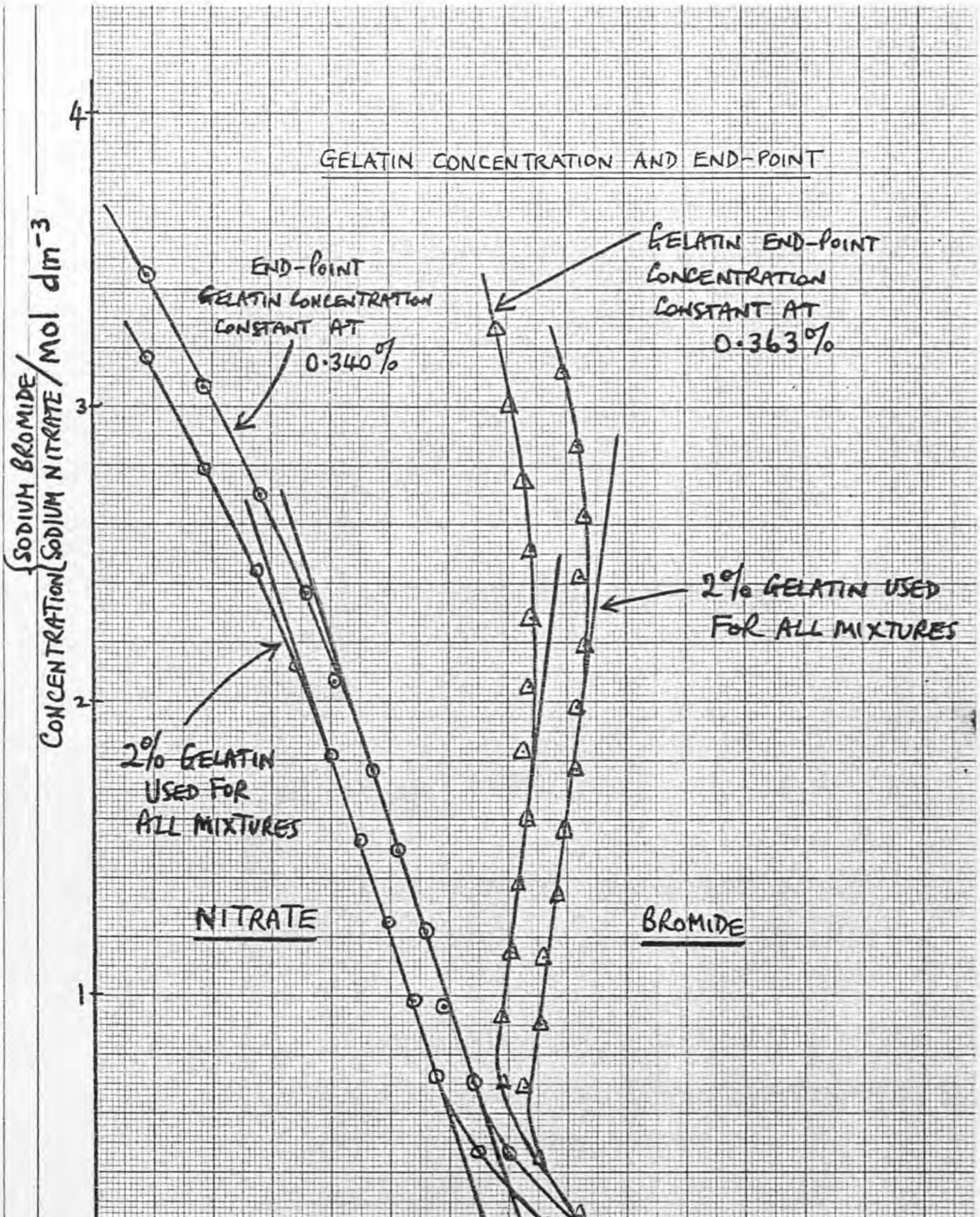

GELATIN CONCENTRATION AND END-POINT
END-POINT
GELATIN CONCENTRATION
CONSTANT AT
0·340%
GELATIN END-POINT
CONCENTRATION
CONSTANT AT
0·363%
2% GELATIN USED
FOR ALL MIXTURES
2% GELATIN
USED FOR
ALL MIXTURES
NITRATE
BROMIDE
CONCENTRATION {SODIUM BROMIDE / SODIUM NITRATE / mol dm⁻³
4
3
2
1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM SULPHATE / mol dm⁻³

FIG. 30

results are shown in Fig. 30 . The gradients along the relevant portion of the curves are effectively unaltered by using 2 % gelatin for every mixture. The slight change of gelatin solubility is no doubt due to a small fluctuation of pH. As has been seen in part (iii) above the position of the curve is most sensitive to pH in the region of pH 5.0, which is the approximate pH of these determinations.

(vi) The use of Agar

Some of the early work on lyotropy was carried out using agar[26]. The author considers agar inferior to gelatin in these determinations for the following reasons:

(1) Agar sols have to be used at a remperature in excess of 40 °C since on further cooling gelation occurs. This means that temperature control is much more difficult than with gelatin at 25 °C. Gelatin sols can be kept at 25 °C for some time (hours rather than minutes) before gelation takes place.

(2) The onset of turbidity is much sharper with gelatin than with agar. Titration of chloride mixtures 1 and 10 at 45 °C using 0.5, 1.0 and 1.5 % agar, and sodium sulphate of concentration 3.00 mol dm^{-3}, gives the results shown in Fig. 31 . The results for two chloride mixtures using 2 % gelatin and sodium sulphate of concentration 1.80 mol dm^{-3} are given for comparison, these being 25 °C determinations. It would

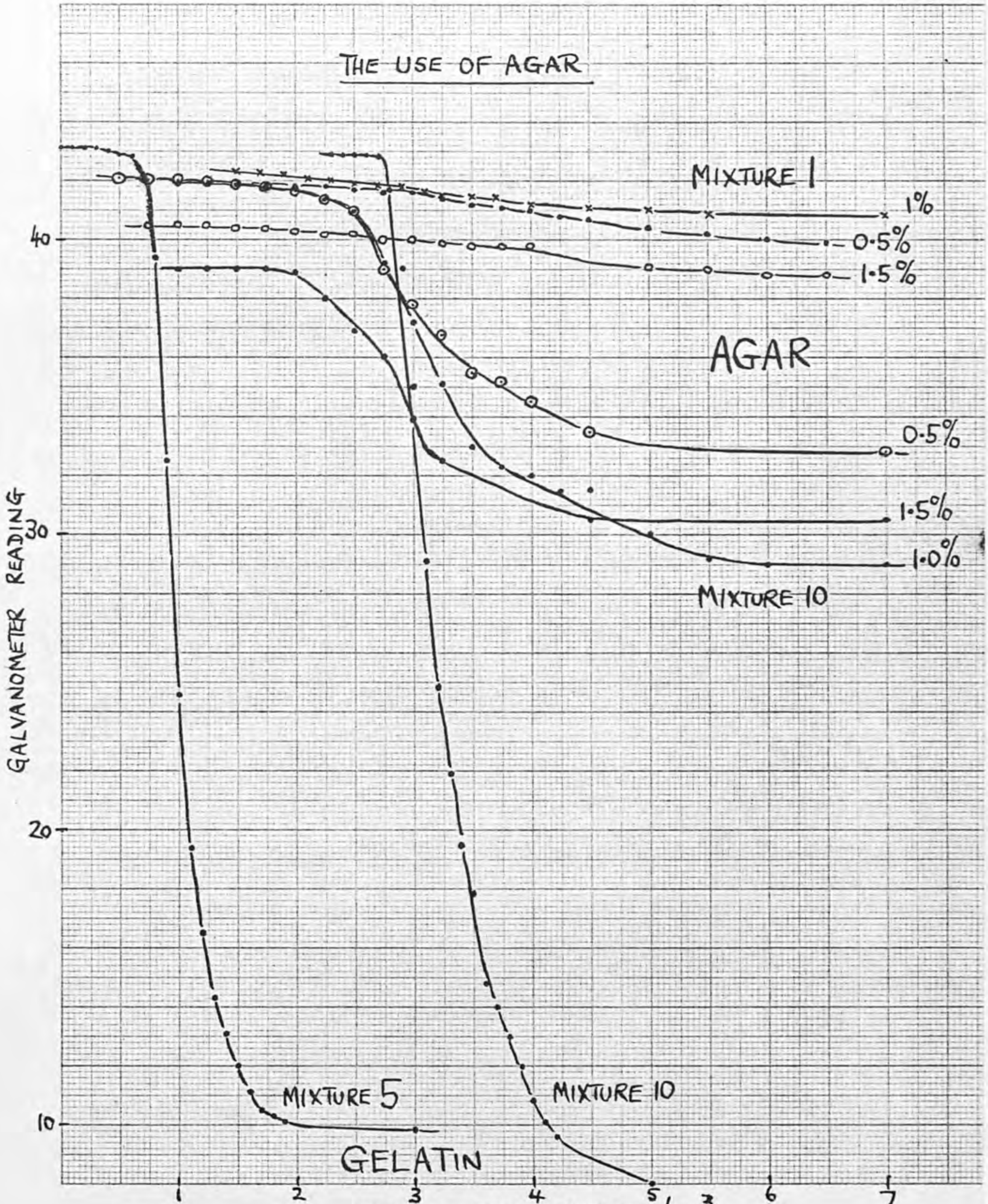

THE USE OF AGAR
MIXTURE 1
1%
0·5%
1·5%
AGAR
0·5%
1·5%
1·0%
MIXTURE 10
MIXTURE 5
MIXTURE 10
GELATIN
GALVANOMETER READING
40
30
20
10
1
2
3
4
5
6
7
VOLUME SODIUM SULPHATE / cm^3

FIG. 31

appear that 1% agar might be the optimum agar sol concentration (sharpest drop in galvanometer readings).

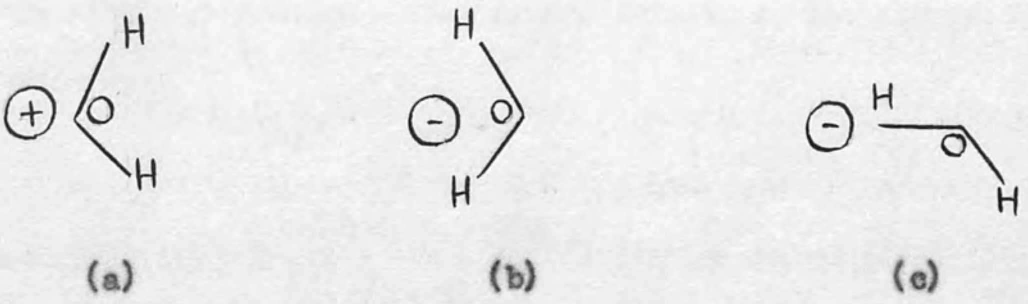
(3) The flocculation of agar does not occur in the same manner as gelatin and galvanometer readings are not as steady.

For these reasons the use of agar produces a greater spread of points on the lyotropic curve and is therefore less satisfactory.

Section 2. Ion hydration; lyotropic curves and lyotropic numbers

It is established[37-39] that at ambient temperatures water has a tetrahedral structure similar to that of ice, so that each water molecule tends to be surrounded by four nearest neighbour water molecules. X-ray scattering experiments[40,41] indicate that the tetrahedral arrangement persists in small regions of the liquid, although no long-range order is found. Water has been described as a broken-down ice structure, each molecule striving to bond itself to four neighbouring molecules, but in which bonds are continually breaking and reforming so that at any instant a molecule is likely to be bonded to less than four others. Frank and Wen[42] postulate that association of water molecules is a co-operative process so that the association of two molecules promotes the further association of these with other molecules. Hence clusters of molecules will tend to form, and break up, giving a picture of "flickering clusters". The life-time of the clusters (10^{-10} to 10^{-11} s) is significant since it is 10^2 to 10^3 times the period of molecular vibration. Increase in temperature causes hydrogen bonds to break and increase the proportion of free molecules. The low solubility of non-polar solutes in water is attributed to a large entropy decrease which accompanies dissolution[42,43], making ΔG positive. This entropy decrease is ascribed to the promotion of water-water interaction in the neighbourhood of the solute particles; such solutes are said to be "structure formers".

Since the electric field in the neighbourhood of an ion in aqueous solution is intense[44], it is to be expected that the nearest-neighbour water molecules will align themselves and become attracted to the ion (ion - dipole attraction), thereby becoming immobilised. This alignment has been discussed by several authors (see for example references 38, 45, 47, 48); plausible orientations are shown in Fig. 32 .



(a) (b) (c)

Fig. 32

Electrostriction has been used to explain the small or negative values of the solute partial molal volumes and compressibilities in salt solutions. Attempts have been made to find hydration numbers, i.e. the number of nearest-neighbour water molecules directly associated with an ion. This is not easy since it is necessary to decide arbitrarily which water molecules are to be regarded as belonging to the primary hydration sphere. Determination of the radial distribution for ion/water systems by measurement of the areas of X-ray diffraction patterns of electrolyte solutions is regarded by Hertz[49] as being, in principle, a satisfactory method of determining hydration numbers. These numbers have also been found[46,49-51] by methods involving mobilities of ions in an applied electric field, the compressibility of solutions compared with that of the pure solvent, and by NMR. Some values of hydration numbers are given in Table 9. Clearly there can be great variation in the values obtained; this is to be expected as different methods use different criteria. The wide variation in magnitude serves to reinforce the doubtful utility of the concept of hydration number.

TABLE 9
Hydration numbers

Ion	Method				Ref.
	X-ray	Mobilities	Compressibilities	NMR	
Li^+		5	4		46
Na^+		4	5		46
K^+	4	4	5		46,49
Mg^{2+}		12	12	6	46,49
Cl^-	6.2 - 7.3	4	2		46,49
Br^-	7.2 - 8.9	2	1		46,49
I^-	8 - 9	1	1		46,49

The early discussions[31] considered that the principal action of an ion is to bind nearest-neighbour water molecules. This was disproved by the fact that a caesium chloride solution, for example, of concentration 0.1 mol dm^{-3}, is more fluid than pure water. Bernal and Fowler[37] interpreted this by proposing that the ions were in some way breaking the water structure, a similar conclusion being later reached by Frank and Evans[43]. Frank and Wen[42] have shown that all the alkali metal ions except Li^{+} and Na^{+}, and all of the halide ions except F^{-}, lose "too little" entropy when dissolved from the gas state to infinite dilution. The entropy of solution for potassium chloride is -51.9 cal mol^{-1} K^{-1}, whereas that for argon is $-\frac{1}{2}$ (60.5) cal mol^{-1} K^{-1}. It follows that the presence of some ions in water causes in some way a more random arrangement of the water molecules. Frank and Wen have proposed the structure in the neighbourhood of an ion as shown in Fig. 33 .

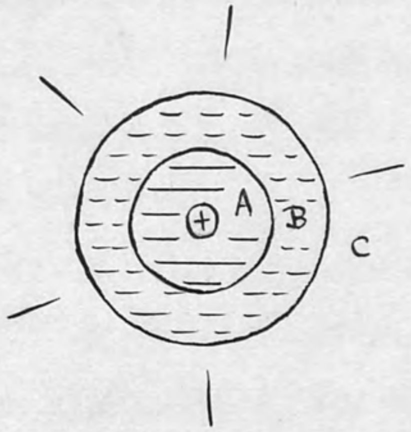


Fig. 33

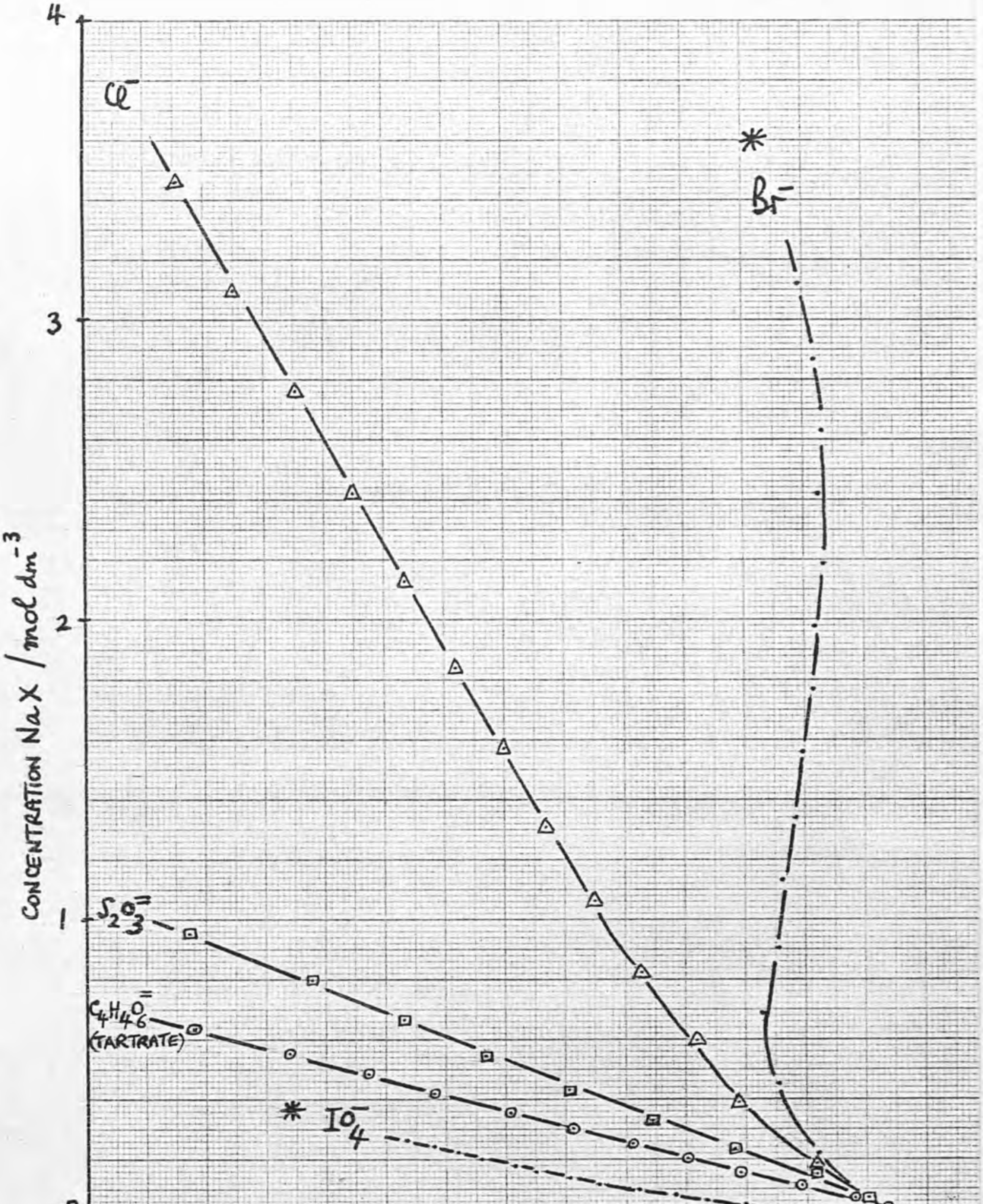
Region A consists of electrostricted water molecules and region C is normal water. In region B there are the competing influences of the ion and the normal (bulk) water so that here there is a disorder greater than in normal water. This picture is supported by data from the diffusion of $H_2{}^{18}O$ through salt solutions and from the temperature coefficient of relative viscosity[52,53]. According to Frank, cations smaller or more highly charged than K^+ are structure-formers. K^+ is slightly structure-breaking and the effect increases from K^+ to Cs^+. F^- is structure-forming but Cl^-, Br^-, and I^- are increasingly structure-breaking. NO_3^- and ClO_4^- are structure-breakers, SO_4^{2-} less so; OH^- is structure-forming. In the case of structure-formers region A encroaches on region B but there will always be some disorder in region B. For large singly-charged ions (structure-breakers) this does not occur. Whereas Frank assumes that region A always exists, Gurney[54] proposes that for ions such as Cs^+ region B extends into region A and may extinguish it completely.

Many models have been used to calculate ion hydration enthalpy.[37,38,45,55] The principle of the methods is to evaluate the energy changes associated with (i) the removal of a group of (n + 1) water molecules leaving a cavity in the water, (ii) the break-up of this group of molecules, (iii) the formation of ion - dipole bonds between the ion and n water molecules, (iv) the transfer of the ion and its primary hydration sheath from vacuum to the solvent cavity,

(v) adjustment of the cavity to fit the hydrated ion, (vi) the return of a single water molecule from vacuum to water. The various treatments represent successive improvements and Bockris[55] reports that, using these steps and allowing for ion-quadrupole interactions in (iii), the process gives agreement with Halliwell and Nyburg values to within 5 %. One of the difficulties in evaluating hydration enthalpies is the question of ion size. For example, radii calculated from electron density maps[56] are quite different from Pauling radii[57] and from van der Waals radii[58]. No single characteristic size can be assigned to an ion; the apparent ionic radius depends on the physical property under discussion and will differ for different properties. Since ions in a crystal are under considerable compression,[58] it is to be expected that the radius of an isolated ion in the gas phase will be greater than its radius in the crystal. Assigning a radius to an aqueous ion is not easy. The small enthalpies of solution of most ionic crystals indicates that the forces acting on ions in water are similar to those in the crystal. A reasonable procedure, therefore, is to use crystal radii for ions in solution. In the hydration process the ion is transferred from the gas phase to aqueous solution so that the question of choice of radius arises. As has previously been mentioned, some workers[20] have used crystal radii to which has been added 0.1 A for anions and 0.85 A for cations.

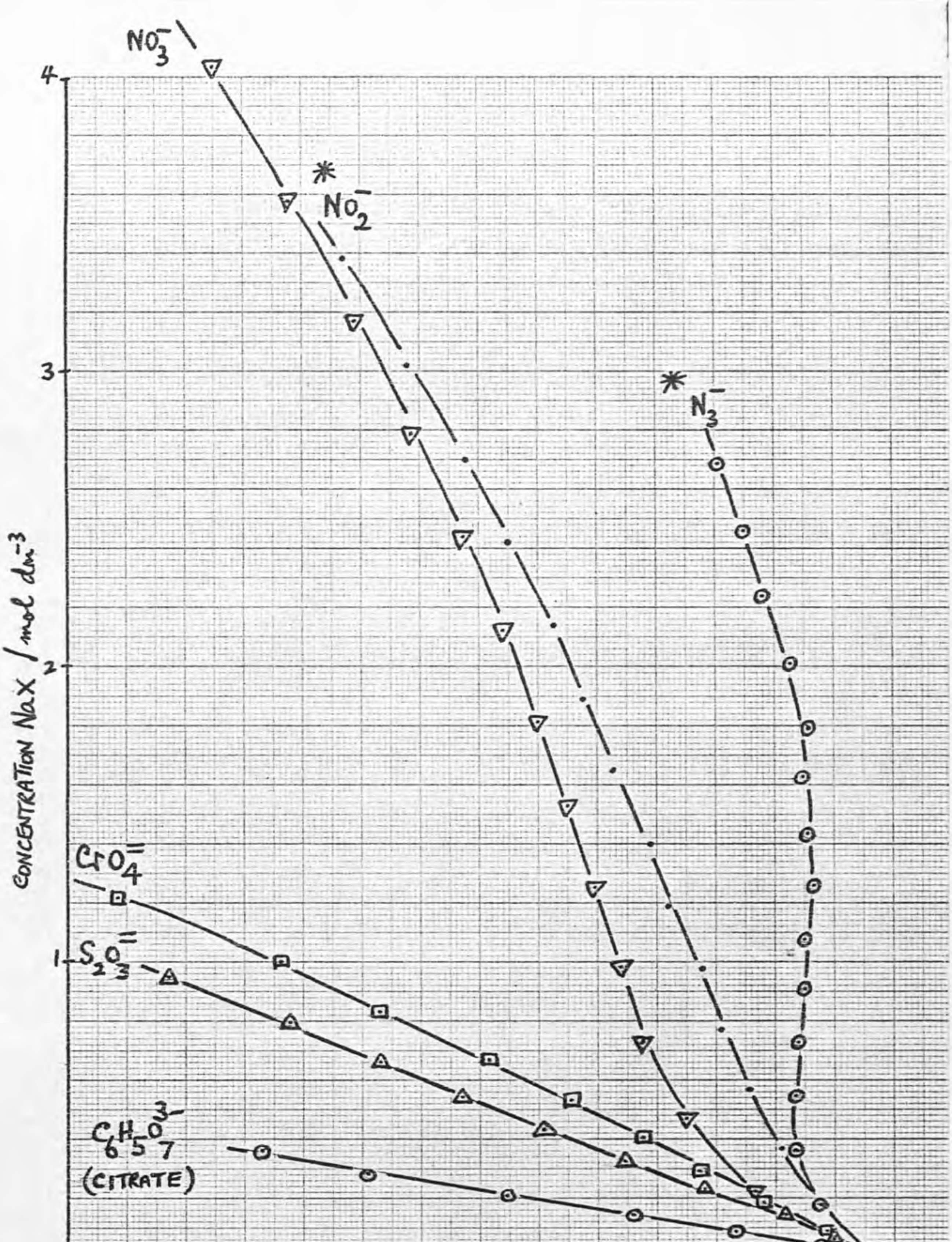
The above discussion of the nature of the ion - water interaction forms an introduction to the present study of the solubility of gelatin in the presence of dissolved electrolytes. The stability of lyophilic colloid systems such as gelatin is due to the charge on the particles and to a layer of water molecules surrounding the particles[59-61]. Since gelatin sols can be quite stable at the isoelectric point, the hydration of the particles is clearly an important factor in their stability; it is through the hydrophilic groupings that the protein is able to bind water to itself. Such a colloidal system can be precipitated by adding acetone or alcohol or by a sufficient concentration of some electrolytes. It is believed that the action of these organic substances and that the lyotropic action of ions is due to their ability to desolvate the colloid particles, hence allowing the particles to coalesce and precipitate. The hydration enthalpy of an ion is a measure of the strength of the ion - water bonding and it is therefore not surprising that a relationship was found between lyotropic number, which measures the ability of an ion to precipitate gelatin, and hydration enthalpy[25,29].

The lyotropic lines which have, in the present work, been determined are shown in Fig. 34 - 38 (an asterisk indicates that the graph is incapable of any appreciable extension because of solubility limitations). Examination of these shows that several are sigmoid. In all but two there is a linear middle section (the dichromate line is



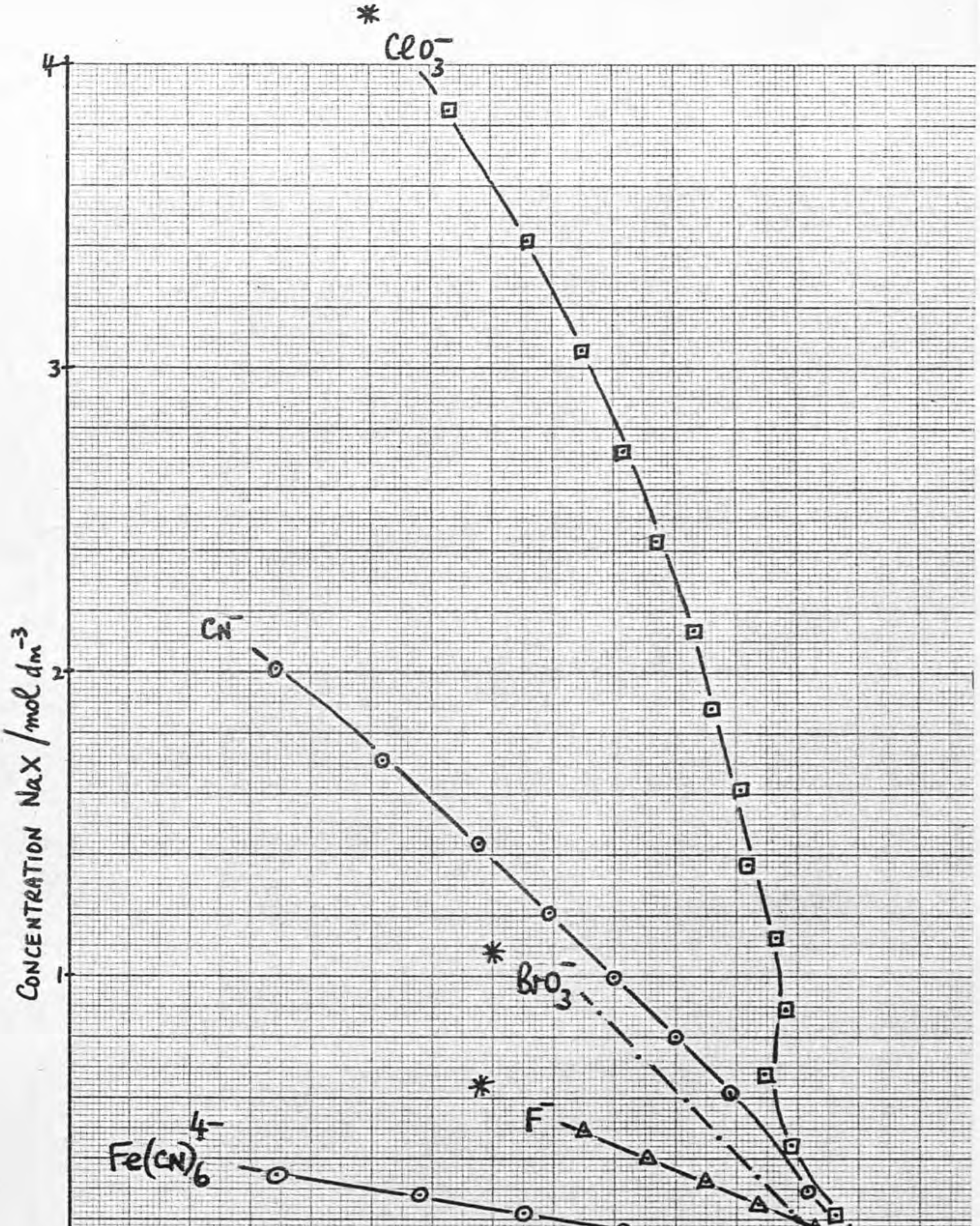
4
3
2
1
0
Cl⁻
* Br⁻
S₂O₃⁼
C₄H₄O₆⁼ (TARTRATE)
* IO₄⁻
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION NaX / mol dm⁻³
CONCENTRATION SODIUM SULPHATE / mol dm⁻³

Fig. 34



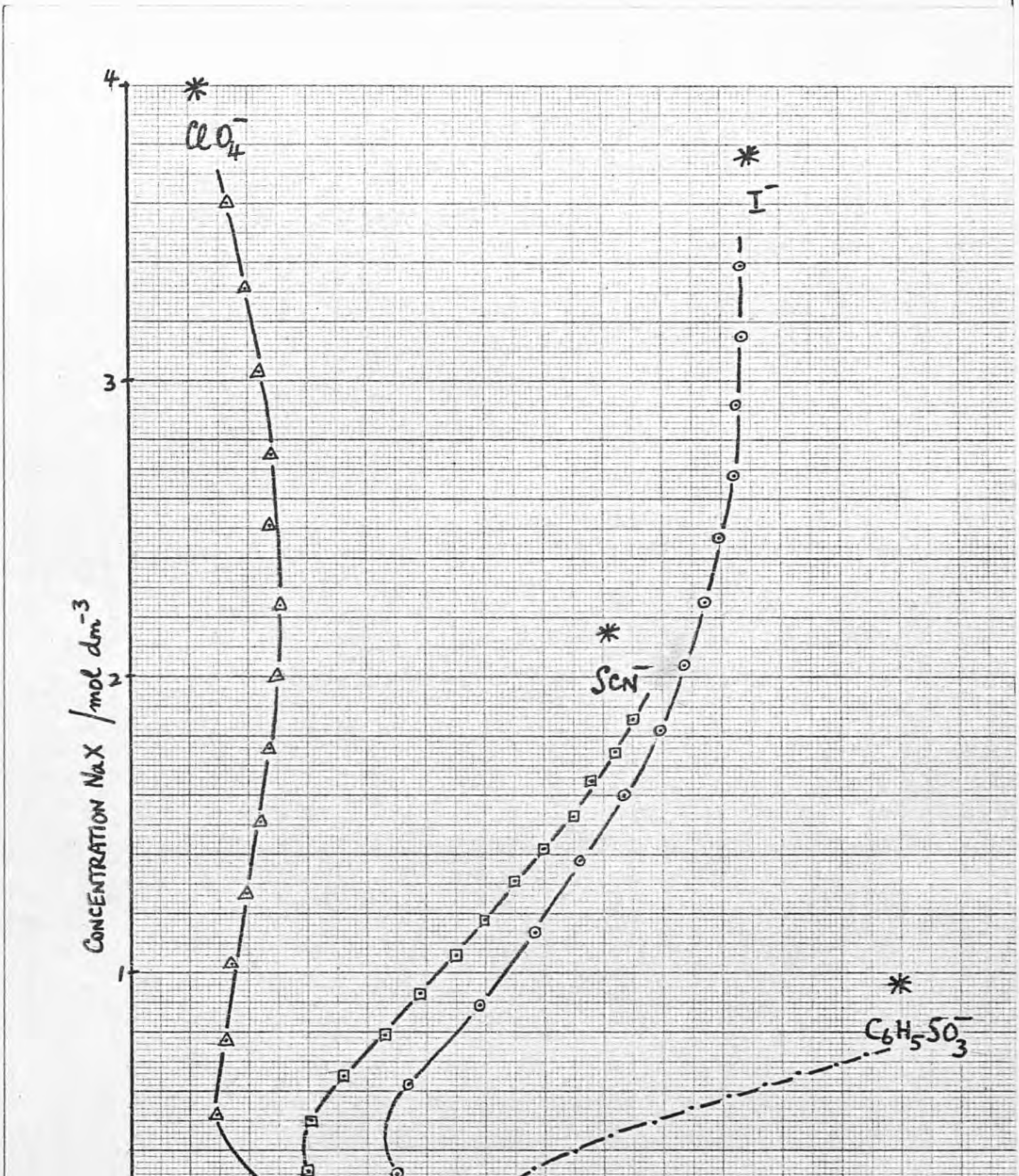
NO_3^-
NO_2^-
*
N_3^-
*
$CrO_4^=$
$S_2O_3^=$
$C_6H_5O_7^{3-}$
(CITRATE)
4
3
2
1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
CONCENTRATION NaX / mol dm^{-3}
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}

Fig. 35



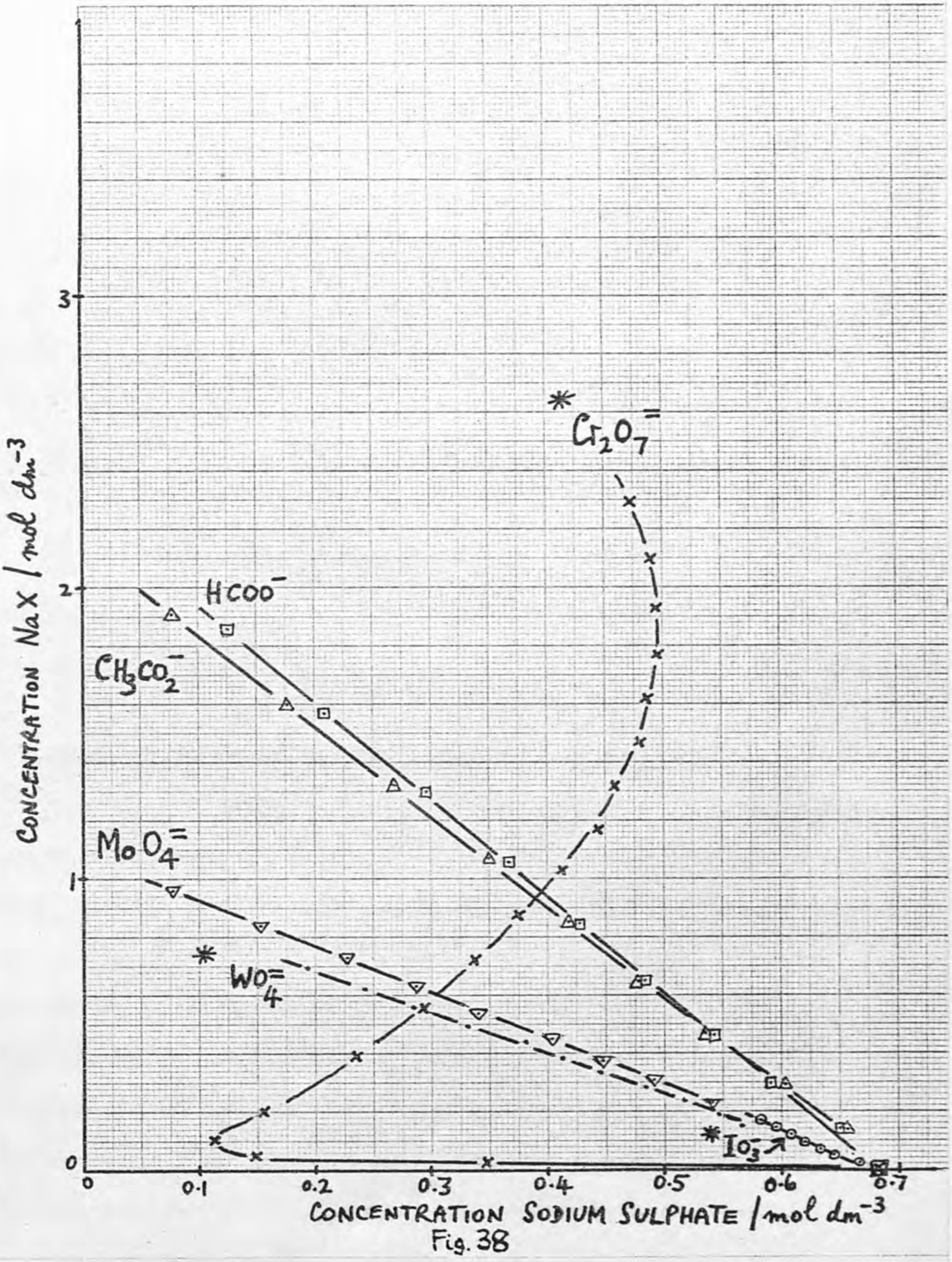
*
ClO_3^-
CN^-
*
BrO_3^-
*
F^-
$Fe(CN)_6^{4-}$
CONCENTRATION NaX / mol dm^{-3}
4
3
2
1
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}

Fig 36



4
3
2
1
0
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
*
ClO_4^-
*
I^-
*
SCN^-
*
$C_6H_5SO_3^-$
Concentration NaX /mol dm^{-3}
Concentration Sodium Sulphate / mol dm^{-3}

Fig. 37



CONCENTRATION NaX / mol dm^{-3}
3
2
1
0
CONCENTRATION SODIUM SULPHATE / mol dm^{-3}
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
* $Cr_2O_7^=$
HCOO$^-$
$CH_3CO_2^-$
$MoO_4^=$
* $WO_4^=$
* IO_3^-

Fig. 38

continuously curved; iodide is similar but of smaller curvature) as sketched in Fig. 39 .

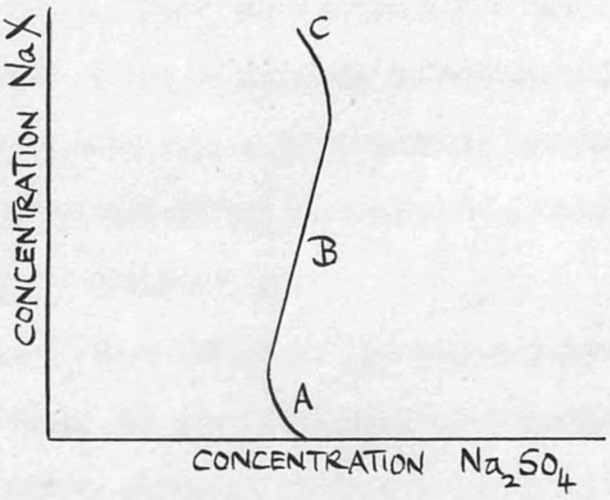


Fig. 39

For many ions no section C is apparent. In the original determinations of Buchner et al. the change of gradient B to C was not detected; at higher concentrations of X^- than section A the line was straight. The gradients used in the evaluation of Buchner's lyotropic numbers were therefore in many cases somewhere between the gradients of sections B and C. It is considered that where all three sections exist section B should be used for the determination of lyotropic number. However high the concentration, solutions of sodium bromide or sodium iodide, for example, will not flocculate a gelatin sol. Br^- and I^- ions are therefore definitely anti-flocculating in that the experimental curve will not intersect the ordinate axis. Section B is therefore used to evaluate lyotropic number, a measure of flocculating power. Throughout the section B concentration range the presence of these ions makes flocculation more difficult since a higher concentration of sulphate is needed. This is a "salting - in" effect. Thus, although the introduction of these ions facilitates the flocculation of gelatin at the extremes of the lyotropic line, they are not singly flocculating.

Consideration must be given where section B of the line is not well - defined. It was found that the transition of section B into section C occurs at an ionic strength (μ) of approximately 3.1 - 3.2 and that the change A to B is completed at an ionic strength not exceeding 2.4 . It was therefore decided that in the above - mentioned graphs the gradient used for the evaluation of lyotropic number should be taken at $\mu = 2.75$. This operationally - defined procedure is applied to sigmoid lines where the linear section B is small, i.e. for $Cr_2O_7^{2-}$ and I^-.

The evaluation of lyotropic numbers has, using the alkali halide crystals as standards for lattice energy, allowed the evaluation of other lattice energies by interpolation of the relationship between hydration enthalpy and lyotropic number.[25] This has been found satisfactory for crystals of the same stoichiometry as that of the alkali halides (M^IX) and in this work the procedure has been extended to the evaluation of the lattice energies of crystals of the type $M^I{}_2Y$, $M^{II}X_2$ and $M^{II}Y$, where M^{II} are the alkaline - earth metals. Consider the following diagram which shows the chloride lyotropic line:

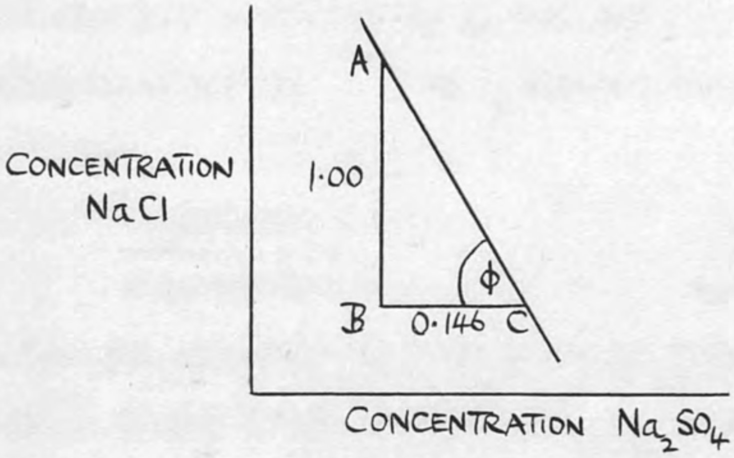


Fig. 40

Since a smaller concentration of sodium sulphate is required to take the place of a given concentration of sodium chloride, clearly the flocculating power of sodium sulphate is the greater. As this work is concerned with mixtures of salts it is appropriate to include in any evaluation of flocculating power some measure of the ionic strength contributions of the two salts. Referring to Fig. 40 we may therefore write:

$$\frac{\text{Flocculating power of } SO_4^{=} \text{ for unit ionic concentration } Na_2SO_4}{\text{Flocculating power of } Cl^{-} \text{ for unit ionic concentration NaCl}} = \frac{1.00}{0.146}$$

where ionic concentration of a salt is the contribution of that salt to the ionic strength ($\frac{1}{2}\Sigma\, cz^2$) of a binary salt mixture, both salts at unit molarity.

For a concentration 1.00 mol dm^{-3} the ionic concentration of a univalent 1:1 electrolyte is 1, that for the type $M^I{}_2Y$ is 3, and for compounds of the type $M^{II}Y$ is 4, assuming complete dissociation. Therefore

$$\frac{\text{Flocculating power of } SO_4^{2-}}{\text{Flocculating power of } Cl^-} = \frac{1.00}{0.146} \times \frac{3}{1}$$

so that the effective cot ϕ value for sulphate is 3.00, for chloride 0.146 . Fixing the lyotropic number, N_Y, of fluoride as 22.0 and that of iodide as 16.7, and using the relationship

$$N_Y = a \cot\phi + b$$

the constants are a = 6.58, b = 17.95 .

Table 10 shows the values of lyotropic number calculated in this way; owing to the different standard values of N used, and the different method of evaluation, these numbers are quite different to the lyotropic numbers of Buchner (see Table 5). It should also be remembered that these (N_Y values) measure the anion flocculating power in the presence of univalent cations.

Graphs of combined ion hydration enthalpy against N_Y are shown in Fig. 41 . These are not quite linear though the error in assuming linearity would only be 2 - 3 kcal mol^{-1} in the interpolation of

TABLE 10

Anion	cot ϕ	Relative flocculating power	Lyotropic number N_Y
Fluoride	+0.615	+ 0.615	22.0
Chloride	+ 0.146	+ 0.146	18.9
Bromide	- 0.0356	- 0.0356	17.7
Iodide	- 0.190	- 0.190	16.7
Sulphate	+ 1.00	+ 3.00	37.7
Chlorate	+ 0.0622	+ 0.0622	18.4
Bromate	+ 0.237	+ 0.237	19.5
Iodate	+ 0.501	+ 0.501	21.2
Perchlorate	- 0.0390	- 0.0390	17.7
Periodate	+ 1.00	+ 1.00	24.5
Formate	+ 0.299	+ 0.299	19.9
Acetate	+ 0.320	+ 0.320	20.0
Nitrate	+ 0.083	+ 0.083	18.5
Nitrite	+ 0.105	+ 0.105	18.6
Tartrate	+ 0.965	+ 2.89	37.0
Citrate	+ 1.60	+ 9.60	81.1
Benzenesulphonate	-0.812	- 0.812	12.6
Cyanide	+ 0.266	+ 0.266	19.7
Azide	- 0.0189	- 0.0189	17.8
Ferrocyanide	+ 1.54	+ 15.4	119
Thiocyanate	- 0.213	- 0.213	16.5
Molybdate	+ 0.633	+ 1.90	30.4
Tungstate	+ 0.702	+ 2.10	31.8
Thiosulphate	+ 0.625	+ 1.87	30.3
Chromate	+ 0.498	+ 1.49	27.8
Dichromate	- 0.306	- 0.918	11.9

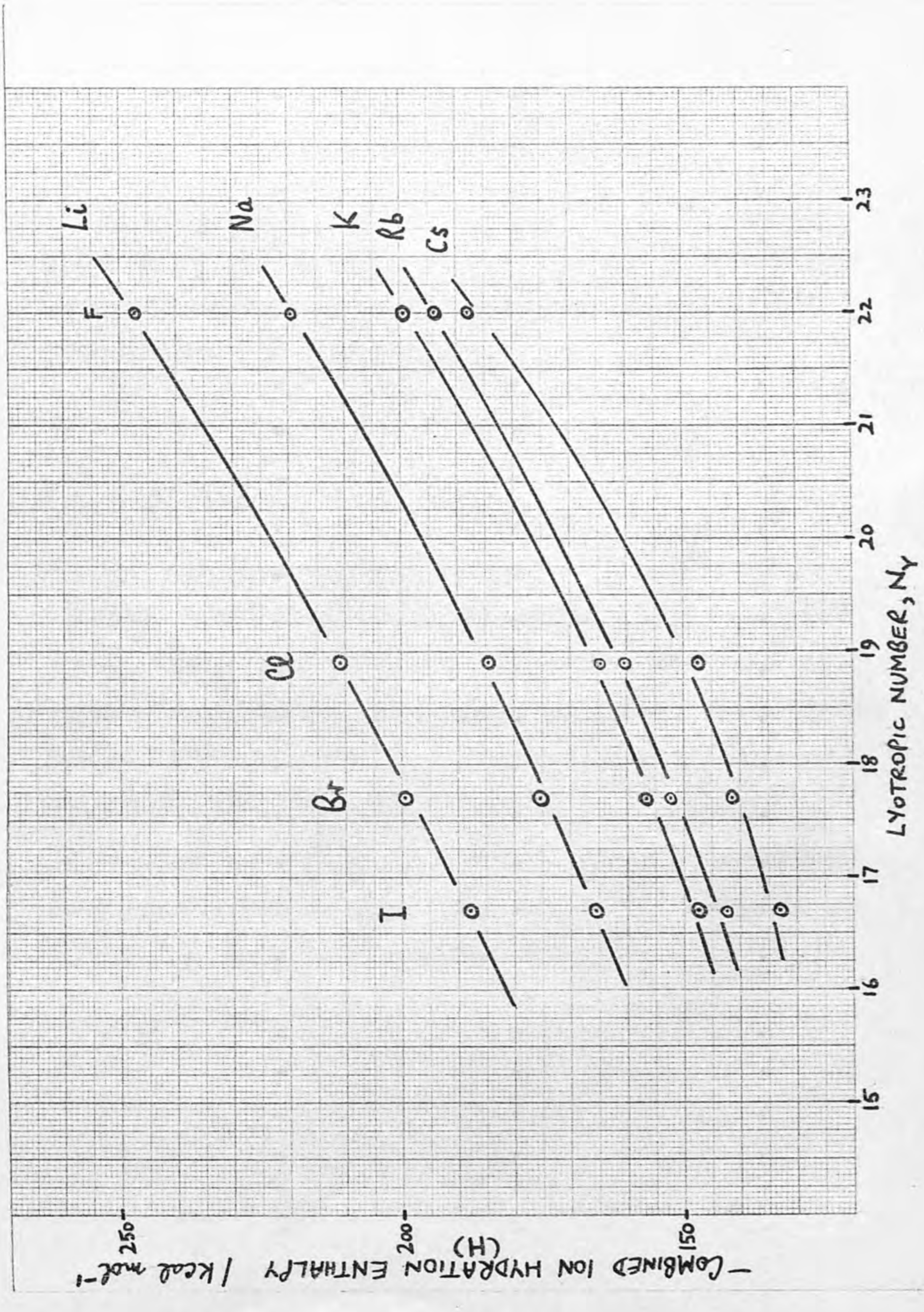

— COMBINED ION HYDRATION ENTHALPY (H) / kcal mol⁻¹
250
200
150
LYOTROPIC NUMBER, N_Y
15
16
17
18
19
20
21
22
23
Li
Na
K
Rb
Cs
F
Cl
Br
I

Fig. 41

combined ion hydration enthalpy for univalent 1:1 salts. However, extrapolation, particularly for salts of the type $M^{I}_{2}Y$, could lead to serious error. Therefore the points were fitted to polynomials of increasing degree:

$$-H = a_o + a_1 N_Y + a_2 N_Y^{2} + \ldots\ldots\, a_n N_Y^{n}$$

where n = 0, 1, 2 and 3.

With only four points for each metal an exact fit to a third degree polynomial could be obtained. There is no reason to suppose that the relation between $-H$ and N_Y is other than monotonic and hence a second degree polynomial was selected as giving the best representation of the results. 'Goodness of fit' was measured in terms of residual mean square (RMS): $\underline{N}^{-1} \sum \left(\left[-H_{calcd} \right] - \left[-H_{exptl} \right] \right)^{2}$ where $\underline{N} = 4$; this was significantly better for the second degree compared with the first degree (linear) polynomial in every case. The coefficients and the RMS values are given in Table 11.

TABLE 11

Polynomial coefficients and RMS values

Metal	n	a_o	a_1	a_2	RMS
Lithium	1	1.6170	11.147		0.696
	2	77.225	3.296	0.20145	0.362
Sodium	1	- 5.5104	10.189		2.435
	2	173.06	- 8.3538	0.47578	0.573
Potassium	1	- 18.270	9.8474		3.370
	2	189.69	- 11.747	0.55409	0.844
Rubidium	1	- 20.615	9.7136		2.404
	2	141.38	- 7.1076	0.43162	0.871
Caesium	1	- 44.793	10.478		11.93
	2	372.94	- 32.900	1.1130	1.742

The data used in the evaluation of -H for the alkali halides, together with the lyotropic numbers, are shown in Table 12. From the lattice enthalpies of the alkali halides (25°C) and their standard enthalpies of solution the corresponding combined ion hydration enthalpies were found from the relationship:

$$\Delta H_L^o = -H + \Delta H_s^o \qquad \text{EQUATION 11}$$

where ΔH_L^o is the lattice enthalpy at 298 K,

H is the combined ion hydration enthalpy at 298 K,

ΔH_s^o is the standard enthalpy of solution.

TABLE 12

Values in kcal mol^{-1}

Compound	ΔH_L^o	ΔH_s^o	$- H$	Lyotropic number, N_Y
Li F	248.4	+ 1.09	247.31	22.0
Li Cl	202.0	- 8.88	210.88	18.9
Li Br	187.9	-11.73	199.63	17.7
Li I	172.9	-15.13	188.03	16.7
Na F	219.7	+ 0.06	219.64	
Na Cl	185.3	+ 0.93	184.37	
Na Br	175.3	- 0.15	175.45	
Na I	163.9	- 1.81	165.71	
K F	195.3	- 4.24	199.54	
K Cl	168.8	+ 4.12	164.68	
K Br	161.6	+ 4.79	156.81	
K I	152.3	+ 4.90	147.4	
Rb F	187.7	- 6.32	194.02	
Rb Cl	164.3	+ 4.01	160.29	
Rb Br	157.5	+ 5.23	152.27	
Rb I	148.6	+ 6.20	142.4	
Cs F	179.0	- 9.00	188.0	
Cs Cl	151.7	+ 4.30	147.4	
Cs Br	147.6	+ 6.20	141.4	
Cs I	140.9	+ 7.90	133.0	

Values of ΔH_L^o were calculated from Born - Haber energy values of Huheey[62] which are in good agreement with Cubicciotti values[63]. Values of ΔH_s^o are from N.B.S. circular 500[35].

It is now possible to find H for an alkali metal salt if the anion lyotropic number is known. Interpolated values will be more reliable than extrapolated values.

Table 13 gives the corresponding data for the alkaline earth halides. Standard enthalpies of solution were taken from N.B.S. Technical Note 270-6[64] with the exception of MgF_2 and SrF_2. The values for magnesium and strontium fluorides were calculated using the relationship

$$\Delta H_s^{\circ} = \Delta H_f^{\circ}\left[M^{++}, aq\right] + 2\,\Delta H_f^{\circ}\left[F^{-}, aq\right] - \Delta H_f^{\circ}\left[MF_2, c\right]$$

and taking necessary data from references 64 and 65.

Graphs of lyotropic number against combined ion hydration enthalpy for the alkaline earth halides are shown in Fig. 42. From these it is now possible to find other values of hydration enthalpy if the appropriate lyotropic numbers are known. Here the hydration enthalpies of compounds of the same stoichiometry as the alkaline earth halides can be obtained by interpolation or extrapolation. If values for compounds of the type $M^{II}Y^{II}$ are required then the previous procedure is applied as follows:

$$\frac{\text{Flocculating power of } Y^{II} \text{ in the presence of } M^{II} \text{ ions}}{\text{Flocculating power of } Cl^{-} \text{ in the presence of } M^{II} \text{ ions}} = \frac{1.00}{0.146} \times \frac{4}{3}$$

Using the same lyotropic numbers for the halide ions as before the sulphate ion now has a lyotropic number of 26.7. Other values are

TABLE 13

Values in kcal mol^{-1}

Compound	ΔH_L^o †	ΔH_s^o	-H	N_Y
$Mg F_2$	698.8	- 3.52	702.3	22.0
$Mg Cl_2$	596.8	-38.2	635.0	18.9
$Mg Br_2$	572.8	-44.38	617.2	17.7
$Mg I_2$	546.8	-50.96	597.8	16.7
$Ca F_2$	623.8	+ 2.76	621.0	
$Ca Cl_2$	531.8	-19.44	551.2	
$Ca Br_2$	508.8	-24.64	533.4	
$Ca I_2$	486.8	-28.62	515.4	
$Sr F_2$	591.8	- 0.19	592.0	
$Sr Cl_2$	507.8	-12.25	520.0	
$Sr Br_2$	486.8	-17.05	503.8	
$Sr I_2$	461.8	-23.43	485.2	
$Ba F_2$	556.8	+ 1.00	555.8	
$Ba Cl_2$	483.8	- 3.20	487.0	
$Ba Br_2$	464.8	- 5.60	470.4	
$Ba I_2$	439.8	-10.98	450.8	

† The lattice enthalpy values were calculated (using $\Delta H_L^o = U + 3RT$) from a self-consistent set of lattice energy values (298 K) evaluated, using the Born - Haber cycle, by Finch and Gardner[66]. These are in good agreement with the values of Brackett and Brackett[67] and with many values calculated by Morris[68].

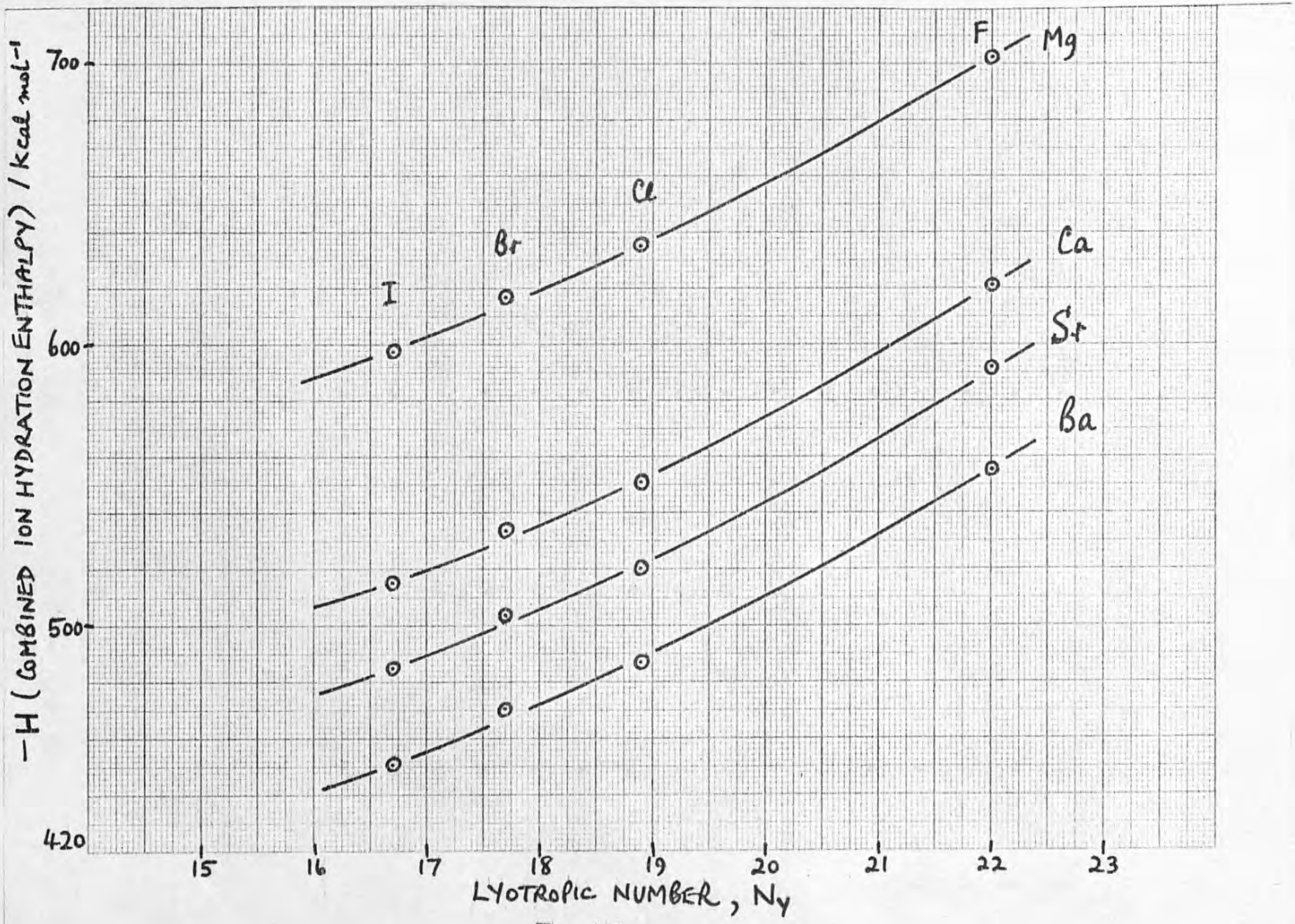

700
600
500
420
15
16
17
18
19
20
21
22
23
−H (COMBINED ION HYDRATION ENTHALPY) / Kcal mol⁻¹
LYOTROPIC NUMBER , Ny
I
Br
Cl
F
Mg
Ca
Sr
Ba

Fig 42

given in Table 14. All univalent anions will have the same lyotropic

TABLE 14

Anion	Lyotropic number, N_Y
Tartrate	26.4
Citrate	39.0
Ferrocyanide	51.7
Molybdate	23.5
Tungstate	24.1
Thiosulphate	23.4
Chromate	22.3
Dichromate	15.3
Sulphate	26.7

numbers as before.

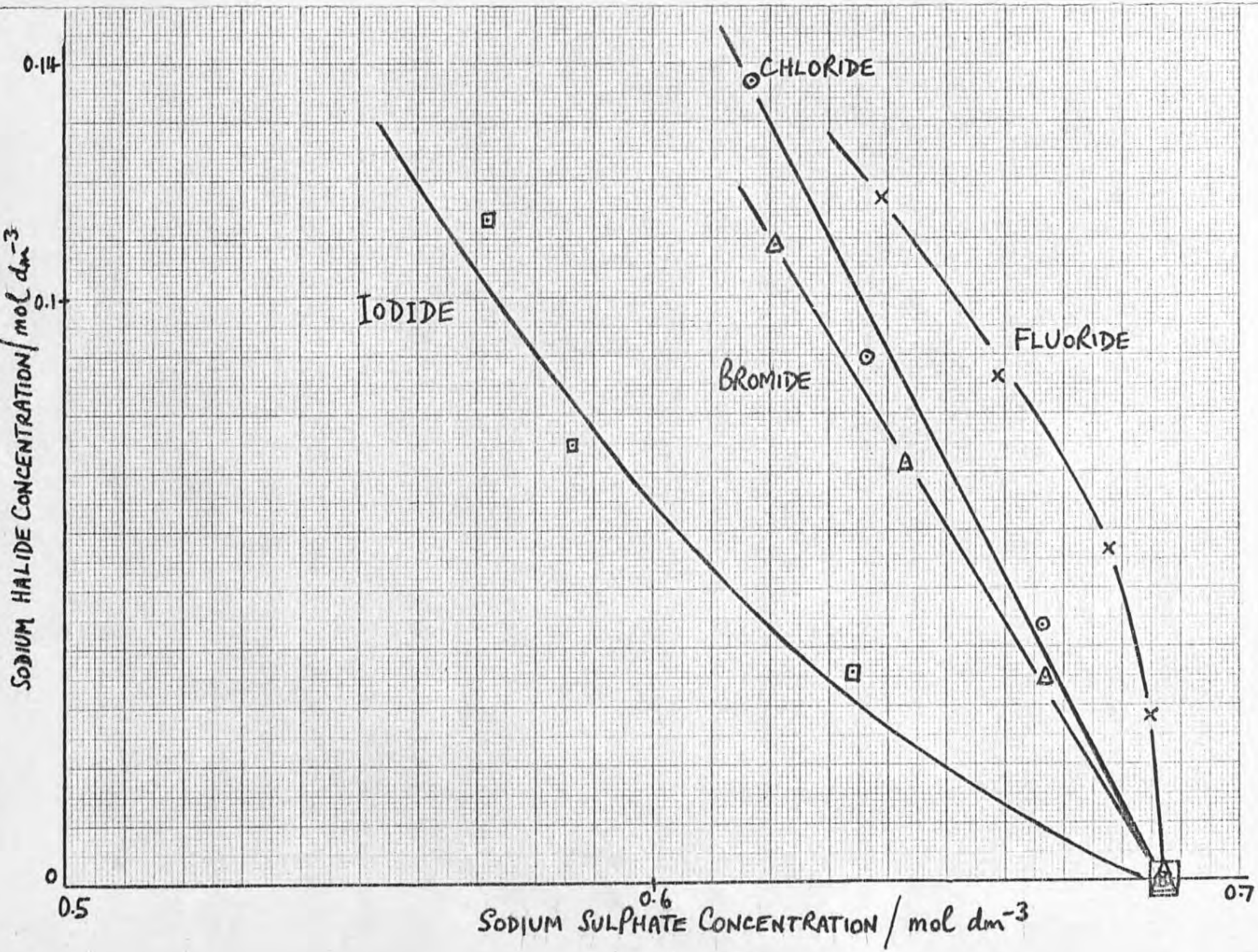
RMS values again indicate that second degree polynomials should be used (see Table 15):

TABLE 15

Polynomial coefficients and RMS values

Metal	n	a_c	a_1	a_2	RMS
Magnesium	1	267.029	+ 19.7102		6.929
	2	557.4705	- 10.4493	+ 0.773865	2.00
Calcium	1	178.317	+ 20.0230		10.825
	2	576.975	- 21.3739	+ 1.06220	1.54
Strontium	1	144.687	+ 20.216		15.62
	2	607.549	- 27.8480	+ 1.23327	3.11
Barium	1	118.427	+ 19.791		10.04
	2	463.324	- 16.02289	+ 0.918960	1.00

The results of flocculation experiments at low concentrations are shown in Fig. 43 . These show clearly that the relative effect of the halide ions at concentrations less than 0.1 mol dm^{-3} is the reverse of their effect at concentrations used for the evaluation of lyotropic number. The reason for this, and for the existence of section C of the lyotropic lines, is not clear. This type of lyotropic reversal has also been reported for the precipitation of collagen fibrils from solutions of electrolytes at low ionic strengths[69]. The lyotropic curves do indicate that low concentrations of the larger ions cause gelatin sols to be more readily flocculated by sodium sulphate, and since these larger ions do not themselves cause flocculation they must be assisting in some other way. It may be that, at low concentrations, the easier flocculation of the gelatin by the larger iodide ion (as compared to the fluoride ion) is due to a smaller number of water molecules in the gelatin - sodium iodide mixtures (than in the gelatin - sodium fluoride mixtures). One might expect a solution of sodium iodide of given concentration (mol dm^{-3}) to contain a smaller number of water molecules than a solution of sodium fluoride of the same concentration because iodide ions themselves take up more space and have a smaller power of electrostriction of water molecules than fluoride ions. The increasing partial molar refraction values of sodium fluoride, sodium chloride, sodium bromide and sodium iodide in aqueous solution[70] confirm this. If



SODIUM HALIDE CONCENTRATION / mol dm^{-3}
0.14
0.1
0
0.5
0.6
0.7
SODIUM SULPHATE CONCENTRATION / mol dm^{-3}
CHLORIDE
FLUORIDE
BROMIDE
IODIDE

Fig. 43

there is a smaller number of water molecules in an iodide - gelatin mixture then a smaller concentration of sodium sulphate is needed to desolvate the gelatin.

Along section B the sodium iodide has a "salting-in" effect. Bockris[55] believes that salting-in is due to one of two influences: (a) the substance being flocculated (gelatin) contains groups of greater dipole than in water; (b) dispersion forces operate between the added ions and the non-electrolyte. (a) is not relevant here since some ions do flocculate gelatin. (b) is a possible explanation since the larger halide ions may reasonably be expected to form stronger dispersion forces with the large gelatin aggregates than would the smaller halides because of their larger polarizability (Bockris quotes alkyl ammonium salts as having good salting-in properties because of the large cation). In addition the larger ions would have smaller primary hydration spheres; this would enable the ion to associate more freely with gelatin aggregates. It has been pointed out[72] that anti-flocculating ions, such as perchlorate and thiocyanate, dissolve in water and in organic solvents. The latter property would indicate a degree of covalency caused by the ability of the larger anion electron cloud to deform. At even higher concentrations (section C) this salting-in effect may be reduced due to a degree of ion-pairing[76] of the added sodium salt, e.g. iodide, so that less sodium sulphate is required for flocculation. The sulphate would also be partly ion-paired, but there could be sufficient free ions for flocculation, and $NaSO_4^-$ pairs might themselves cause flocculation.

In general, decrease in charge and increase in ion radius (r) causes a decrease in flocculating power. As the thermochemical radius increases within the halate series so the flocculating power (measured by N_Y) decreases. Likewise there is a decrease of flocculating power as the Pauling radius increases within the halide series. It is interesting that the decrease in thermochemical radius in the series $ClO_3^- \longrightarrow IO_3^-$ is in agreement with the lyotropic properties of the ions, whereas most chemists would intuitively expect the halate ion radius to increase through the series. Formate and acetate ions have similar radii and similar lyotropic numbers. The more highly charged ions such as tartrate and citrate have good flocculating power. It is reasonable therefore to try to connect flocculating power with ionic potential[77], but this is not easy because of the extreme difficulty of assigning consistent radii for a large number of ions. Fig. 44 shows a graph of 1/r against lyotropic number for the halide ions, a restricted group for which ion radius is consistent. Fig. 45 is a similar graph for the halate ions. Both lines are gentle curves and not far removed from linearity. For the halide ions much depends on the choice of fluoride ion radius; Table 16 shows how the magnitude of ion radius depends on the source.

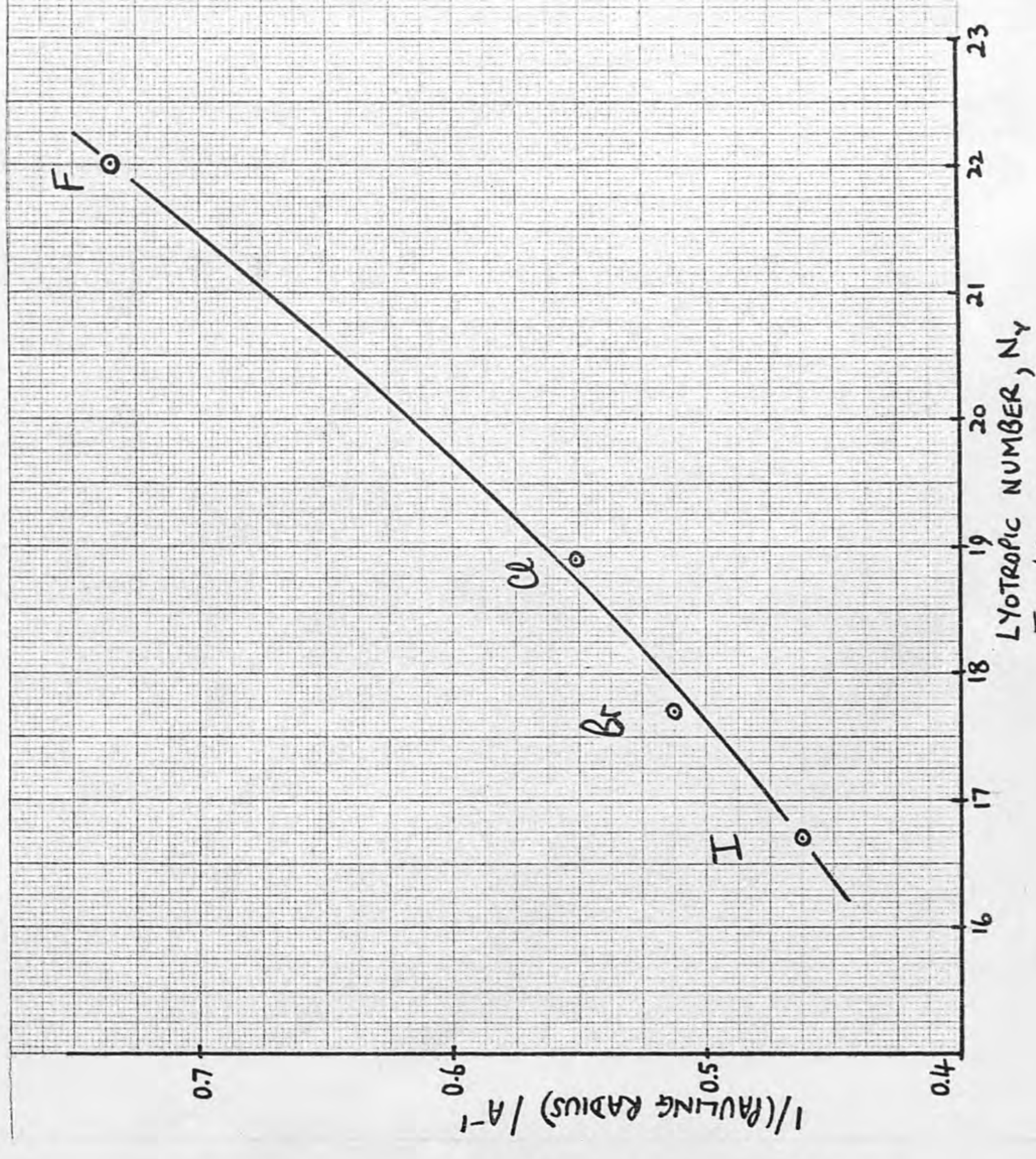
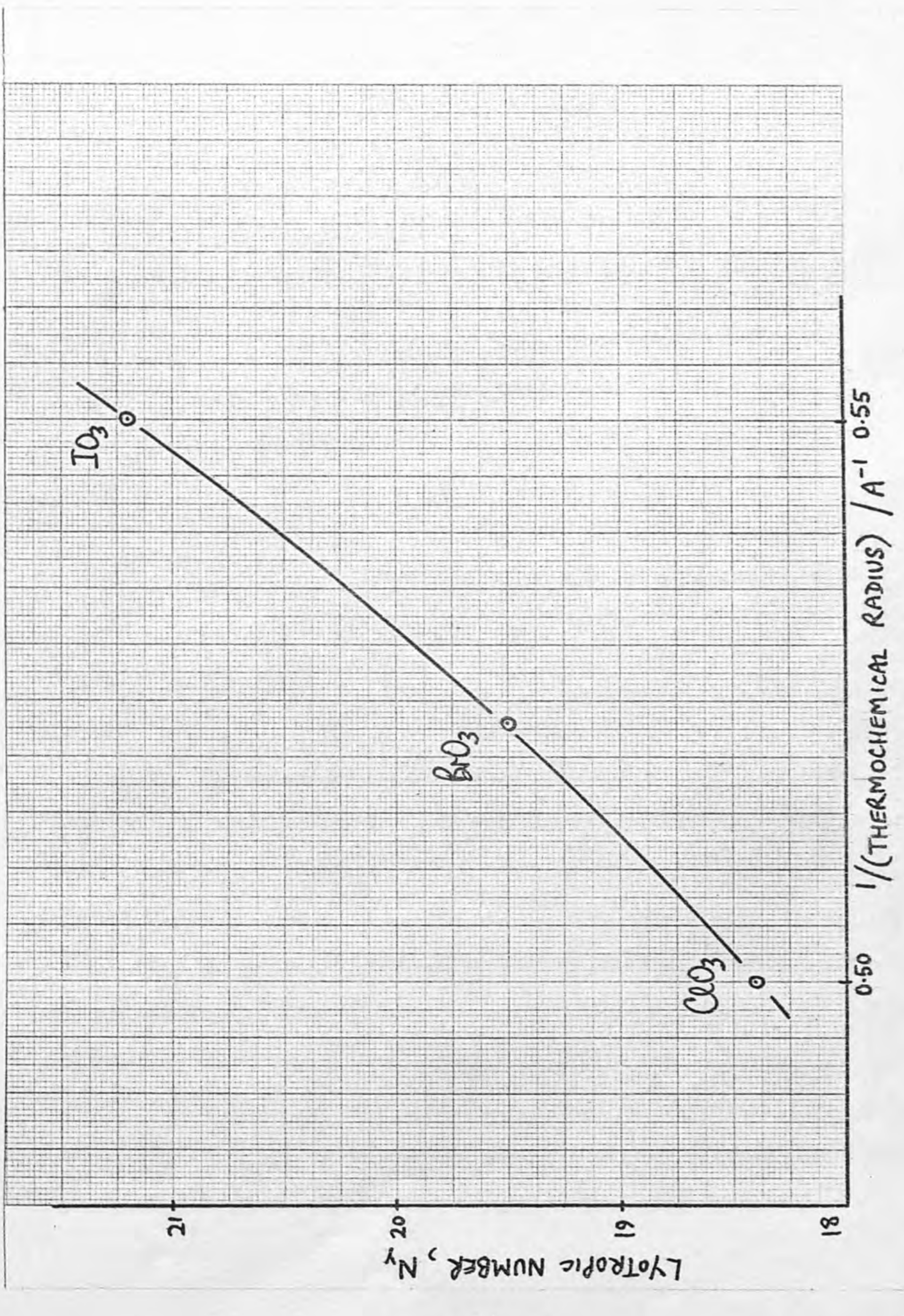

F
Cl
Br
I
0.4
0.5
0.6
0.7
1/(PAULING RADIUS) /A^{-1}
16
17
18
19
20
21
22
23
LYOTROPIC NUMBER, N_Y

Fig. 44



IO_3
BrO_3
ClO_3
21
20
19
18
LYOTROPIC NUMBER, N_y
0·50
0·55
1/(THERMOCHEMICAL RADIUS) /A^{-1}

Fig. 4-5

TABLE 16

Ion	Ion radius / A		
	Pauling[57]	Electron density maps[24]	Goldschmidt[24]
Li^+	0.60	0.93	0.78
Na^+	0.95	1.17	0.98
K^+	1.33	1.49	1.33
Rb^+	1.48	1.64	1.49
Cs^+	1.69	1.83	1.65
F^-	1.36	1.16	1.33
Cl^-	1.81	1.64	1.81
Br^-	1.95	1.80	1.96
I^-	2.16	2.04	2.20

During the last 25 years work in the field of lyotropy has been scant and has consisted of attempts to relate the lyotropic series to other properties. The work of Meyerstein and Treinin has been already mentioned in the Introduction. Others[71-75] have investigated the effects of flocculating and anti-flocculating ions on the osmotic pressure of alcohol - water solutions and on the vapour pressure of aqueous solutions of acetone; they also note that anti-flocculating compounds show a tendency to dissolve in organic solvents as well as in water. The results are consistent with a correlation between loss of flocculating power and an increase in structure-breaking tendency and an increase in the deformability of the ion. Thus the increase in the osmotic pressure of such solutions caused by anti-flocculating ions is in line with an increase in the structural temperature caused by these ions. More recently[78] the order of some ions in the lyotropic series has been confirmed and the importance of protein dehydration during flocculation re-iterated.

(b) LATTICE ENTHALPIES FROM LYOTROPIC NUMBERS

Section 1. Comparison of some present values with values from other sources

The procedure used for finding the combined ion hydration enthalpy, H, of a particular Group I or Group II salt may be summarised as follows. The appropriate anion lyotropic number (N_Y) was taken from Table 10 or Table 14. Table 10 gives N_Y values of anions in the presence of univalent cations (Group I salts); Table 14 gives N_Y values of anions in the presence of bivalent cations (Group II salts). Only univalent anions have the same lyotropic numbers in both cases (these numbers are given in Table 10). The combined ion hydration enthalpy was then found from the appropriate relationship connecting -H and N_Y. Fig. 41 and Fig. 42 were used to interpolate -H values and the following equations were used for extrapolation:

LITHIUM	$-H = 77.22 + 3.296\ N_Y + 0.2014\ N_Y^2$	EQUATION 21
SODIUM	$-H = 173.1 - 8.354\ N_Y + 0.4758\ N_Y^2$	EQUATION 22
POTASSIUM	$-H = 189.7 - 11.75\ N_Y + 0.5541\ N_Y^2$	EQUATION 23
RUBIDIUM	$-H = 141.4 - 7.108\ N_Y + 0.4316\ N_Y^2$	EQUATION 24
CAESIUM	$-H = 372.9 - 32.90\ N_Y + 1.113\ N_Y^2$	EQUATION 25
MAGNESIUM	$-H = 557.5 - 10.45\ N_Y + 0.7739\ N_Y^2$	EQUATION 26
CALCIUM	$-H = 577.0 - 21.37\ N_Y + 1.062\ N_Y^2$	EQUATION 27
STRONTIUM	$-H = 607.5 - 27.85\ N_Y + 1.233\ N_Y^2$	EQUATION 28
BARIUM	$-H = 463.3 - 16.02\ N_Y + 0.919\ N_Y^2$	EQUATION 29

As has been previously pointed out, second degree polynomials give the best representation of the results (see p. 84 and Tables 11 and 15).

The lattice enthalpies (298 K) were then found using equation 11:

$$\Delta H^{o}_{L} = -H + \Delta H^{o}_{s}$$

ΔH_s values were mostly enthalpies to infinite dilution. An asterisk indicates that an enthalpy of solution to MX. nH_2O (n is the mole ratio water to MX) has been used. The value of n was not less than 220. The effect of using these latter values is a change in the lattice enthalpy of only a small fraction of 1%.

Lattice enthalpy values for Group I and Group II azides and cyanides are shown in Tables 17 and 18 respectively, with the corresponding lattice energies for comparison with other calculated values. It can be seen that values from the present work are comparable with other calculated values.

In Sections 2 and 3 present values of lattice enthalpy for Group I and Group II salts respectively are given. A double asterisk indicates that the value was not previously available.

TABLE 17

Alkali metal azides and cyanides

(values in kcal mol^{-1})

Compound	-H	ΔH_s^o	ΔH_L^o	U	Yatsimirskii[16]	Ladd & Lee[79]	Gray & Waddington[13]
Li N_3	199.5	- 2.60 †	197	196			194
Na N_3	175.0	+ 3.17 †	178	177			175
K N_3	156.5	+ 5.82 †	162	161			157
Rb N_3	152.0	+ 6.70 †	159	158			150
Cs N_3	140.5	+ 8.70 †	149	148			143
Li CN	220.0	- 8.9 ††	211	210			
Na CN	193.0	+ 1.2 ††	194	193	185	178	
K CN	173.5	+ 7.0 ††	180	179	167	161	
Rb CN	169.0	+ 6.6 ††	176	175			
Cs CN	157.5	+ 7.4 ††	165	164			

† Values from Gray & Waddington[80] (*)
†† Values from Ladd[81]

TABLE 18

Alkaline earth azides and cyanides

(values in kcal mol^{-1} at 298 K)

Compound	-H	ΔH_s^o	ΔH_L^o	U	Gray & Waddington[13]	Yatsimirskii[16]
$Ca(N_3)_2$	532	- 1.72 †	530	528	517	
$Sr(N_3)_2$	502	- 1.03 †	501	499	494	
$Ca(CN)_2$	568	-12.8 ††	555	553		542
$Ba(CN)_2$	504	- 2.8 ††	501	499		489

† Calculated using $\Delta H_s^o = \Delta H_f^o\left[M^{2+}, aq\right] + 2\,\Delta H_f^o\left[N_3^-, aq\right] - \Delta H_f^o\left[M(N_3)_2, c\right]$

Data from ref. 64 & 82

†† Data from ref. 64

Section 2 Group I salts

(values in kcal mol^{-1} at 298 K)

Chlorates

Salt	− H	ΔH_s^o [35]	ΔH_L^o
Sodium	180.5	+ 4.95	185
Potassium	161.5	+ 9.96	171
Rubidium	157.0	+11.4	168
Caesium	144.0	+13.26	157

Bromates

Salt	− H	ΔH_s^o [83]	ΔH_L^o
** Lithium	217.5	+ 0.34	218
** Sodium	191.0	+ 6.35	197
** Potassium	171.5	+ 9.70	181
** Rubidium	167.0	+11.69	179
** Caesium	155.0	+12.00	167

Iodates

Salt	− H	ΔH_s^o	ΔH_L^o
** Lithium	237.5	+ 1.59 †	239
** Sodium	209.5	+ 4.83 ††	214
Potassium	189.5	+ 6.63 ††	196
** Rubidium	185.0	+11.2 †††	196
** Caesium	176.0	+12.5 †††	188

† see ref. 84

†† see ref. 85

††† calculated using $\Delta H_s^o = \Delta H_f^o\left[M^+,aq\right] + \Delta H_f^o\left[IO_3^-,aq\right] - \Delta H_f^o\left[MIO_3,c\right]$

Data from ref. 35, 82, 86.

Nitrates

Salt	$-H$	ΔH^{o}_{s} [35]	ΔH^{o}_{L}
Lithium	207.0	-0.65	206
Sodium	181.5	$+4.89$	186
Potassium	162.5	$+8.34$	171
Rubidium	158.0	$+8.74$	167
Caesium	146.0	$+9.51$	156

Nitrites

Salt	$-H$	ΔH^{o}_{s} [35]	ΔH^{o}_{L}
Sodium	182.5	$+3.3$	186
Potassium	163.0	$+3.3$ *	166

Thiocyanates

Salt	$-H$	ΔH^{o}_{s} [35]	ΔH^{o}_{L}
Sodium	164.0	$+1.63$	166
Potassium	147.0	$+5.82$	153

Formates

Salt	$-H$	ΔH^{o}_{s} [35]	ΔH^{o}_{L}
Sodium	195.0	$+0.11$ *	195
Potassium	175.5	$+0.30$	176

Acetates

Salt	$-H$	ΔH^{o}_{s} [35]	ΔH^{o}_{L}
Sodium	196.0	-4.32	192
Potassium	176.5	-3.68	173

Molybdates

Salt	− H	ΔH^{o}_{s} †	ΔH^{o}_{L}
** Lithium	363.4	− 8.1	355
** Sodium	359.3	− 2.18	357
** Potassium	344.0	− 1.11	343
** Rubidium	324.0	+ 0.94	325

† calculated from $2\,\Delta H^{o}_{f}\left[M^{+},aq\right] + \Delta H^{o}_{f}\left[MoO_4^{-},aq\right] - \Delta H^{o}_{f}\left[M_2\,MoO_4,c\right] = \Delta H^{o}_{s}$

Data from ref. 35, 87, 88 .

Tungstates

Salt	− H	ΔH^{o}_{s}	ΔH^{o}_{L}
** Sodium	388.4	+ 14.1 [35]	402
Rubidium	351.9	+ 1.1 †	353

† calculated from $\Delta H^{o}_{s} = 2\,\Delta H^{o}_{f}\left[M^{+},aq\right] + \Delta H^{o}_{f}\left[WO_4^{2-},aq\right] - \Delta H^{o}_{f}\left[M_2WO_4,c\right]$

Data from ref.35,88,89.

Chromates

Salt	− H	ΔH^{o}_{s}	ΔH^{o}_{L}
** Lithium	324.7	− 10.8 † *	314
Sodium	308.9	− 3.00 †† *	306
Potassium	291.1	+ 4.49 ††	296
** Rubidium	277.0	+ 5.9 † *	283

† ref. 90 †† ref. 35

Perchlorates

Salt	- H	ΔH_s^o [91]	ΔH_L^o
** Lithium	198	- 6.35	192
Sodium	174	+ 3.32	177
Potassium	156	+12.20	168
Rubidium	151	+13.56	165
Caesium	140	+13.25	153

Periodates

Salt	- H	ΔH_s^o [92]	ΔH_L^o
** Sodium	254	+ 9.00	263

Section 3 Group II salts

(values in kcal mol^{-1} at 298 K)

Chlorates, bromates, iodates

Salt	- H	ΔH_s^o	ΔH_L^o
** Calcium bromate	564	+ 1.4 [64] *	565
** Calcium iodate	602	+ 5.5 †	607
** Strontium iodate	571	+ 8.75 †	580
Barium chlorate	479	+ 6.1 [64] *	485
** Barium bromate	500	+11.44 [64] *	511
** Barium iodate	537	+11.2 [64]	548

† calculated as for calcium azide (Table 18) using the same sources.

Perchlorates

Salt	- H	ΔH_s^o [64]	ΔH_L^o
** Magnesium	614	-37.43	577
Calcium	530	-15.47	515
Strontium	501	- 9.96	491
Barium	467	+ 1.00 *	468

Nitrates

Salt	- H	ΔH_s^o [64]	ΔH_L^o
** Magnesium	628	-21.73	606
Calcium	544	- 4.58	539
Strontium	514	+ 4.23	518
Barium	481	+ 9.49	490

Nitrites

Salt	- H	ΔH_s^o [64]	ΔH_L^o
Calcium	546	- 2.3 *	544
Strontium	516	+ 1.7 *	518
Barium	483	+ 5.1 *	488

Formates

Salt	- H	ΔH_s^o	ΔH_L^o
Calcium	572	- 1.10 [64] *	571
Strontium	542	- 0.87 †	541
Barium	508	+ 2.0 [64] *	510

† calculated as for calcium azide (Table 18) using the same sources.

Acetates

Salt	$-H$	ΔH_s^o [64]	ΔH_L^o
Calcium	574	- 8.46	566
Strontium	544	- 5.90	538
Barium	510	- 6.02	504

Tungstates

Salt	$-H$	ΔH_s^o	ΔH_L^o
** Magnesium	755	- 2.38 †	753
** Calcium	679	+ 6.4 [64]	685
** Strontium	652.5	+ 4.35 †	657
** Barium	611	+ 3.4 †	614

† calculated as for calcium azide (Table 18) using ref. 64 and 89.

Molybdates

Salt	$-H$	ΔH_s^o	ΔH_L^o
** Magnesium	739	-15.07 †	724
** Calcium	662	+ 0.2 [64]	662
** Strontium	634.5	+ 1.25 †	636
** Barium	594.5	+ 3.2 †	598

† calculated as for calcium azide (Table 18) using ref. 64 and 87.

Chromates

Salt	$-H$	ΔH_s^o	ΔH_L^o
** Magnesium	712.2	- 2.9 [64]	709
Calcium	628.5	- 0.8 †	628
** Strontium	600.0	+ 1.2 [90]	601
Barium	563.3	+ 6.4 [90]	570

† estimated

Sulphates

Salt	- H	ΔH^{o}_{s} [64]	ΔH^{o}_{L}
** Magnesium	830.5	-21.8	809
Calcium	763.5	- 6.42	757
Strontium	742.5	- 0.47	742
Barium	690.0	+ 6.28	696

Section 4. The Application of Lyotropic Methods to the Determination of Lattice Enthalpies

This method of determining lattice enthalpies involves two stages: (1) the experimental determination of lyotropic numbers, and (2) the use of alkali halide lattice energies and standard enthalpies of solution, which are accurately known, to find the ion hydration enthalpies of other crystals and hence their lattice enthalpies provided that the corresponding standard enthalpies of solution are known.

The experimental determinations in (1) which have been carried out are considered much more precise than the original determinations of Buchner et al. The affects of temperature and pH are known and are not significant, but it is essential to use reproducible gelatin indicator; agar is less suitable. Two factors may reduce the accuracy of the lyotropic number determinations: (a) pronounced and continuous curvature in the lyotropic lines, which, though rarely, makes gradient determination more difficult, and (b) a degree of insolubility in the compound under investigation which allows only a limited range of concentrations to be examined.

Regarding (2) values of combined ion hydration enthalpy can be readily interpolated on the halide combined ion hydration enthalpy - lyotropic number curves. For extrapolation the values should be found by calculation. The greater the amount of extrapolation the greater any error is likely to be; it is considered that with the amount of extrapolation attempted here the error due to this procedure is not likely to be more than 1 - 2%.

Thus, for soluble salts, the lyotropic method can be readily applied to the determination of lattice enthalpies. Values are comparable with those found by other methods (see, for example, reference 93) and no knowledge of structural parameters is needed. In this work about 100 values of lattice enthalpy have been found; approximately 35 were not previously available. For the uses of such values see references 2 and 94.

APPENDIX 1

Determination of lyotropic lines at 25 °C

In all cases the standard procedure given in EXPERIMENTAL, Section 4, was used. Titres are all in cm^3, concentrations in mol dm^{-3}, and pH values are for end-point gelatin - salt mixtures.

A 1.00 M solution has a concentration 1.00 mol dm^{-3}.

CHLORIDE

5.00 M solution used

pH: 5.0

Mixture	Titre	Sodium chloride concentration	Sodium sulphate concentration
2	0.40	3.46	0.0766
3	0.67	3.10	0.125
4	0.98	2.76	0.177
5	1.32	2.42	0.230
6	1.57	2.13	0.268
7	1.87	1.84	0.310
8	2.17	1.57	0.350
9	2.45	1.31	0.385
10	2.78	1.06	0.425
11	3.12	0.825	0.463
12	3.55	0.597	0.509
13	3.90	0.388	0.544
14	4.60	0.184	0.608
15	5.50	0.000	0.683

BROMIDE

6.00 M solution used

pH: 5.4

Mixture	Titre	Sodium bromide concentration	Sodium sulphate concentration
1	4.46	3.12	0.597
2	4.60	2.87	0.609
3	4.68	2.63	0.616
4	4.63	2.42	0.611
5	4.70	2.19	0.617
6	4.60	1.98	0.609
7	4.58	1.77	0.607
8	4.48	1.56	0.598
9	4.42	1.34	0.593
10	4.28	1.13	0.580
11	4.25	0.906	0.577
12	4.10	0.687	0.564
13	4.25	0.453	0.577
14	4.60	0.220	0.609
15	5.50	0.000	0.682

IODIDE

8.00 M solution used

pH: 5.8

Mixture	Titre	Sodium iodide concentration	Sodium sulphate concentration
1	7.50	3.39	0.818
2	7.48	3.15	0.817
3	7.42	2.92	0.813
4	7.38	2.68	0.811
5	7.17	2.47	0.798
6	6.98	2.25	0.786
7	6.70	2.04	0.768
8	6.40	1.82	0.748
9	5.95	1.60	0.717
10	5.48	1.38	0.680
11	5.00	1.14	0.643
12	4.45	0.892	0.595
13	3.80	0.625	0.535
14	3.70	0.315	0.524
15	5.50	0.000	0.683

FLUORIDE

0.820 solution used

pH: 6.4

Mixture	Titre	Sodium fluoride concentration	Sodium sulphate concentration
1	2.78	0.487	0.425
3	3.25	0.401	0.477
5	3.70	0.323	0.524
7	4.15	0.250	0.568
9	4.65	0.180	0.614
10	4.75	0.149	0.621
11	4.95	0.117	0.639
12	5.20	0.0866	0.659
13	5.45	0.0567	0.678
14	5.53	0.0282	0.685
15	5.55	0.000	0.686

CHLORATE

6.00 M solution used

pH: 7.7

Mixture	Titre	Sodium chlorate concentration	Sodium sulphate concentration
1	1.92	3.85	0.316
2	2.42	3.42	0.381
3	2.77	3.06	0.424
4	3.10	2.73	0.461
5	3.33	2.43	0.486
6	3.62	2.14	0.516
7	3.77	1.88	0.531
8	4.00	1.61	0.553
9	4.08	1.37	0.561
10	4.30	1.13	0.582
11	4.40	0.895	0.591
12	4.20	0.682	0.573
13	4.45	0.446	0.595
14	4.85	0.217	0.630
15	5.50	0.000	0.683

BROMATE

1.50 M solution used

pH: 5.4

Mixture	Titre	Sodium bromate concentration	Sodium sulphate concentration
1	2.90	0.882	0.438
3	3.17	0.739	0.469
5	3.55	0.597	0.509
7	3.82	0.468	0.536
9	4.15	0.342	0.568
11	4.45	0.223	0.595
13	4.95	0.107	0.639
15	5.50	0.000	0.683

IODATE

0.328 M solution used

pH: 5.4

Mixture	Titre	Sodium iodate concentration	Sodium sulphate concentration
1	4.30	0.173	0.582
3	4.45	0.146	0.596
5	4.58	0.121	0.607
7	4.73	0.0955	0.619
9	4.88	0.0709	0.633
11	5.03	0.0467	0.645
13	5.30	0.0230	0.667
15	5.50	0.000	0.683

PERCHLORATE

5.88 M solution used

pH: 5.5

Mixture	Titre	Sodium perchlorate concentration	Sodium sulphate concentration
1	2.43	3.60	0.382
2	2.55	3.31	0.398
3	2.65	3.03	0.410
4	2.75	2.75	0.421
5	2.73	2.51	0.418
6	2.80	2.24	0.427
7	2.78	2.00	0.425
8	2.72	1.76	0.418
9	2.65	1.51	0.410
10	2.55	1.27	0.398
11	2.45	1.03	0.385
12	2.40	0.773	0.379
13	2.35	0.518	0.372
14	2.75	0.250	0.422
15	5.50	0.000	0.683

PERIODATE

0.400 solution used

pH: 4.9

Mixture	Titre	Sodium periodate concentration	Sodium sulphate concentration
1	1.57	0.265	0.267
2	1.73	0.242	0.290
3	1.87	0.221	0.310
4	2.03	0.199	0.331
5	2.23	0.178	0.357
6	2.38	0.158	0.376
7	2.60	0.138	0.403
8	2.80	0.118	0.427
9	3.10	0.0990	0.461
10	3.37	0.0810	0.490
11	3.63	0.0630	0.517
12	3.95	0.0460	0.549
13	4.33	0.0300	0.584
14	4.70	0.0150	0.617
15	5.50	0.000	0.683

FORMATE

4.00 M solution used

pH: 7.0

Mixture	Titre	Sodium formate concentration	Sodium sulphate concentration
6	0.67	1.86	0.125
7	1.18	1.57	0.208
8	1.77	1.30	0.296
9	2.30	1.06	0.366
10	2.80	0.847	0.427
11	3.30	0.650	0.483
12	3.87	0.466	0.542
13	4.40	0.298	0.591
14	5.10	0.142	0.651
15	5.50	0.000	0.682

ACETATE

4.00 M solution used
pH: 7.5

Mixture	Titre	Sodium acetate concentration	Sodium sulphate concentration
6	0.40	1.91	0.0766
7	0.97	1.60	0.176
8	1.57	1.32	0.268
9	2.17	1.07	0.350
10	2.72	0.854	0.418
11	3.25	0.652	0.477
12	3.80	0.469	0.534
13	4.52	0.296	0.602
14	5.12	0.142	0.654
15	5.50	0.000	0.682

TARTRATE

1.00 M solution used

pH: 6.7

Mixture	Titre	Sodium tartrate concentration	Sodium sulphate concentration
3	0.48	0.633	0.091
4	0.93	0.554	0.169
5	1.35	0.483	0.235
6	1.72	0.419	0.289
7	2.20	0.357	0.353
8	2.62	0.301	0.406
9	3.05	0.249	0.456
10	3.47	0.201	0.501
11	3.92	0.155	0.546
12	4.45	0.111	0.596
13	4.95	0.0717	0.639
14	5.30	0.0350	0.667
15	5.50	0.000	0.682

BENZENESULPHONATE

1.90 M solution used

pH: 5.9

Mixture	Titre	Sodium benzenesulphonate concentration	Sodium sulphate concentration
1	9.43	0.724	0.920
2	8.88	0.693	0.894
3	8.30	0.660	0.863
4	7.78	0.625	0.835
5	7.27	0.586	0.805
6	6.77	0.544	0.773
7	6.33	0.497	0.742
8	5.80	0.451	0.705
9	5.40	0.397	0.675
10	4.97	0.341	0.641
11	4.70	0.278	0.617
12	4.55	0.211	0.604
13	4.50	0.141	0.600
14	4.85	0.0687	0.630
15	5.50	0.000	0.683

CITRATE

1.20 M solution used

pH: 7.4

Mixture	Titre	Sodium citrate concentration	Sodium sulphate concentration
9	0.90	0.364	0.164
10	1.55	0.284	0.254
11	2.35	0.211	0.373
12	3.28	0.146	0.481
13	4.12	0.0914	0.566
14	4.95	0.0430	0.638
15	5.50	0.000	0.683

THIOSULPHATE (adjusted with NaOH to pH 7.0)

2.00 M solution used
pH: 7.0

Mixture	Titre	Sodium thiosulphate concentration	Sodium sulphate concentration
6	0.45	0.952	0.0857
7	1.05	0.796	0.188
8	1.55	0.663	0.265
9	2.05	0.543	0.334
10	2.60	0.431	0.403
11	3.20	0.328	0.472
12	3.85	0.233	0.539
13	4.58	0.147	0.608
14	5.10	0.0709	0.651
15	5.70	0.000	0.698

NITRATE

6.00 M solution used

pH: 5.1

Mixture	Titre	Sodium nitrate concentration	Sodium sulphate concentration
1	0.20	4.57	0.0391
2	0.67	4.03	0.125
3	1.05	3.58	0.188
4	1.42	3.17	0.245
5	1.75	2.79	0.293
6	2.07	2.44	0.337
7	2.32	2.12	0.369
8	2.58	1.81	0.401
9	2.77	1.53	0.424
10	2.98	1.25	0.448
11	3.17	0.986	0.469
12	3.35	0.729	0.488
13	3.70	0.472	0.524
14	4.30	0.226	0.582
15	5.50	0.000	0.682

NITRITE

5.00 M solution used

pH: 7.2

Mixture	Titre	Sodium nitrite concentration	Sodium sulphate concentration
1	1.35	3.38	0.235
2	1.73	3.02	0.290
3	2.10	2.70	0.341
4	2.37	2.42	0.375
5	2.68	2.14	0.413
6	2.90	1.89	0.438
7	3.12	1.65	0.463
8	3.43	1.40	0.496
9	3.55	1.19	0.509
10	3.83	0.974	0.537
11	4.00	0.768	0.553
12	4.25	0.566	0.578
13	4.55	0.369	0.605
14	4.95	0.179	0.639
15	5.50	0.000	0.682

CHROMATE

2.50 M solution used

pH: 8.6

Mixture	Titre	Sodium chromate concentration	Sodium sulphate concentration
6	0.22	1.22	0.043
7	1.00	1.00	0.180
8	1.55	0.830	0.264
9	2.23	0.667	0.357
10	2.80	0.529	0.427
11	3.35	0.405	0.488
12	3.80	0.293	0.535
13	4.37	0.187	0.589
14	5.00	0.0893	0.643
15	5.50	0.000	0.682

MOLYBDATE

1.50 M solution used

pH: 7.1

Mixture	Titre	Sodium molybdate concentration	Sodium sulphate concentration
3	0.37	0.960	0.0771
4	0.83	0.840	0.152
5	1.30	0.727	0.227
6	1.70	0.631	0.286
7	2.10	0.541	0.340
8	2.60	0.453	0.403
9	2.97	0.376	0.447
10	3.38	0.303	0.491
11	3.87	0.233	0.541
12	4.28	0.169	0.581
13	4.60	0.110	0.610
14	5.20	0.0528	0.659
15	5.50	0.000	0.683

TUNGSTATE

1.00 M solution used

pH: 8.5

Mixture	Titre	Sodium tungstate concentration	Sodium sulphate concentration
1	1.08	0.694	0.193
2	1.40	0.625	0.242
3	1.68	0.562	0.283
4	2.03	0.498	0.331
5	2.42	0.438	0.381
6	2.67	0.386	0.412
7	2.95	0.335	0.444
8	3.30	0.285	0.483
9	3.62	0.237	0.516
10	3.92	0.193	0.546
11	4.13	0.152	0.565
12	4.40	0.112	0.591
13	4.70	0.0730	0.617
14	4.85	0.0361	0.630
15	5.50	0.000	0.682

THIOCYANATE

4.00 M solution used

pH: 5.4

Mixture	Titre	Sodium thiocyanate concentration	Sodium sulphate concentration
1	6.07	1.86	0.726
2	5.85	1.75	0.709
3	5.57	1.65	0.689
4	5.37	1.53	0.674
5	5.07	1.42	0.649
6	4.77	1.31	0.624
7	4.50	1.18	0.600
8	4.22	1.06	0.575
9	3.90	0.930	0.544
10	3.60	0.793	0.515
11	3.28	0.651	0.481
12	3.02	0.499	0.453
13	3.00	0.333	0.450
14	3.45	0.161	0.499
15	5.60	0.000	0.691

AZIDE

5.00 M solution used

pH: 7.4

Mixture	Titre	Sodium azide concentration	Sodium sulphate concentration
1	4.00	2.69	0.553
2	4.22	2.46	0.575
3	4.38	2.24	0.589
4	4.65	2.01	0.613
5	4.82	1.81	0.628
6	4.77	1.63	0.624
7	4.83	1.44	0.628
8	4.87	1.26	0.632
9	4.80	1.08	0.626
10	4.80	0.906	0.626
11	4.73	0.728	0.619
12	4.70	0.547	0.617
13	4.70	0.365	0.617
14	4.95	0.179	0.638
15	5.60	0.000	0.691

FERROCYANIDE

0.500 M solution used

pH: 6.0

Mixture	Titre	Sodium ferrocyanide concentration	Sodium sulphate concentration
1	0.95	0.352	0.172
3	1.72	0.280	0.289
5	2.37	0.220	0.376
7	3.07	0.166	0.458
9	3.75	0.118	0.530
11	4.27	0.0754	0.580
13	4.75	0.0364	0.622
15	5.50	0.000	0.682

CYANIDE

4.00 M solution used
pH: 10.3

Mixture	Titre	Sodium cyanide concentration	Sodium sulphate concentration
5	0.95	2.01	0.172
6	1.52	1.71	0.260
7	2.10	1.44	0.341
8	2.50	1.21	0.397
9	3.00	1.00	0.450
10	3.47	0.802	0.501
11	3.90	0.620	0.545
13	4.60	0.294	0.608
15	5.55	0.000	0.686

DICHROMATE

4.00 M solution used

pH: 4.3

Mixture	Titre	Sodium dichromate concentration	Sodium sulphate concentration
1	3.20	2.29	0.472
2	3.37	2.10	0.491
3	3.40	1.93	0.494
4	3.43	1.77	0.496
5	3.33	1.62	0.486
6	3.27	1.47	0.480
7	3.07	1.32	0.458
8	2.95	1.17	0.444
9	2.67	1.03	0.412
10	2.38	0.878	0.376
11	2.08	0.722	0.337
12	1.75	0.558	0.293
13	1.35	0.386	0.235
14	0.85	0.203	0.155
15	5.50	0.000	0.682

0.500 M solution used

Volume sodium dichromate/cm^3	Volume of water/cm^3	Volume of 2% gelatin/cm^3	Titre	Sodium dichromate concn.	Na_2SO_4 concn.
2.00	5.00	2.00	0.60	0.104	0.112
1.00	6.00	2.00	0.80	0.051	0.147
0.50	6.50	2.00	2.15	0.022	0.347

APPENDIX 2

Dependence of lyotropic line on gelatin sample

The chloride line was determined (5.00 M NaCl used) as indicated in EXPERIMENTAL, Section 4, using in turn three different gelatin samples. Except for the gelatin the substances used were the same throughout. Determinations were carried out at 25.0 °C.

Titres are in cm^3, concentrations in mol dm^{-3}.

B.D.H. GELATIN

Mixture	Titre	Sodium chloride concentration	Sodium sulphate concentration
2	0.40	3.46	0.077
3	0.67	3.10	0.125
4	0.98	2.76	0.177
5	1.32	2.42	0.230
6	1.57	2.13	0.268
7	1.87	1.84	0.310
8	2.17	1.57	0.350
9	2.45	1.31	0.385
10	2.78	1.06	0.425
11	3.12	0.83	0.463
12	3.55	0.60	0.509
13	3.90	0.390	0.544
14	4.60	0.180	0.608
15	5.50	0.000	0.683

GELATIN: ROYAL HOLLOWAY COLLEGE CHEMICAL STORE

Mixture	Titre	Sodium chloride concentration	Sodium sulphate concentration
1	0.50	3.69	0.095
2	0.82	3.31	0.150
3	1.05	2.98	0.188
4	1.35	2.66	0.235
5	1.72	2.33	0.289
6	1.97	2.05	0.324
7	2.20	1.79	0.353
8	2.57	1.51	0.400
9	2.90	1.26	0.438
10	3.20	1.03	0.472
11	3.60	0.790	0.514
12	4.10	0.570	0.563
15	6.25	0.000	0.738

GELATIN: SERVA ENTWICKLUNGSLABOR, HEIDELBERG

Mixture	Titre	sodium chloride concentration	Sodium sulphate concentration
1	3.95	2.70	0.549
2	4.28	2.44	0.580
3	4.55	2.21	0.604
4	4.78	1.99	0.624
5	5.07	1.78	0.649
6	5.38	1.56	0.674
7	5.65	1.37	0.694
8	5.93	1.17	0.715
9	6.22	0.990	0.737
10	6.50	0.810	0.755
12	7.10	0.470	0.794
15	8.10	0.000	0.853

APPENDIX 3

The effect of temperature on lyotropic curves

Investigations were carried out at 25 °C and 30 °C, using the same solutions, for chloride, bromide, nitrate and chlorate. The mixtures are those quoted in EXPERIMENTAL, Section 4, the titres are volumes (cm^3) of 1.80 M sodium sulphate, and concentrations tabulated are in mol dm^{-3}.

CHLORIDE - 5.00 M solution used

30 °C				25 °C		
Mixture	Titre	NaCl concn.	Na_2SO_4 concn.	Titre	NaCl concn.	Na_2SO_4 concn.
2	0.22	3.52	0.043	0.40	3.46	0.077
3	0.65	3.11	0.121	0.67	3.10	0.125
4	0.90	2.78	0.164	0.98	2.76	0.177
5	1.25	2.44	0.219	1.32	2.42	0.230
6	1.52	2.14	0.260	1.57	2.13	0.268
7	1.77	1.86	0.296	1.87	1.84	0.310
8	2.12	1.57	0.343	2.17	1.57	0.350
9	2.40	1.32	0.379	2.45	1.31	0.385
10	2.75	1.06	0.421	2.78	1.06	0.425
11	3.12	0.830	0.464	3.12	0.830	0.463
12	3.55	0.590	0.510	3.55	0.590	0.509
13	4.10	0.380	0.563	3.90	0.390	0.544
14	4.70	0.180	0.617	4.60	0.180	0.608
15	5.50	0.000	0.682	5.52	0.000	0.683

BROMIDE

6.00 M solution used

	30.0 °C			25.0 °C		
Mixture	Titre	NaBr concn.	Na_2SO_4 concn.	Titre	NaBr concn.	Na_2SO_4 concn.
1	4.27	3.17	0.580	4.46	3.12	0.597
2	4.42	2.90	0.593	4.60	2.87	0.609
3	4.43	2.68	0.593	4.68	2.63	0.616
4	4.53	2.44	0.602	4.63	2.42	0.611
5	4.53	2.22	0.602	4.70	2.19	0.617
6	4.47	2.01	0.598	4.60	1.98	0.609
7	4.45	1.79	0.596	4.58	1.77	0.607
8	4.37	1.57	0.590	4.48	1.56	0.598
9	4.28	1.36	0.580	4.42	1.34	0.593
10	4.25	1.13	0.578	4.28	1.13	0.580
11	4.13	0.910	0.566	4.25	0.910	0.577
12	4.10	0.680	0.563	4.10	0.680	0.564
13	4.40	0.450	0.591	4.25	0.450	0.577
14	4.65	0.220	0.613	4.60	0.220	0.609
15	5.50	0.000	0.682	5.55	0.000	0.686

NITRATE

6.00 M solution used

		30.0 °C			25.0 °C	
Mixture	Titre	$NaNO_3$ concn.	Na_2SO_4 concn.	Titre	$NaNO_3$ concn.	Na_2SO_4 concn.
1	0.10	4.62	0.0198	0.20	4.57	0.0391
2	0.60	4.07	0.112	0.67	4.03	0.125
3	0.98	3.61	0.177	1.05	3.58	0.188
4	1.37	3.18	0.238	1.42	3.17	0.245
5	1.67	2.81	0.282	1.75	2.79	0.293
6	1.95	2.47	0.320	2.07	2.44	0.337
7	2.22	2.14	0.356	2.32	2.12	0.369
8	2.48	1.83	0.389	2.58	1.81	0.401
9	2.72	1.54	0.418	2.77	1.53	0.424
10	2.93	1.25	0.442	2.98	1.25	0.448
11	3.08	0.990	0.459	3.17	0.990	0.469
12	3.30	0.730	0.483	3.35	0.730	0.488
13	3.75	0.470	0.529	3.70	0.470	0.524
14	4.25	0.230	0.577	4.30	0.230	0.582
15	5.30	0.000	0.667	5.50	0.000	0.683

CHLORATE

6.00 M solution used

	30.0 °C			25.0 °C		
Mixture	Titre	$NaClO_3$ concn.	Na_2SO_4 concn.	Titre	$NaClO_3$ concn.	Na_2SO_4 concn.
1	2.10	3.78	0.341	1.92	3.85	0.316
2	2.58	3.37	0.401	2.42	3.42	0.381
3	2.82	3.04	0.430	2.77	3.06	0.424
4	3.13	2.72	0.464	3.10	2.73	0.461
5	3.37	2.43	0.490	3.33	2.43	0.486
6	3.67	2.13	0.521	3.62	2.14	0.516
7	3.78	1.88	0.532	3.77	1.88	0.531
8	3.97	1.62	0.551	4.00	1.62	0.553
9	4.05	1.38	0.558	4.08	1.37	0.561
10	4.25	1.13	0.577	4.30	1.13	0.582
11	4.50	0.890	0.600	4.40	0.890	0.591
12	4.65	0.660	0.613	4.20	0.680	0.573
13	4.80	0.430	0.626	4.45	0.450	0.595
14	5.05	0.210	0.647	4.85	0.220	0.630
15	5.30	0.000	0.667	5.50	0.000	0.682

APPENDIX 4

The influence of pH

In the following tables concentrations are in mol dm^{-3}, titres in cm^3 of 1.80 M sodium sulphate.

CHLORIDE

All the determinations were carried out at 25 °C. The mixtures quoted in EXPERIMENTAL, Section 4, were modified to include hydrochloric acid or sodium hydroxide solution. Mixtures 1 and 2 were therefore not involved; the following mixtures will serve to illustrate the procedure.

Mixture	Volume of 5.00 M NaCl/cm^3	Volume of HCl or NaOH/cm^3	Volume of water/cm^3	Volume of 2% gelatin/cm^3
3	6.00	1.00	0.00	2.00
14	0.50	1.00	5.50	2.00

The concentrations used were:

pH of mixtures	Concentration of hydrochloric acid	Concentration of sodium hydroxide
4.0	0.010	
4.6	0.005	
4.9	0.001	
5.2		0.001
6.4		0.010
10.7		0.100

pH: 4.0

Mixture	Titre	Sodium chloride concn.	Sodium sulphate concn.
7	0.55	2.09	0.104
8	0.78	1.79	0.143
9	1.07	1.49	0.191
10	1.55	1.18	0.264
11	1.80	0.930	0.300
12	2.22	0.67 0	0.356
13	3.00	0.420	0.450
14	3.70	0.200	0.524
15	5.00	0.000	0.643

pH: 4.6

Mixture	Titre	sodium chloride concn.	Sodium sulphate concn.
4	0.15	3.01	0.0295
5	0.50	2.63	0.095
6	0.80	2.29	0.147
7	1.15	1.97	0.204
8	1.40	1.68	0.242
9	1.70	1.40	0.286
10	2.05	1.13	0.334
11	2.40	0.880	0.379
13	3.35	0.400	0.489
15	5.00	0.000	0.643

pH: 4.9

Mixture	Titre	Sodium chloride concn.	Sodium sulphate concn.
3	0.50	3.16	0.095
4	0.90	2.78	0.164
5	1.05	2.49	0.188
6	1.30	2.19	0.227
7	1.65	1.88	0.279
8	1.90	1.60	0.314
9	2.25	1.33	0.360
10	2.60	1.08	0.403
11	3.05	0.830	0.456
12	3.50	0.600	0.504
13	3.85	0.390	0.540
14	4.55	0.180	0.604
15	5.20	0.000	0.658

pH: 5.2

Mixture	Titre	Sodium chloride concn.	Sodium sulphate concn.
3	0.85	3.05	0.155
4	1.20	2.69	0.212
5	1.45	2.39	0.250
6	1.70	2.10	0.286
7	2.00	1.82	0.327
8	2.30	1.55	0.366
9	2.60	1.29	0.403
10	3.00	1.04	0.450
11	3.30	0.810	0.483
13	4.30	0.380	0.582
15	5.85	0.000	0.709

pH: 6.4

Mixture	Titre	Sodium chloride concn.	Sodium sulphate concn.
3	1.75	2.79	0.293
4	1.95	2.51	0.320
5	2.17	2.24	0.350
6	2.45	1.96	0.385
7	2.72	1.70	0.418
8	2.92	1.47	0.442
9	3.22	1.23	0.478
10	3.55	1.00	0.510
11	3.77	0.780	0.531
13	4.55	0.370	0.604
15	5.70	0.000	0.698

pH: 10.7

Mixture	Titre	Sodium chloride concn.	Sodium sulphate concn.
3	2.40	2.63	0.379
4	2.65	2.36	0.410
5	2.90	2.10	0.439
6	3.15	1.85	0.467
7	3.40	1.61	0.493
8	3.75	1.37	0.529
9	3.90	1.16	0.544
10	4.15	0.950	0.568
11	4.30	0.750	0.582
15	5.60	0.000	0.691

BROMIDE

Determinations were carried out as for chloride using the following concentrations of sodium hydroxide and hydrobromic acid, and using a 6.00 M sodium bromide solution.

pH of mixtures	Hydrobromic acid concentration	Sodium hydroxide concentration
4.2	0.010	
5.1	0.001	
5.4	NIL	NIL
6.4		0.010
10.9		0.100

pH: 4.2

Mixture	Titre	Sodium bromide concentration	Sodium sulphate concentration
3	1.22	3.52	0.215
4	1.42	3.17	0.245
5	1.55	2.84	0.264
6	1.55	2.56	0.264
7	1.70	2.24	0.286
8	1.82	1.94	0.303
9	1.75	1.67	0.293
10	1.85	1.38	0.307
11	1.87	1.10	0.310
13	2.40	0.527	0.379
15	4.50	0.000	0.600

pH: 5.1

Mixture	Titre	Sodium bromide concentration	Sodium sulphate concentration
3	4.10	2.75	0.563
4	4.10	2.52	0.563
5	4.12	2.29	0.566
6	4.05	2.07	0.558
7	4.10	1.83	0.563
8	3.95	1.62	0.548
9	3.95	1.39	0.548
10	3.85	1.17	0.538
11	3.80	0.940	0.534
13	3.95	0.460	0.549
15	5.40	0.000	0.676

pH: 5.4

Mixture	Titre	Sodium bromide concentration	Sodium sulphate concentration
1	4.46	3.12	0.597
2	4.60	2.87	0.609
3	4.68	2.63	0.616
4	4.63	2.42	0.611
5	4.70	2.19	0.617
6	4.60	1.98	0.609
7	4.58	1.77	0.607
8	4.48	1.56	0.598
9	4.42	1.34	0.593
10	4.28	1.13	0.580
11	4.25	0.910	0.577
12	4.10	0.690	0.564
13	4.25	0.450	0.577
14	4.60	0.220	0.609
15	5.50	0.000	0.682

pH: 6.4

Mixture	Titre	Sodium bromide concentration	Sodium sulphate concentration
3	4.75	2.62	0.621
4	4.95	2.32	0.625
5	4.90	2.16	0.634
6	4.95	1.93	0.638
7	4.95	1.72	0.638
8	4.90	1.51	0.634
9	4.95	1.29	0.638
10	4.85	1.08	0.630
11	4.85	0.870	0.630
13	4.70	0.440	0.617
15	5.90	0.000	0.713

pH: 10.9

Mixture	Titre	Sodium bromide concentration	Sodium sulphate concentration
3	5.95	2.41	0.716
5	6.05	1.99	0.724
7	6.00	1.60	0.720
9	5.80	1.22	0.705
11	5.50	0.830	0.682
13	5.10	0.000	0.651

ACETATE

A 4.00 M sodium acetate solution was used and the determinations were carried out as for chloride using the following concentrations of acetic acid and sodium hydroxide:

pH of mixtures	Concentration of acetic acid	Concentration of sodium hydroxide
5.4	1.00	
6.4	0.10	
7.5	NIL	NIL
7.8		0.01
11.1		0.10

pH: 5.4

Mixture	Titre	Sodium acetate concentration	Sodium sulphate concentration
6	0.25	1.94	0.049
7	0.95	1.61	0.172
8	1.47	1.33	0.253
9	2.15	1.07	0.348
10	2.72	0.850	0.418
11	3.15	0.660	0.467
12	3.75	0.470	0.529
13	4.37	0.300	0.589
14	4.75	0.140	0.622

pH: 6.4

Mixture	Titre	Sodium acetate concentration	Sodium sulphate concentration
6	0.45	1.90	0.086
7	1.05	1.59	0.188
8	1.75	1.30	0.293
9	2.30	1.06	0.366
10	2.95	0.840	0.444
11	3.45	0.640	0.499
12	3.92	0.460	0.547
13	4.70	0.290	0.618
14	5.20	0.140	0.659
		pH: 7.5	
6	0.40	1.91	0.077
7	0.97	1.60	0.176
8	1.57	1.32	0.268
9	2.17	1.07	0.350
10	2.72	0.850	0.418
11	3.25	0.650	0.477
12	3.80	0.470	0.534
13	4.52	0.300	0.602
14	5.12	0.140	0.654

pH: 7.8

Mixture	Titre	Sodium acetate concentration	Sodium sulphate concentration
7	1.00	1.60	0.180
8	1.60	1.32	0.271
9	2.20	1.07	0.353
10	2.65	0.860	0.410
11	3.25	0.650	0.477
12	3.95	0.460	0.549
13	4.50	0.300	0.600
14	5.25	0.140	0.663
		pH: 11.1	
6	0.70	1.86	0.130
7	1.20	1.57	0.212
8	1.70	1.31	0.286
9	2.20	1.07	0.353
10	2.80	0.850	0.427
11	3.25	0.650	0.478
12	3.70	0.470	0.524
13	4.25	0.300	0.577
14	4.65	0.150	0.613

FORMATE

A 4.00 M sodium formate solution was used. The determinations were carried out as for chloride, using the following concentrations of formic acid and sodium hydroxide:

pH of mixtures	Formic acid concentration	Sodium hydroxide concentration
4.3	1.00	
5.4	0.10	
7.0	NIL	NIL
10.9		0.10

pH: 4.3

Mixture	Titre	Sodium formate concentration	Sodium sulphate concentration
9	1.15	1.18	0.204
10	1.55	0.950	0.264
11	1.90	0.730	0.314
12	2.50	0.520	0.391
13	3.05	0.330	0.456
14	3.55	0.160	0.509

pH: 5.4

Mixture	Titre	Sodium formate concentration	Sodium sulphate concentration
6	0.55	1.88	0.103
7	1.10	1.58	0.196
8	1.65	1.31	0.278
9	2.20	1.07	0.354
10	2.75	0.850	0.421
11	3.20	0.660	0.472
12	3.75	0.470	0.529
13	4.30	0.300	0.582
14	4.65	0.150	0.614

pH: 7.0

Mixture	Titre	Sodium formate concentration	Sodium sulphate concentration
5	0.30	2.15	0.058
6	0.70	1.86	0.130
7	1.25	1.56	0.219
8	1.75	1.30	0.293
9	2.25	1.06	0.360
10	2.85	0.840	0.433
11	3.40	0.640	0.493
12	3.90	0.460	0.545
13	4.45	0.300	0.596
14	5.20	0.140	0.659

pH: 10.9

Mixture	Titre	Sodium formate concentration	Sodium sulphate concentration
5	0.55	2.09	0.103
6	1.00	1.80	0.180
7	1.45	1.53	0.250
8	1.95	1.28	0.320
9	2.50	1.04	0.391
10	2.85	0.840	0.433
11	3.20	0.660	0.472
12	3.75	0.470	0.529
13	4.25	0.300	0.577
14	4.75	0.145	0.622

APPENDIX 5

Effect of gelatin concentration on the sharpness of the end-point

Gelatin sols were prepared of concentrations 0.5, 0.75, 1.00, 1.25, 1.50, 1.75 and 2.00%. The mixture used was:

NaCl (5.00 M) /cm^3	De-ionised water /cm^3	Gelatin sol /cm^3
2.00	5.00	2.00

Seven mixtures of this composition were titrated with 1.80 M sodium sulphate solution, using a different gelatin concentration in each mixture. The same materials were used in all the determinations and these were carried out at 25.0 °C. The sulphate was added in 0.10 cm^3 portions, at half-minute intervals, the galvanometer reading being taken at the end of the interval.

0.5% GELATIN

Volume of 1.8 M sodium sulphate cm^3	Galvanometer reading
4.40	41.7
4.50	41.7
4.60	41.7
4.70	41.6
4.80	41.3
4.90	41.1
5.00	40.9
5.10	40.6
5.20	40.0
5.30	39.6
5.40	39.0
5.50	38.5
5.60	37.9
5.70	37.2
5.80	36.7
5.90	36.0
6.00	35.6
6.10	35.1
6.20	34.5
6.30	34.0
6.40	33.4
6.50	32.9
6.60	32.4
6.70	32.0
6.80	31.3
6.90	30.9
7.00	30.4
7.10	30.0
7.20	29.6
7.30	29.0
7.40	28.6
7.50	28.0
7.60	27.6
7.70	27.1
7.80	26.8
7.90	26.2
8.00	25.8
8.10	25.5
8.20	25.0
8.30	24.7
8.40	24.3
8.50	23.9
8.60	23.7
8.70	23.2
8.80	22.8
8.90	22.6
9.00	22.2

0.75% GELATIN

Volume of 1.8 M sodium sulphate cm^3	Galvanometer reading	Volume of 1.8 M sodium sulphate cm^3	Galvanometer reading
3.60	39.6	5.50	31.2
3.70	39.6	5.60	30.7
3.80	39.6	5.70	29.9
3.90	39.6	5.80	29.2
4.00	39.6	5.90	28.7
4.10	39.5	6.00	27.9
4.20	39.3	6.10	27.2
4.30	39.1	6.20	26.5
4.40	38.8	6.30	25.7
4.50	38.3	6.40	25.0
4.60	37.8	6.50	24.2
4.70	37.1	6.60	23.6
4.80	36.3	6.70	22.9
4.90	35.7	6.80	22.2
5.00	34.8	6.90	21.6
5.10	34.0	7.00	21.0
5.20	33.2	7.10	20.3
5.30	32.8	7.20	19.8
5.40	32.0	7.30	19.2

1.00% GELATIN

Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading	Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading
3.70	40.0	5.20	27.2
3.80	40.0	5.30	26.0
3.90	39.9	5.40	24.9
4.00	39.7	5.50	23.7
4.10	39.2	5.60	22.2
4.20	38.6	5.70	21.1
4.30	37.8	5.80	20.2
4.40	36.9	5.90	19.2
4.50	35.8	6.00	18.2
4.60	34.8	6.10	17.1
4.70	33.4	6.20	16.3
4.80	32.2	6.30	15.5
4.90	31.0	6.40	14.8
5.00	29.8	6.50	14.0
5.10	28.7	6.60	13.4

1.25% GELATIN

Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading	Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading
3.40	39.5	5.00	25.8
3.50	39.4	5.10	24.8
3.60	39.3	5.20	23.0
3.70	39.2	5.30	21.6
3.80	39.0	5.40	20.2
3.90	38.5	5.50	19.2
4.00	37.8	5.60	17.9
4.10	36.8	5.70	16.7
4.20	35.8	5.80	15.7
4.30	34.7	5.90	14.7
4.40	33.2	6.00	13.8
4.50	32.1	6.10	13.0
4.60	30.9	6.20	12.1
4.70	29.7	6.30	11.2
4.80	28.4	6.40	10.8
4.90	27.2	6.50	10.0
		6.60	9.6

1.50% GELATIN

Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading	Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading
3.30	41.0	4.80	24.8
3.40	41.0	4.90	23.0
3.50	41.0	5.00	21.4
3.60	40.8	5.10	19.8
3.70	40.3	5.20	18.3
3.80	39.8	5.30	16.9
3.90	39.0	5.40	15.7
4.00	37.8	5.50	14.2
4.10	36.4	5.60	13.1
4.20	35.0	5.70	12.1
4.30	33.4	5.80	11.0
4.40	32.0	5.90	10.2
4.50	30.0	6.00	9.3
4.60	28.2	6.10	8.7
4.70	26.4	6.20	8.1

1.75% GELATIN

Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading	Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading
3.00	41.8	4.70	22.0
3.10	41.8	4.80	20.0
3.20	41.8	4.90	18.0
3.30	41.8	5.00	16.2
3.40	41.7	5.10	14.7
3.50	41.4	5.20	13.1
3.60	41.0	5.30	11.8
3.70	40.1	5.40	10.6
3.80	39.0	5.50	9.4
3.90	37.6	5.60	8.7
4.00	35.8	5.70	8.0
4.10	34.0	5.80	7.2
4.20	32.1	5.90	6.7
4.30	30.1	6.00	6.1
4.40	28.1	6.10	5.7
4.50	26.0	6.20	5.2
4.60	24.0		

2.00% GELATIN

Volume of 1.80 M sodium sulphate cm^3	Galvanometer reading
3.30	39.8
3.40	39.8
3.50	39.8
3.60	39.4
3.70	38.5
3.80	37.2
3.90	35.8
4.00	33.9
4.10	32.0
4.20	29.8
4.30	27.5
4.40	25.2
4.50	23.0
4.60	21.0
4.70	18.9
4.80	16.8
4.90	14.8
5.00	13.2
5.10	11.8
5.20	10.4
5.30	9.0
5.40	8.3
5.50	7.7
5.60	6.9
5.70	6.2

APPENDIX 6

The effect of gelatin concentration on end-point

Three chloride mixtures were determined using 2%, 3%, and 4% gelatin. The titrant was 1.80 M sodium sulphate and determinations were carried out at 25 °C.

Mixture	Gelatin concentration %	Titre cm^3	Gelatin concentration at end-point / %
2	4	0.28	0.862
2	3	0.37	0.640
2	2	0.45	0.423
6	4	1.45	0.765
6	3	1.60	0.566
6	2	1.70	0.374
14	4	4.30	0.601
14	3	4.50	0.444
14	2	4.70	0.292

Adjustment of titres over the linear part of the curve to those for a common end-point concentration gives a change of gradient which corresponds to a change in lyotropic number of approximately 0.4%.

The nitrate and bromide lyotropic lines were determined at 25 °C using a constant gelatin end-point concentration (different gelatin concentration in each mixture before titration) and the gradients were compared to those determinations using 2% gelatin sol in all mixtures (varying end-point gelatin concentration). These latter results are given in Appendix 3 (25 °C).

NITRATE

6.00 M solution used

Gelatin end-point concentration: 0.340%

Mixture	Titre cm^3	Sodium nitrate concn./mol dm^{-3}	Sodium sulphate concn./mol dm^{-3}
1	0.63	4.36	0.118
2	1.07	3.88	0.191
3	1.43	3.45	0.246
4	1.75	3.07	0.293
5	2.10	2.70	0.341
6	2.40	2.37	0.379
7	2.60	2.07	0.403
8	2.87	1.77	0.436
9	3.05	1.49	0.456
10	3.28	1.22	0.481
11	3.42	0.970	0.496
12	3.65	0.710	0.519
13	3.95	0.460	0.549
14	4.60	0.220	0.609

BROMIDE

6.00 M solution used

Gelatin end-point concentration: 0.363%

Mixture	Titre cm^3	Sodium bromide concn./mol dm^{-3}	Sodium sulphate concn./mol dm^{-3}
1	3.87	3.26	0.542
2	4.00	3.00	0.554
3	4.12	2.74	0.566
4	4.17	2.51	0.571
5	4.17	2.28	0.571
6	4.15	2.05	0.568
7	4.10	1.83	0.563
8	4.15	1.60	0.568
9	4.05	1.38	0.559
10	4.00	1.15	0.553
11	3.95	0.930	0.546
12	3.95	0.690	0.546

APPENDIX 7

Use of Agar

Mixtures 1 and 10 (chloride) were titrated with 3.00 M sodium sulphate at 45 °C using 0.5, 1.0 and 1.5% agar. Additions of titrant were made at 15-second intervals, the galvanometer reading being taken at the end of the interval.

Mixture 1 : Agar 0.5%

Volume of titrant/cm^3	Galvanometer reading
1.75	41.8
2.00	41.8
2.25	41.8
2.50	41.7
2.75	41.6
3.00	41.6
3.25	41.4
3.50	41.2
3.75	41.1
4.00	41.0
4.25	40.8
4.50	40.7
5.00	40.4
5.50	40.2
6.00	40.0
6.50	39.9
8.00	39.7

Mixture 1 : Agar 1.0%

Volume of titrant/cm^3	Galvanometer reading
1.50	42.3
1.70	42.3
1.90	42.2
2.10	42.1
2.30	42.0
2.50	41.9
2.70	41.8
2.90	41.8
3.10	41.6
3.30	41.5
3.50	41.5
3.70	41.4
4.00	41.2
4.50	41.1
5.00	41.0
5.50	40.9
7.00	40.8

Mixture 1 : Agar 1.5%

Volume of titrant/cm^3	Galvanometer reading
0.75	40.5
1.00	40.5
1.25	40.5
1.50	40.4
1.75	40.4
2.00	40.3
2.25	40.2
2.50	40.2
2.75	40.0
3.00	40.0
3.25	39.9
3.50	39.8
3.75	39.8
4.00	39.8
5.00	39.1
5.50	39.0
6.00	38.8
6.50	38.8

Mixture 10 : Agar 0.5%

Volume of titrant/cm^3	Galvanometer reading
0.50	42.1
0.75	42.0
1.00	42.0
1.25	42.0
1.50	41.9
1.75	41.8
2.00	41.7
2.25	41.4
2.50	41.0
2.75	39.0
3.00	37.8
3.25	36.8
3.50	35.5
3.75	35.2
4.00	34.5
4.50	33.5
7.00	32.8

Mixture 10 : Agar 1.0%

Volume of titrant/cm^3	Galvanometer reading
1.00	41.9
1.25	41.9
1.50	41.9
1.75	41.8
2.00	41.8
2.25	41.5
2.50	41.0
2.75	39.2
3.00	37.2
3.25	35.1
3.50	33.0
3.75	32.3
4.00	32.0
4.25	31.5
4.50	30.5
5.00	30.0
5.50	29.2
6.00	29.0
7.00	29.0

Mixture 10 : Agar 1.5%

Volume of titrant/cm^3	Galvanometer reading
1.00	39.0
1.25	39.0
1.50	39.0
1.75	39.0
2.00	38.9
2.25	38.0
2.50	36.9
2.75	36.0
3.00	35.0
3.25	32.5
4.50	31.5
7.00	30.5
9.00	30.4

GELATIN

Titrant 1.80 M sodium sulphate

Mixture 5 - 2% sol		Mixture 10 - 2% sol	
Titrant volume cm^3	Galvanometer reading	Titrant volume cm^3	Galvanometer reading
0.00	43.1	2.30	42.9
0.10	43.1	2.40	42.9
0.20	43.1	2.50	42.9
0.30	43.1	2.60	42.9
0.40	43.0	2.70	42.8
0.50	42.9	2.80	41.7
0.60	42.8	2.90	39.0
0.70	42.2	3.00	33.9
0.80	39.4	3.10	29.1
0.90	32.5	3.20	24.8
1.00	24.6	3.30	21.9
1.10	19.4	3.40	19.5
1.20	16.5	3.50	17.8
1.30	14.3	3.60	14.8
1.40	13.1	3.70	14.0
1.50	12.0	3.80	13.0
1.60	11.1	3.90	12.0
1.70	10.5	4.00	10.8
1.80	10.3	4.10	10.1
1.90	10.1	4.20	9.6
3.00	9.8	5.00	8.0

APPENDIX 8

Burette temperature calibration

A solution of 1.80 M sodium sulphate was allowed to reach equilibrium (over a period of two hours) in the electrically heated burette (10 cm^3) for various potential differences applied across it. The results were:

P.D. / volt	Temperature excess / °C
1.42	2.70
1.69	4.40
1.86	5.70
2.06	6.35
2.40	9.00
2.60	9.90

APPENDIX 9

Examination of the halide lines at low concentrations

Volumes and titres are in cm^3, concentrations in mol dm^{-3}.

The titrant was 1.80 M sodium sulphate.

FLUORIDE - results given in Appendix 1.

CHLORIDE -

Volume of 1.25 M NaCl	Volume of water	Volume of 2% gelatin	Titre	Sodium chloride concn.	Sodium sulphate concn.
1.50	5.50	2.00	4.70	0.137	0.617
1.00	6.00	2.00	4.93	0.090	0.637
0.50	6.50	2.00	5.30	0.044	0.666
0.00	7.00	2.00	5.55	0.000	0.686

BROMIDE -

Volume of 1.00 M NaBr	Volume of water	Volume of 2% gelatin	Titre	Sodium bromide concn.	Sodium sulphate concn.
1.50	5.50	2.00	4.75	0.109	0.621
1.00	6.00	2.00	5.00	0.071	0.643
0.50	6.50	2.00	5.30	0.035	0.667
0.00	7.00	2.00	5.55	0.000	0.686

IODIDE -

Volume of 1.00 M NaI	Volume of water	Volume of 2% gelatin	Titre	Sodium iodide concn.	Sodium sulphate concn.
2.00	5.00	2.00	3.85	0.155	0.540
1.50	5.50	2.00	4.20	0.113	0.572
1.00	6.00	2.00	4.35	0.075	0.586
0.50	6.50	2.00	4.90	0.036	0.634
0.00	7.00	2.00	5.55	0.000	0.686

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