1062. *Initial Thermoelectric Power Measurements on Thermocells with Iodine–Iodide Electrodes at a Mean Temperature of* 30°.

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Thermocells with iodine–iodide electrodes give very reproducible values of initial thermoelectric powers. An equation relating this quantity to the iodine and iodide concentrations in the cell is derived, together with a simple extrapolation procedure to eliminate the entropy of transfer of the complex tri-iodide ion. This has been tested for a series of iodides with univalent cations, and the extrapolation errors shown to be small. The experimental data have been used to compute values of the Soret coefficients of the iodides studied relative to that of one iodide selected as a standard. These are consistent with some recent direct measurements of Soret coefficients by a conductimetric method. The standard transported entropy of the iodide ion, apart from a small correction term, has been calculated to be 27·4 cal. g.-ion^{-1} deg.$^{-1}$ which agrees quite well with the value of 28·1 units obtained by Haase, Hoch, and Schönert from data on silver–silver iodide thermocells.

EXPERIMENTAL data on the initial thermoelectric power (ε_0) of thermocells can be used to calculate relative values of Soret coefficients for a series of salts having a common ion.[1] Such calculations depend on the determination of small differences between ε_0 values for thermocells having the same electrodes but different electrolytes; these may be no more than a few microvolts per degree and accurate values of ε_0 are needed. Silver–silver halide electrodes have been most commonly used in studies on thermocells but they are not ideal for the purpose. A redox electrode in which the electron-transfer process takes place between two dissolved species should in principle be more reproducible, and it is known that measurements of extreme precision are possible with the platinum–iodine–iodide electrode.[2] When this work began the best available Soret coefficient measurements on dilute alkali iodide solutions were those due to Alexander,[3] obtained at a mean temperature of 30°. Accordingly, measurements on thermocells containing these electrodes have been carried out at this mean temperature with electrolytes prepared from a number of univalent iodides.

The thermocell can be written:

$$\begin{array}{ccc|c|ccc} \text{Pt} & \text{———} & \text{Pt} & \text{Solution of MI,} & \text{Pt} & \text{———} & \text{Pt} \\ & & & \text{and iodine} & & & \\ T_0 & & T & & T+\Delta T & & T_0 \end{array}$$

the electrode reactions being,

$$\text{I}^- \longrightarrow \tfrac{1}{2}\text{I}_2 + \varepsilon^- \text{ at } T \quad \ldots\ldots\ldots \quad (a)$$

$$\tfrac{1}{2}\text{I}_2 + \varepsilon^- \longrightarrow \text{I}^- \text{ at } T + \Delta T \quad \ldots\ldots\ldots \quad (b)$$

if the right-hand (heated) electrode is taken as positive. T_0 is the temperature of the potentiometer terminals. It is not difficult to show[4] that, if the temperature interval is small, the initial thermoelectric power, ε_0, of this cell is given by

$$\boldsymbol{F}\varepsilon_0 = -S^*_{\text{el. Pt}} + \Delta S_{\text{R}} - \sum_{\text{k}} t_{\text{k}}S^*_{\text{k}}/z_{\text{k}} \quad \ldots\ldots\ldots \quad (1)$$

$S^*_{\text{el. Pt}}$ is the entropy of transfer of the electron in the platinum conductor, and ΔS_{R} the

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[1] *E.g.*, Tyrrell and Hollis, *Trans. Faraday Soc.*, 1952, **48**, 893; Tyrrell and Colledge, *ibid.*, 1954, **50**, 1056.

[2] *E.g.*, MacInnes and Dayhoff, *J. Chem. Phys.*, 1952, **20**, 1034; Agar and Breck, *Nature*, 1955, **175**, 298.

[3] Alexander, *Z. phys. Chem.* (*Leipzig*), 1954, **203**, 213.

[4] *E.g.*, Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworth, London, 1961.

entropy change in the reaction (*b*). S^*_{k} and z_{k} are respectively the entropy of transfer and valency of the ion species k, the sum being taken over all the ion species present. By definition,

$$\Delta S_{\mathrm{R}} = s_{\mathrm{I}^-} - \tfrac{1}{2}s_{\mathrm{I}_2} - s_{\mathrm{el.\,Pt}}$$

and

$$s_{\mathrm{I}^-} = s^{\circ}_{\mathrm{I}^-} - \boldsymbol{R} \ln a_{\mathrm{I}^-} - \boldsymbol{R}T\ \partial/\partial T\ (\ln a_{\mathrm{I}^-})$$

$$s_{\mathrm{I}_2} = s^{\circ}_{\mathrm{I}_2} - \boldsymbol{R} \ln a_{\mathrm{I}_2} = \boldsymbol{R}T\ \partial/\partial T\ (\ln a_{\mathrm{I}_2})$$

where s_{j}, s°_{j} are respectively the partial molar entropy, and the standard partial molar entropy of the species j. Inserting these values into equation (1), it follows that

$$\boldsymbol{F}\varepsilon_0 = -\bar{\bar{S}}_{\mathrm{el.\,Pt}} + (s^{\circ}_{\mathrm{I}^-} - \tfrac{1}{2}s^{\circ}_{\mathrm{I}_2}) - \boldsymbol{R} \ln (a_{\mathrm{I}^-}/a^{\frac{1}{2}}_{\mathrm{I}_2}) - \boldsymbol{R}T\ \partial/\partial T \ln (a_{\mathrm{I}^-}/a^{\frac{1}{2}}_{\mathrm{I}_2}) - \textstyle\sum t_{\mathrm{k}}S^*_{\mathrm{k}}/z_{\mathrm{k}}. \quad . \quad (2)$$

$\bar{\bar{S}}_{\mathrm{el.\,Pt}}$ is the transported entropy of the electron in the platinum conductor, defined as $(S^*_{\mathrm{el.\,Pt}} + s_{\mathrm{el.\,Pt}})$, and the activity terms refer to the *free* iodine and iodide ions. The solutions also contain the complex ion I_3^- as the only complex species present when the iodine : iodide ratio is as small as in the present experiments. It is convenient to eliminate the activity of free iodine from equation (2) by introducing the association constant β_1:

$$\beta_1 = a_{\mathrm{I}_3^-}/a_{\mathrm{I}_2}a_{\mathrm{I}^-}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (3),

$$\boldsymbol{R} \ln (a_{\mathrm{I}^-}/a^{\frac{1}{2}}_{\mathrm{I}_2}) + \boldsymbol{R}T\ \partial/\partial T \ln (a_{\mathrm{I}^-}/a^{\frac{1}{2}}_{\mathrm{I}_2})$$

$$= \frac{\boldsymbol{R}}{2} (\ln \frac{m^3_{\mathrm{I}^-}}{m_{\mathrm{I}_3^-}} + T\ \partial/\partial T \ln m^3_{\mathrm{I}^-}/m_{\mathrm{I}_3^-} + \ln \beta_1 + T\ \partial/\partial \mathrm{T} . \ln \beta_1)$$

$$+ \boldsymbol{R}(\ln \gamma_{\mathrm{I}^-} + T\partial/\partial T . \ln \gamma_{\mathrm{I}^-}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\gamma_{\mathrm{I}_3^-}$ has been taken as equal to γ_{I^-}, and m_{j} is the molality of species j. β_1 is of the order of 10^3 l. mole^{-1}, and in these experiments the ratio (total iodine) : (total iodide) never exceeded 0·1. The free iodine concentration was thus always negligible, and it is legitimate to write

$$m_{\mathrm{I}^-} = [\mathrm{I}^-] - [\mathrm{I}_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$m_{\mathrm{I}_3^-} = [\mathrm{I}_2], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $[\mathrm{I}^-]$, $[\mathrm{I}_2]$, are respectively the total iodide and total iodine concentrations (molalities) in the solution. The change in the ratio of the concentrations of free iodide and of tri-iodide due to the shift in equilibrium with temperature is negligible in the experimental conditions, and all thermoelectric-power measurements were made before concentration gradients due to the Soret phenomenon could be established. Hence the term including $\partial/\partial T . \ln (m^3_{\mathrm{I}^-}/m_{\mathrm{I}_3^-})$ can be omitted from (4). Furthermore, $\boldsymbol{R}(\ln \beta_1 + T . \partial/\partial T . \ln \beta_1)$ is ΔS°, the standard entropy change in the association process which has the form:

$$\Delta S^{\circ} = s^{\circ}_{\mathrm{I}_3^-} - s^{\circ}_{\mathrm{I}_2} - s^{\circ}_{\mathrm{I}^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From equations (2), and (4)—(7),

$$\boldsymbol{F}\varepsilon_0 + \frac{\boldsymbol{R}}{2} \ln ([\mathrm{I}^-] - [\mathrm{I}_2])^3/[\mathrm{I}_2] + \boldsymbol{R}(\ln \gamma_{\mathrm{I}^-} + T . \partial/\partial\ T . \ln \gamma_{\mathrm{I}^-})$$

$$= -\bar{\bar{S}}_{\mathrm{el.\,Pt}} + s^{\circ}_{\mathrm{I}^-} - \tfrac{1}{2}(s^{\circ}_{\mathrm{I}_3^-} - s^{\circ}_{\mathrm{I}^-}) - \sum_{\mathrm{k}} t_{\mathrm{k}}S^*_{\mathrm{k}}/z_{\mathrm{k}} \quad . \quad . \quad . \quad . \quad (8)$$

For a given iodide concentration, the activity coefficient terms are substantially independent of the iodine concentration, and changes in the function $(\boldsymbol{F}\varepsilon_0 + \frac{\boldsymbol{R}}{2} \ln ([\mathrm{I}^-] - [\mathrm{I}_2])^3/[\mathrm{I}_2])$, which are in practice small and arise mainly from the entropy of transfer terms, do not prevent extrapolation of values of this function, measured at constant iodide but varying iodine concentrations, to zero iodine concentration; this extrapolated value can be denoted by $P_{\varepsilon,0}$. For an iodide MI, the Soret coefficient σ_{MI}, defined as shown, is related to ionic entropies of transfer by

$$\sigma_{\mathrm{MI}} = -\left(\frac{\mathrm{d}}{\mathrm{d}T}\ln m\right)_{\mathrm{stat}} = \frac{S^*_{\mathrm{M}^+} + S^*_{\mathrm{I}^-}}{2\boldsymbol{R}T\,(1 + \partial \ln \gamma_{\pm 1}/\partial \ln m)_{T,P}}, \quad . \quad . \quad . \quad (9)$$

the suffix denoting that the concentration gradient is measured in the stationary state. Equation (8) then becomes,

$$\boldsymbol{F}P_{\varepsilon,0} + \boldsymbol{R}(\ln \gamma_{\mathrm{I}^-} + T\,.\,\partial/\partial T\,.\ln \gamma_{\mathrm{I}^-}) = \bar{\bar{S}}{}^\circ_{\mathrm{I}^-} + \Delta S^*_{\mathrm{I}^-} - \bar{\bar{S}}_{\mathrm{el.\,Pt}} - \tfrac{1}{2}(s^\circ_{\mathrm{I}_3^-} - s^\circ_{\mathrm{I}^-})$$
$$-2t_{\mathrm{M}}\boldsymbol{R}T\,(1 + \partial \ln \gamma_{\pm}/\partial \ln m)_{T,R}\sigma_{\mathrm{MI}} \quad . \quad (10)$$

$\bar{\bar{S}}{}^\circ_{\mathrm{I}^-}$ is the standard transported entropy of the iodide ion, that is, the sum of the standard molar entropy and the entropy of transfer in an infinitely dilute solution, and $\Delta S^*_{\mathrm{I}^-}$ is the difference between the entropy of transport of the iodide ion in the solution considered and in an infinitely dilute solution.

For a second iodide, NI, the extrapolated thermoelectric power can be denoted by $P'_{\varepsilon,0}$, and the Soret coefficient by σ_{NI}. For dilute solutions, $\ln \gamma_{\mathrm{I}^-}$, $\Delta S^*_{\mathrm{I}^-}$ will be almost independent of the cation species and, from (9) and (10), for measurements taken in solutions of the same ionic strength,

$$\Delta P_{\varepsilon,0} = P_{\varepsilon,0} - P'_{\varepsilon,0} = -\frac{2\boldsymbol{R}T}{\boldsymbol{F}}\left\{t_{\mathrm{M}}\left[1 + \left(\frac{\partial \ln \gamma_\pm}{\partial \ln m}\right)_{T,P}\right]_{\mathrm{MI}}\cdot\sigma_{\mathrm{MI}}\right.$$
$$\left.-t_{\mathrm{N}}\left[1 + \left(\frac{\partial \ln \gamma_\pm}{\partial \ln m}\right)_{T,P}\right]_{\mathrm{NI}}\cdot\sigma_{\mathrm{NI}}\right\} \quad . \quad . \quad (11)$$

Experimental.—The cell used was basically that used by Tyrrell and Hollis,[1] modified to take account of the tendency of iodine to distil out of the solutions during the measurements by extending the thermostat jackets above the closures on each side of the cell (Fig. 1). The liquid junction was made in the inverted Y tube by releasing the air pressure at A after the screw-clips on the short lengths of silicone rubber tubing had been opened at B,B′. The temperature interval between the two half-cells was measured with two single copper–constantan thermocouples which had been calibrated by means of the secondary fixed points provided by the sodium chromate decahydrate-hexahydrate transition [5] and the sodium sulphate decahydrate–anhydrous sodium sulphate transition.[6] The e.m.f.s on the thermocell and on the thermocouples were measured on a Cambridge Vernier potentiometer.

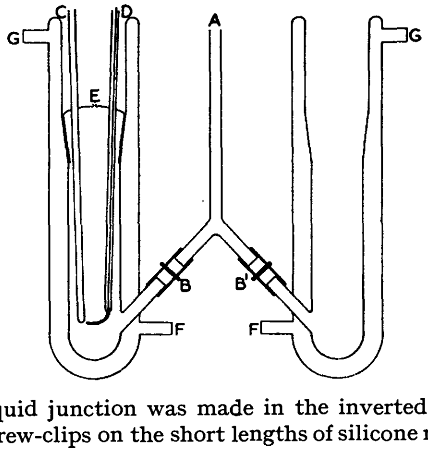

FIG. 1. Modified thermocell for iodine–iodide electrodes.

A, to manostat; B, B′ screw clips; C, thermocouple pocket; D, platinum electrode and lead; E, air leak; F, inlets to constant-temperature jackets; G, exits from constant-temperature jackets.

The right-hand side of the cell is not shown complete.

Solutions of iodine in the appropriate iodide, with ionic strengths of approximately 0·2, 0·1,

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[5] Richards and Kelly, *J. Amer. Chem. Soc.*, 1911, **33**, 847.

[6] Dickinson and Mueller, *J. Amer. Chem. Soc.*, 1907, **29**, 1381.

and 0·05m, and iodine concentrations between 2×10^{-2} and 10^{-4} m. were prepared, and the compositions checked by weight titration. The elementary iodine was determined directly by titration with sodium arsenite, and the iodide by oxidising it to iodine and then determining the total iodine by a similar titration. The iodides used were of the purest available grade, and were purified by recrystallisation except in the case of ammonium iodide where Smith and Eastlack's method [7] was used.

Results and Discussion.—It follows from equation (8) that, for a particular concentration of a given salt, the quantity, $\varepsilon_0 + \frac{\boldsymbol{R}}{2\boldsymbol{F}} \ln ([\mathrm{I}^-] - [\mathrm{I}_2])^3/[\mathrm{I}_2]$, will change with the iodine : iodide ratio only to the extent that the term $\sum_{\mathrm{k}} t_{\mathrm{k}} S^*{}_{\mathrm{k}}/z_{\mathrm{k}}\boldsymbol{F}$ changes, provided that the assumptions made in the derivation of eqn. (8) are correct. In Fig. 2 this quantity is plotted against the iodine : iodide ratio for different iodide solutions. Errors in the extrapolation to zero iodine concentration are clearly small, and the effect of the added iodine, essential to the operation of the electrode system, can therefore be eliminated and equation (11) used. Extrapolated values of $\left\{\varepsilon_0 + \frac{\boldsymbol{R}}{2\boldsymbol{F}} \ln ([\mathrm{I}^-] - [\mathrm{I}_2])^3/[\mathrm{I}_2]\right\}$ or $P_{\varepsilon,0}$, are shown in Table 1.

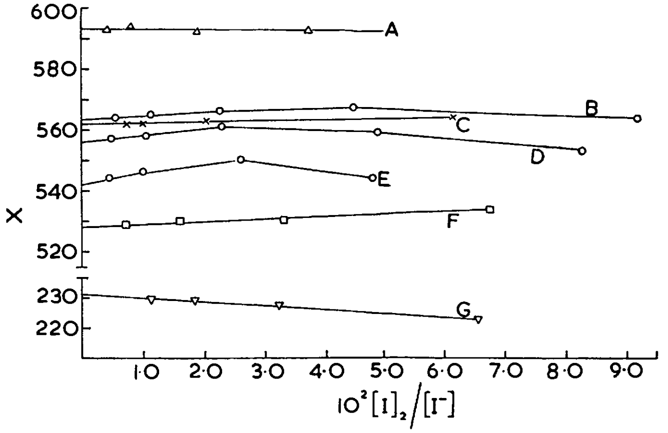

FIG. 2. Extrapolation of thermocell data to zero iodine concentration. The ordinate (X) records $\varepsilon_0 + \frac{\boldsymbol{R}}{2\boldsymbol{F}} \ln ([\mathrm{I}^-] - [\mathrm{I}_2]^3)/[\mathrm{I}_2]$ (μv deg.$^{-1}$).

A, 0·0496M-NH_4I. B, 0·215M-KI. C, 0·053M-LiI. D, 0·090M-KI. E, 0·053M-KI. F, 0·0492M-NaI. G, 0·048M-HI.

TABLE 1.

Values of $P_{\varepsilon,0}$ derived from experimental thermocell data (μv deg.$^{-1}$). Figures in parentheses have been "corrected" for variations in the ionic activity coefficient terms (see text).

Salt	Molality	$P_{\varepsilon,0}$	Salt	Molality	$P_{\varepsilon,0}$
NH_4I	0·0496	593	KI	0·215	563 (521)
LiI	0·053	562		0·090	556 (522)
NaI	0·0492	528		0·053	542 (516)
HI	0·048	231			

The variation of $P_{\varepsilon,0}$ with iodide concentration for potassium iodide solutions may be due partly to changes in the term involving the activity coefficient of the iodide ion and its variation with temperature, and partly to changes in the $\sum t_{\mathrm{k}} S^*{}_{\mathrm{k}}/z_{\mathrm{k}}\boldsymbol{F}$ term. The first

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[7] Smith and Eastlack, *J. Amer. Chem. Soc.*, 1916, **38**, 1500.

can be estimated by calculating $\ln f_{\pm} + T \,.\, \partial/\partial T \,.\, (\ln f_{\pm})$ from a suitable semi-empirical equation such as that suggested by Davies,[8] and the approximate relationship between the activity coefficient and its temperature coefficient derived by Tyrrell and Hollis,[1] writing

$$\log f_{-} = z_{-}/z_{+} \log f_{\pm},$$

a relationship which is consistent with the definition of the mean activity coefficient but not required by it, and ignoring the distinction between the molarity and molality concentration scales. The figures in parentheses in Table 1 (KI only) show values of $[P_{\varepsilon,0} + \boldsymbol{R}(\ln \gamma_{\mathrm{I}^-} + T \,.\, \partial/\partial T \,.\, \ln \gamma_{\mathrm{I}^-})]$ obtained in this way. For this salt, the entropy of transfer term is probably almost constant for solutions between 0·053 and 0·215 molal.

In order to apply equation (11) it is necessary to have values of transport numbers, and of the terms involving mean activity coefficients at 30° and a molality of about 0·05. The quantity $(1 + \partial \ln \gamma_{\pm}/\partial \ln m)_{T,P}$ is about 0·97 for all the salts included in Table 1 under these conditions. Cation transport numbers were calculated from the Onsager equation [9]

$$t_{+} = \frac{\lambda^{\circ}_{+} - (\tfrac{1}{2}|z_{+}|B_{2}I^{\frac{1}{2}})/(1 + \kappa a)}{\Lambda^{\circ} - \tfrac{1}{2}(|z_{+}| + |z_{-}|)B_{2}I^{\frac{1}{2}}/(1 + \kappa a)}$$

where λ°_{+}, Λ° are respectively the equivalent conductance of the cation and of the salt at 30° and at infinite dilution. Also,

$$B_{2} = \frac{82{\cdot}5}{\eta(\ni T)^{\frac{1}{2}}};\ \kappa a = Ba^{\circ}I^{\frac{1}{2}}$$

where η is the viscosity, and $\ni$ the dielectric constant of the solvent. I is the ionic strength, and, at 30°, B has the value 0·3297 for aqueous solutions. This equation gives good agreement with experiment for uni-univalent electrolytes at $I = 0{\cdot}05$. Limiting ionic conductances at 30° were obtained from published data by interpolation,[9] and the ion-size parameters a° tabulated by Robinson and Stokes [9] were used, except in the case of ammonium iodide. No data were available for this salt, and a value of 4·15 was selected by comparing the known figures for ammonium chloride with those for the alkali-metal chlorides and iodides. Ammonium iodide was taken as the reference substance, and, if this salt has its Soret coefficient, etc., denoted by the suffix MI, or M, it can be seen from (11) that

$$\sigma_{\mathrm{NI}} = \frac{\boldsymbol{F}\Delta P_{\varepsilon,0}}{0{\cdot}97\ (2\boldsymbol{R}Tt_{\mathrm{N}})} + \frac{t_{\mathrm{M}}}{t_{\mathrm{N}}} \,.\, \sigma_{\mathrm{MI}}$$

or

$$\sigma_{\mathrm{NI}} = \alpha + \beta\sigma_{\mathrm{MI}}$$

where α and β are parameters which can be calculated from experimental data on $\Delta P_{\varepsilon,0}$ and transport numbers. These, and the derived values of α and β are summarised in Table 2 and compared with some figures derived earlier from measurements on silver–silver iodide electrodes,[1] by using iodide solutions with $I = 0{\cdot}01$.

TABLE 2.

Parameters for the calculation of Soret coefficients.

Salt	Molality	$\Delta P_{\varepsilon,0}$ (μv deg.$^{-1}$)	t_{+}	$10^{3}\alpha$ (deg.$^{-1}$)	β	Data from ref. 1	
						$10^{3}\alpha$ (deg.$^{-1}$)	β
NH_4I	0·053	—	0·490	—	—	—	—
LiI	0·053	31	0·324	1·9	1·51	0·8	1·5
KI	0·0496	51	0·488	2·1	1·00	1·3	1·0
NaI	0·0492	65	0·389	3·4	1·26	2·5	1·2
HI	0·048	362	0·823	8·9	0·60	—	—

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[8] Davies, *J.*, 1938, 2093.

[9] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 2nd edn., 1959.

The values of α and β obtained agree roughly with those derived from Preston's measurements[1] on 0·01M-solutions in silver–silver iodide thermocells and should be more accurate. Fig. 3 shows plots of σ_{NI} against σ_{MI} ($\text{MI} = \text{NH}_4\text{I}$) for sodium, lithium, and potassium iodides derived from these data. Each pair of horizontal lines represents an experimental value for σ_{NI}, the error in which is assumed to be $\pm 10^{-5}$ deg.$^{-1}$, derived either from Snowdon and Turner's conductimetric measurements[10] at a mean temperature of 25·3° (NaI, KI), or from Alexander's thermogravitational measurements[3] (LiI, NaI, KI: $T_{\text{m}} = 30°$). Both sets of experimental data were obtained for 0·05M-solutions. It can be seen that Snowdon and Turner's values for sodium iodide and potassium iodide in conjunction with the thermocell data lead to almost the same value for σ_{MI}. A much larger spread in this quantity is obtained if Alexander's values are used to calculate it, in spite of the fact that they were obtained at the same mean temperature as the thermocell data. If it is assumed that the *relative* values of the Soret coefficients of these iodides are not much changed between 25° and 30°, the best value for the Soret coefficient of ammonium iodide in 0·05M-solution at 25·3° can be taken to be $-2{\cdot}50 \times 10^{-3}$ deg.$^{-1}$. This is consistent with the conductimetric values for both sodium iodide and potassium iodide, and predicts a Soret coefficient of $-1{\cdot}88 \times 10^{-3}$ deg.$^{-1}$ for 0·05M-lithium iodide at this temperature. No value is available from direct measurements, but, if the difference between the coefficients for sodium and lithium iodide is not very dependent on concentration, Snowdon and Turner's measurements on 0·05M- and 0·01M-solutions lead to a value of about $-1{\cdot}8 \times 10^{-3}$ deg.$^{-1}$ for this solution. Some earlier conductimetric measurements by Agar and Turner[11] gave values for 0·01M-lithium iodide which differed according to whether they were calculated from measurements made during the approach to the steady state or in the steady state itself. Combination of these values with Snowdon and Turner's measurements, with the above assumption, suggests that the value for 0·05M-lithium iodide lies between $-0{\cdot}9$ and $-2{\cdot}2 \times 10^{-3}$ deg.$^{-1}$. In view of the difficulties encountered in the direct measurement of the Soret coefficients of salts with negative Soret coefficients the agreement can be considered good, and, for the limited range of iodides considered here, Snowdon and Turner's measurements fit the thermocell data most satisfactorily.

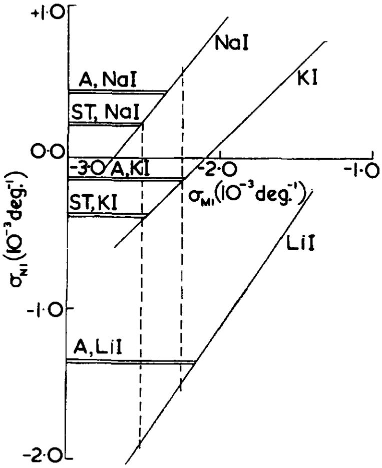

FIG. 3. Graphical test of mutual consistency of thermocell data and Soret coefficient measurements (0·05M-iodide solutions).

A, Alexander's Soret coefficient data[3] at 30°. ST, Snowdon and Turner's Soret coefficient data[10] at 25·3°.

Table 3 shows Soret coefficients and heats of transfer for 0·05M-iodide solutions at 25° and 30° obtained by using respectively $\sigma_{\text{MI}} = -2{\cdot}50 \times 10^{-3}$ and $-2{\cdot}35 \times 10^{-3}$ deg.$^{-1}$ and

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[10] Snowdon and Turner, *Trans. Faraday Soc.*, 1960, **56**, 1409.

[11] Agar and Turner, *Proc. Roy. Soc.*, 1960, *A*, **255**, 307.

the parameters shown in Table 2. Heats of transfer have been calculated by assuming that $\left(1 + \frac{\partial \ln \gamma_{\pm}}{\partial \ln m}\right)_{T,P}$ is 0·97 for all salts studied, as before; the error in this is small.

TABLE 3.

Soret coefficients and heats of transfer (Q_2^*) for 0·05M-iodide solutions.

Salt	Soret coefficient (10^{-3} deg.$^{-1}$)		Q_2^* (cal. mol.$^{-1}$)	
	25°	30°	25°	30°
NH_4I	−2·50	−2·35	−855	−822
LiI	−1·88	−1·50	−643	−530
KI	−0·40	−0·15	−140	−50
NaI	+0·24	+0·56	+80	+200
HI	+7·40	+7·51	+2530	+2660

Not all of these have been measured directly, but, where this is the case, the values in Table 3 are not inconsistent with the general body of data on Soret coefficients. For example, the high positive value for hydrogen iodide solution is not surprising in view of Tanner's measurements [12] on more concentrated chloride solutions including solutions of hydrogen chloride.

The standard transported entropy of the iodide ion $\bar{\bar{S}}^{\circ}_{I^-}$ can be calculated, apart from $\Delta S^*_{I^-}$, by using equation (10). $P_{\varepsilon,0}$ and σ vary from salt to salt, but the method of calculating the Soret coefficients given in Table 3 ensures that they are consistent with the thermocell measurements, and it is only necessary to carry through the calculation for one salt. For 0·053M-potassium iodide $P_{\varepsilon,0} + \frac{\boldsymbol{R}}{\boldsymbol{F}} (\ln \gamma_{I^-} + T \,.\, \partial/\partial T \,.\, \ln \gamma_{I^-})$ is 516 μv deg.$^{-1}$ (Table 2). Uncertainties in the activity-coefficient term are of minor importance in this connection. On using tabulated [13] values of the standard entropies of the aqueous tri-iodide and iodide ions at 25°, and assuming the difference in these quantities to be substantially the same at 30°, it is found that $\frac{1}{2}(s^{\circ}_{I_3^-} - s^{\circ}_{I^-})$ is 15·48 entropy units. The Soret coefficient of potassium iodide at 30° is, from Table 3, $-0{\cdot}15 \times 10^{-3}$ deg.$^{-1}$, and $2\boldsymbol{R}Tt_M(1 + \partial \ln \gamma_{\pm}/\partial \ln m)\, \sigma_M$ is approximately −0·10 entropy unit. When Khoroshin and Temkin's value [14] for the transported entropy of the electron in platinum (4·67 μv deg.$^{-1}$ at 303° K) is included, $(\bar{\bar{S}}^{\circ}_{I^-} + \Delta S^*_{I^-})$ proves to be 27·4 cal. g.-ion^{-1} deg.$^{-1}$. Haase, Hoch, and Schönert [15] obtained values of 28·1 and 28·4 units, depending on the Soret coefficient values chosen, for $\bar{\bar{S}}^{\circ}_{I^-}$, using some recent data on silver–silver iodide thermocells, and conductimetric Soret coefficients obtained by Snowdon and Turner and by Agar and Turner. They were able to estimate the variation in the entropy of transfer of the iodide ion with concentration and concluded that it was very small. No such estimate can be obtained from the present data, but the agreement between the transported entropies ($\Delta S^*_{I^-}$ being ignored) is quite good and shows that the two sets of thermocell data are consistent.

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[12] Tanner, *Trans. Faraday Soc.*, 1927, **23**, 75.

[13] Latimer, " Oxidation Potentials," Prentice-Hall, New York, 2nd edn., 1959.

[14] Khoroshin and Temkin, *Zhur. fiz. Khim.*, 1952, **26**, 500.

[15] Haase, Hoch, and Schönert, *Z. phys. Chem.* (*Frankfurt*), 1961, **27**, 421.