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Standard Potentials of the Silver–Silver Iodide Electrode in Diethylene Glycol–Water Mixtures at Different Temperatures and the Related Thermodynamic Quantities

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Standard electrode potentials of the silver–silver iodide electrode were determined at four temperatures in the temperature range 5–35 °C in 20, 40, 60, and 80 wt % diethylene glycol–water mixtures by emf measurements on the cells Pt,H_2(g, 1 atm)|HBO_2(m_1),$NaBO_2$(m_2),KBr(m_3)[diethylene glycol (x)-water (y)]|AgBr–Ag and Pt,H_2(g, 1 atm)|HBO_2(m_1),$NaBO_2$(m_2),KI(m_3)[diethylene glycol (x)-water (y)]|AgI–Ag. The standard molal potential, $_sE^\circ_m$, in the various solvent mixtures is expressed as a function of temperature. The various thermodynamic parameters for the transfer of HI from water to these media at 25 °C are reported and the variation of these parameters with solvent composition is discussed both in terms of the basicity of the solvent mixtures and also in terms of their structural effects on the transfer process. The standard molal free energies of transfer of the H^+ and the halide ions are also evaluated at 25 °C on the basis of the Feakins extrapolation method in these mixtures.

In earlier communications from this laboratory (*8*, *11*), the standard potentials of silver–silver chloride and silver–silver bromide electrodes in the temperature range 5–45 °C in diethylene glycol–water mixtures of varying composition were reported. In continuation of this work, the present paper deals with the determination of the standard potentials of the silver–silver iodide electrode in diethylene glycol–water mixtures of varying composition in order to evaluate the proton medium effects in these mixtures in conjunction with the data obtained earlier and thereby gain an insight into the acid–base nature of these media. Although such studies on galvanic cells involving hydrogen and silver, silver iodide electrodes were made in a few amphiprotic media (*2*, *3*, *9*), no data have been reported in diethylene glycol or its aqueous mixtures. The results on buffered cells (1) and (2) in the composition range 20–80 wt % diethylene glycol–water mixtures and in the temperature range 5–35 °C are reported, and by combining these data and also utilizing the standard potentials of the Ag–AgBr electrode in these mixtures determined earlier (*11*), the standard potentials of the silver–silver iodide electrode are obtained.

$$Pt,H_2(g,\ 1\ atm)|HBO_2(m_1),NaBO_2(m_2),KBr(m_3)|AgBr\text{–}Ag \quad (1)$$

$$Pt,H_2(g,\ 1\ atm)|HBO_2(m_1),NaBO_2(m_2),KI(m_3)|AgI\text{–}Ag \quad (2)$$

Experimental Section

The solvents were purified as described previously (*8*). The hydrogen (*8*), silver–silver bromide, and silver–silver iodide electrodes (*7*) were prepared according to the methods described elsewhere. Boric acid (AnalaR, BDH), dried at 120 °C was used in the preparation of borate buffers. Sodium borate was prepared in situ by appropriately neutralizing the acid with sodium hydroxide in the desired solvent. Other salts such as potassium bromide and potassium iodide used in these measurements were of reagent grade and suitably dried before use. The experimental setup and the general procedure used for emf measurements are identical with those described earlier (*8*). All measurements were made with two hydrogen and four silver–silver halide electrodes. The cells were thermostated at each temperature with an accuracy ±0.05 °C. Both Ag–AgBr and Ag–AgI electrodes were found to be stable over the entire temperature range and constancy of cell emf to ±0.05 mV over a period of 0.5 h was considered as an adequate criterion of equilibrium in the emf measurements. The emf values recorded initially at 25 °C were redetermined when increasing the temperature of the thermostat from 5 to 35 °C and finally again at the end. All the values agreed within ±0.05 mV.

The determination of the standard potential of the Ag–AgI electrode in these mixtures is based on Owen's method (*10*) which involves the use of buffered cell 2 to prevent the aerial oxidation of I^- to I_2. Using identical molalities of HBO_2, $NaBO_2$, and KBr or KI, we measured the emf of cells 1 and 2 in various solvent mixtures. These data, corrected to a partial pressure of 1 atm of hydrogen, are given in Table I.

Results and Discussion

The difference in the emf of cells 2 (E_2) and 1 (E_1) at a given molality, m, of the electrolytes can be expressed as

$$E_2 - E_1 = E^\circ_2 - E^\circ_1 - \frac{RT}{F} \ln \gamma_{I^-}/\gamma_{Br^-} = E^\circ_m + f(\mu) \quad (3)$$

where f(μ) represents the variation of the activity coefficient term with the ionic strength. The ionic strength was taken to be equal to 2 m and in this calculation it was assumed that the dissociation of HBO_2 is negligible and that other electrolytes are completely dissociated. In obtaining eq 3, we assumed that the activity coefficients of the species involved in cells 1 and 2 are the same and this was a reasonable assumption in view of the identical conditions maintained in the two cells.

A plot of $E_2 - E_1$ against μ was linear in all solvent compositions with an intercept at $\mu = 0$ equal to $\Delta E^\circ_m = E^\circ_{Ag\text{–}AgI} - E^\circ_{Ag\text{–}AgBr}$. The data so obtained are given in Table II.

Using the $_sE^\circ_m$ of Ag–AgBr electrode determined earlier in these solvent mixtures (*11*), we obtained the standard electrode potential of the Ag–AgI electrode. Table III gives the $_sE^\circ_m$ values at all temperatures as well as $_sE^\circ_c$ and $_sE^\circ_N$, i.e., the $_sE^\circ$ values on the molar and mole fraction scale at 25 °C calculated from

$$_sE^\circ_c = {}_sE^\circ_m + 2k \log d_0 \quad (4)$$

and

$$_sE^\circ_N = {}_sE^\circ_m - 2k \log (1000/M_{xy}) \quad (5)$$

In the above equations, d_0 is the density of the solvent, $k = (RT/F) \ln 10$, and M_{xy} is the mean molecular weight of the solvent, as defined earlier (*8*). The standard error in E°_m is about ±0.25 mV in all the mixtures at different temperatures. The $_sE^\circ_m$ can be expressed as a function of temperature according to

$$_sE^\circ_m = {}_sE^\circ_{m(25\,°C)} + b(t - 25) + c(t - 25)^2 \quad (6)$$

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Table I. Emf Data of Cells (1) and (2) (Corrected for 1 Atm Pressure of H_2) from 5 to 35 °C in Volts in Various Diethylene Glycol-Water Mixtures (X = wt % Diethylene Glycol (g/100 g), m = molality (mol kg^{-1}))

	emf, V			
m,[a] mol kg^{-1}	5 °C	15 °C	25 °C	35 °C
	X = 20 (Ag-AgBr)			
0.006 56	0.713 72	0.726 17	0.739 05	0.750 92
0.008 20	0.711 92	0.722 50	0.735 47	0.746 94
0.010 25	0.702 88	0.715 67	0.727 59	0.740 07
0.012 80	0.701 58	0.711 51	0.723 42	0.734 67
0.016 00	0.695 93	0.708 25	0.720 50	0.732 30
0.020 00	0.691 76	0.704 45	0.716 24	0.727 86
	X = 20 (Ag-AgI)			
0.006 56	0.494 96	0.510 93	0.525 18	0.538 46
0.008 20	0.492 16	0.506 21	0.520 71	0.535 00
0.010 25	0.484 81	0.499 37	0.513 06	0.527 69
0.012 80	0.481 83	0.495 65	0.510 15	0.523 64
0.016 00	0.476 00	0.490 08	0.504 34	0.517 39
0.020 00	0.470 72	0.485 86	0.499 28	0.513 10
	X = 40 (Ag-AgBr)			
0.006 56	0.730 20	0.755 23	0.767 84	0.779 26
0.008 20	0.726 00	0.750 07	0.763 70	0.774 97
0.010 25	0.723 00	0.736 89	0.754 09	0.765 90
0.012 80	0.721 90	0.735 78	0.750 97	0.763 00
0.016 00	0.719 42	0.730 39	0.743 62	0.755 20
0.020 00	0.713 22	0.726 68	0.738 58	0.750 32
	X = 40 (Ag-AgI)			
0.006 56	0.520 78	0.548 56	0.561 10	0.577 50
0.008 20	0.516 45	0.543 16	0.557 26	0.573 15
0.010 25	0.513 90	0.530 51	0.550 40	0.563 09
0.012 80	0.512 45	0.529 41	0.547 20	0.560 58
0.016 00	0.510 24	0.524 50	0.538 83	0.552 42
0.020 00	0.504 38	0.519 48	0.534 46	0.547 88
	X = 60 (Ag-AgBr)			
0.008 20	0.752 47	0.758 18	0.770 11	0.782 10
0.010 25	0.747 77	0.757 15	0.767 11	0.781 38
0.012 80	0.741 76	0.753 56	0.763 57	0.774 55
0.016 00	0.735 61	0.746 26	0.758 34	0.769 71
0.020 00	0.731 45	0.740 16	0.752 61	0.763 50
	X = 60 (Ag-AgI)			
0.008 20	0.555 35	0.565 26	0.578 64	0.592 27
0.010 25	0.550 60	0.563 20	0.574 57	0.589 62
0.012 80	0.544 17	0.559 08	0.570 54	0.583 18
0.016 00	0.538 52	0.552 12	0.564 60	0.578 00
0.020 00	0.534 38	0.546 60	0.559 49	0.571 86
	X = 80 (Ag-AgBr)			
0.006 56	0.759 50	0.765 33	0.778 70	0.789 26
0.008 20	0.756 11	0.762 64	0.777 71	0.788 78
0.010 25	0.750 09	0.760 13	0.776 68	0.787 06
0.012 80	0.745 14	0.757 35	0.769 20	0.780 88
0.016 00	0.740 40	0.748 66	0.760 36	0.773 11
0.020 00	0.734 09	0.746 20	0.755 29	0.768 28
	X = 80 (Ag-AgI)			
0.006 56	0.567 35	0.574 66	0.594 39	0.608 01
0.008 20	0.566 38	0.573 70	0.593 46	0.606 81
0.010 25	0.561 34	0.572 80	0.592 76	0.605 92
0.012 80	0.557 68	0.571 90	0.586 23	0.599 30
0.016 00	0.555 82	0.567 42	0.580 27	0.592 95
0.020 00	0.554 24	0.565 08	0.575 59	0.589 01

[a] $m = m_1 = m_2 = m_3$. $m_1 = m_{HBO_2}$. $m_2 = m_{NaBO_2}$. $m_3 = m_{KBr}$ or m_{KI}.

Table II. $\Delta E°_m$ Data (Eq 3) at Different Temperatures in Various Diethylene Glycol-Water Mixtures

diethylene glycol, wt % (g/100 g)	$\Delta E°_m$			
	5 °C	15 °C	25 °C	35 °C
20	−0.2175	−0.2138	−0.2126	−0.2105
40	−0.2090	−0.2070	−0.2065	−0.2015
60	−0.1975	−0.1928	−0.1916	−0.1900
80	−0.1980	−0.1945	−0.1870	−0.1830

where t is the temperature in degrees Celsius and b and c are empirical coefficients. These data are summarized in Table IV. The standard deviations in ${}_sE°_m$ calculated from eq 6 were found to be within ±0.2–0.3 mV. The standard free energy change, $\Delta G°_t$, associated with the transfer of 1 mol of HI from water to the given solvent at infinite dilution according to

$$\text{HI(water)} = \text{HI(diethylene glycol–water mixture)} \qquad (7)$$

was calculated on the mole fraction scale for the various solvent mixtures at 25 °C from the expression

$$\Delta G°_t = F({}_wE°_N - {}_sE°_N) \qquad (8)$$

where ${}_wE°_N$ and ${}_sE°_N$ represent the standard electrode potentials of the Ag–AgI electrode in water and in mixed solvent, respectively, on the mole fraction scale. The transfer process (eq 7) is associated with a transfer of charged species, i.e., of H^+ and I^- ion from water to the mixed solvents at infinite dilution, and it is generally agreed (*4*) that it consists of an electrostatic part, $\Delta G°_{t(el)}$, and a nonelectrostatic part, $\Delta G°_{t(nonel)}$. While the electrostatic transfer free energy arises mainly due to the differences in the dielectric constants of the solvents, the nonelectrostatic transfer free energy reflects the contributions of solvation and other specific ion–solvent interactions which depend on the basicity of solvent. Thus

$$\Delta G°_t = \Delta G°_{t(el)} + \Delta G°_{t(nonel)} \qquad (9)$$

The standard entropy of transfer, $\Delta S°_t$, was calculated from

$$\begin{aligned}\Delta S°_t &= (-d/dT)F({}_wE°_N - {}_sE°_N) \\ &= F[(b_s - b_w) + 2(c_s - c_w)(t - 25) + (K_w - K_s)]\end{aligned} \qquad (10)$$

where b_s and c_s and b_w and c_w are the coefficients from Table IV in the solvent and water, respectively, and $K_w = (2R/F)\ln(1000/18.0154) = 6.92 \times 10^{-4}$ and $K_s = (2R/F)\ln(1000/M_{xy})$. The last term arises in the conversion of ${}_sE°_m$ to ${}_sE°_N$. The standard enthalpy of transfer, $\Delta H°_t$, was then calculated from the equation

$$\Delta H°_t = \Delta G°_t + T(\Delta S°_t) \qquad (11)$$

All these thermodynamic quantities are recorded in Table V. The $\Delta G°_t$ values are accurate to ±40 J and the expected errors in $\Delta S°_t$ and $\Delta H°_t$ are ±0.5 J deg^{-1} and ±160 J, respectively. It is seen from Table V that $\Delta G°_t$ is negative and increases (in the negative direction) up to about 60 wt % diethylene glycol and then becomes less negative after passing through a minimum at this composition which is similar to the observations in the case of HBr in these media. Thus the transfer of HI from water to all diethylene glycol–water mixtures is a thermodynamically favorable process. The nature of the variation of $\Delta G°_t$ with solvent composition can be qualitatively explained from eq 9 where $\Delta G°_{t(el)}$ becomes more and more positive due to the decreasing dielectric constant of the solvent with increasing additions of diethylene glycol while $\Delta G°_{E(nonel)}$ possibly decreases continuously under the same conditions. $\Delta H°_t$ passes through an endothermic maximum at about 20 wt % diethylene glycol as in the case of HCl and HBr but subsequently it becomes continuously negative up to 60 wt % diethylene glycol and then becomes less negative at 80 wt % organic solvent. The significance for the existence of the endothermic maximum at 20 wt % diethylene glycol has been discussed earlier (*8*, *11*). According to Franks and Ives (*6*) and Feakins and Voice (*4*), the effect of the ionic fields on the structure of the solvent will appear as compensating contributions in $\Delta H°_t$ and $T(\Delta S°_t)$ and

Table III. ${}_sE^\circ_m$ at Different Temperatures and ${}_sE^\circ_N$ and ${}_sE^\circ_c$ for the Ag-AgI Electrode at 25 °C (in Volts) in Various Diethylene Glycol-Water Mixtures

diethylene glycol, wt % (g/100 g)	${}_sE^\circ_m$ 5 °C	15 °C	25 °C	${}_sE^\circ_c$	${}_sE^\circ_N$	${}_sE^\circ_m$ 35 °C
0[a]	−0.14718	−0.14951	−0.15242	−0.15260	−0.35890	−0.15589
20	−0.1448	−0.1452	−0.1481	−0.1465	−0.3495	−0.1516
40	−0.1390	−0.1407	−0.1473	−0.1444	−0.3330	−0.1488
60	−0.1330	−0.1368	−0.1427	−0.1385	−0.3137	−0.1513
80	−0.1576	−0.1671	−0.1726	−0.1675	−0.3230	−0.1821

[a] See: Hetzer, H. B., Robinson, R. A., Bates R. G., *J. Phys. Chem.*, 68, 1929 (1964).

Table IV. Coefficients of the Empirical Equation ${}_sE^\circ_m = {}_sE^\circ_{m(25\,^\circ C)} + b(t-25) + C(t-25)^2$

diethylene glycol, wt % (g/100 g)	${}_sE^\circ_{m(25\,^\circ C)}$	$-b \times 10^4$	$-C \times 10^6$
0	−0.15242	3.190	2.840
20	−0.1478	3.105	7.750
40	−0.1458	3.550	−0.500
60	−0.1427	7.280	12.000
80	−0.1738	7.900	0.000

Table V. Thermodynamic Quantities for the Transfer of HI from Water to Various Diethylene Glycol-Water Mixtures at 25 °C on the Mole Fraction Scale[a]

diethylene glycol, wt % (g/100 g)	ΔG°_t	ΔS°_t	ΔH°_t
20	−907	3.9	241
40	−2499	3.3	−1523
60	−4362	−28.0	−12680
80	−3464	−27.2	−11568

[a] ΔG°_t and ΔH°_t in J, ΔS°_t in J K^{-1} mol^{-1}.

Table VI. Transfer Free Energies of H$^+$ and Halide Ions in Various Diethylene Glycol-Water Mixtures at 25 °C on the Molal Scale[a]

diethylene glycol, wt % (g/100 g)	ΔG°_t H$^+$	Cl$^-$	Br$^-$	I$^-$
20	−9 830	11 480	10 510	9 400
40	−15 900	18 500	17 050	15 110
60	−24 270	29 250	26 480	23 200
80	−28 450	37 950	33 910	28 630

[a] ΔG°_t in J mol^{-1}.

the structural effects of the solvent on the transfer process are revealed through these quantities. The continuous decrease of ΔH°_t with addition of diethylene glycol beyond 20 wt % organic solvent is associated with structure-making ion-solvent interactions although this effect decreases somewhat beyond 60 wt % diethylene glycol.

An examination of ΔS°_t (Table V) in the presence of increasing amounts of diethylene glycol in general supports the above conclusions. The positive value of ΔS°_t up to about 40 wt % diethylene glycol, which is similar to the observations in the case of HCl and HBr, is indicative of the net structure breaking effect of the ions of the acid which promote the hydrogen-bonded structure of water at these low compositions of the organic solvent. At higher compositions of diethylene glycol, ΔS°_t becomes continuously negative showing the net structure making effect of the ions which is aided by the strong electrostatic fields in media of low dielectric constant. It must, however, be mentioned that the small differences in the variation of ΔH°_t and ΔS°_t with solvent compostion between HCl and HBr on one side and HI on the other are most possibly associated with the nonelectrolytic contributions to the thermodynamic transfer parameters in the present case as suggested by Andrews et al. (*1*) for HI in methanol-water mixtures.

A plot of the standard molal free energy of transfer, ΔG°_t(HX), for the three halogen acids against the reciprocal of the anionic radius, "$1/r^-$" (*5*), in the solvent compositions from 20 to 80 wt % diethylene glycol at 25 °C according to the relation (*5*)

$$\Delta G^\circ_{t(HX)} = \Delta G^\circ_{t(H^+)} + ar_-^{-1} \tag{12}$$

where *a* is a constant and is linear and from the intercept at $1/r_- = 0$, $\Delta Gf^\circ_{t(H^+)}$, the free energy of transfer of the proton (molal scale), was obtained in all the compositions.

The transfer free energy of the halide ions in different solvent mixtures was then evaluated from the relation

$$\Delta G^\circ_{t(HX)} = \Delta G^\circ_{t(H^+)} + \Delta G^\circ_{t(X^-)} \tag{13}$$

These data are recorded in Table VI.

It is seen from this table that the transfer free energy of the proton is negative and decreases continuously with increasing additions of diethylene glycol which shows that all diethylene glycol-water mixtures are more basic than water and that the basicity increases with increasing amounts of organic solvent. These results are in qualitative agreement with those obtained (*12*) on the basis of the ferrocene redox couple reference method in these media. The transfer free energies of the halide ions, on the other hand, are positive and increase with increasing amount of the organic solvent. Thus the transfer of the halide ions from water to the diethylene glycol-water mixtures is thermodynamically not a favorable process. Similar results have been reported in other aqueous-organic solvent mixtures (*9*).

Glossary

E°_m, ${}_sE^\circ_c$, ${}_sE^\circ_N$	standard electrode potentials on molality, molarity, and mole fraction scales in solvent, V
${}_wE^\circ_m$, ${}_wE^\circ_c$, ${}_wE^\circ_N$	standard electrode potentials on molality, molarity, and mole fraction scales in water, V
k	(RT ln 10)/F, V
M_{xy}	$100/(x/M_x + y/M_y)$ average molecular weight of the solvent (x = wt % diethylene glycol (g/100 g), M_x = molecular weight of diethylene glycol, y = wt % water (g/100 g), M_y = molecular weight of water
ΔG°_t, ΔH°_t, ΔS°_t	free energies, enthalpies, and entropies of transfer on mole fraction scale, J
$\Delta G^\circ_{t(el)}$	electrostatic Gibbs free energy of transfer, J
$\Delta G^\circ_{t(nonel)}$	nonelectrostatic Gibbs free energy of transfer, J
K_s	$2R/F$ ln $(1000/M_{xy})$
K_w	$2R/F$ ln (1000/18.0154)

Literature Cited

(1) Andrews, A. L., Bennetto, H. P., Feakins, D., Tomkins, R. P. T., *J. Chem. Soc.*, 1486 (1968).

(2) Bax, D., DeLigny, C. L., Alfenaar, M., Mohr, N. J., *Recl. Trav. Chim. Pays-Bas*, **91**, 601 (1972).

(3) Feakins, D., Tomkins, R. P. T., *J. Chem. Soc.*, 1458 (1967).

(4) Feakins, D., Voice, P. J., *J. Chem. Soc., Faraday Trans.*, **68**, 1390 (1972).
(5) Feakins, D., Watson, P., *J. Chem. Soc.*, 4734 (1963).
(6) Franks, F., Ives, D. J. G., *Chem. Soc. Rev.*, **20**, 1 (1966).
(7) Janz, G. J., "Reference Electrodes", D. J. G. Ives and G. J. Janz, Eds., Academic Press, New York, 1961, Chapter 4, pp 209-11.
(8) Kalidas, C., Srinivas Rao, V., *J. Chem. Eng. Data*, **19**, 201 (1974).
(9) Kundu, K. K., Jana, D., Das, M. N., *Electrochim. Acta*, **18**, 95 (1973).
(10) Owen, B. B., *J. Am. Chem. Soc.*, **57**, 1526 (1935).
(11) Srinivas Rao, V., Kalidas, C., *J. Chem. Eng. Data*, **21**, 314 (1976).
(12) Srinivas Rao, V., Kalidas, C., *Indian J. Chem.*, **13**, 1303 (1975).

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Solvent Effects on Solubility and Dehydration of Strontium Chloride

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The solubility of $SrCl_2$ in mixtures of water with methanol, ethanol, 2-propanol, formic acid, acetic acid, and lactic acid at 25, 50, and 70 °C and the extent of dehydration of $SrCl_2 \cdot 6H_2O$ in the presence of these solvents have been studied. Achumow's equation is applied for the prediction of solubility of the salt in alcohols.

The salting out phenomenon is well-known, where a salt is added to a homogeneous mixture of two solvents to split this homogeneous phase into two partially miscible liquid phases. Likewise, addition of a nonaqueous solvent (water miscible) to a binary aqueous salt solution can considerably change the solubility and the nature of the equilibrating phase. The effect of such solvents can be known quantitatively by examining the phase diagrams of ternary systems, comprising the salt, water, and different water-miscible solvents, at various temperatures. Such diagrams would give the nature of phase transformation, if any, and the data on the extent of dehydration of a salt. The role of organic solvents in the dehydration of hydrated salts has been studied by many workers.[1-6]

The present work was undertaken to study the solubility of strontium chloride in different organic solvents, such as methanol, ethanol, 2-propanol, formic acid, acetic acid, and lactic acid. The same data indicate the extent of dehydration of hydrates of strontium chloride in the presence of these solvents. The relevant available literature and the solubility data pertaining to these systems at different temperatures are reported elsewhere.[7]

Experimental Section

All chemicals used were of analytical reagent grade. Karl Fisher reagent, for determination of water content, was prepared by a procedure described in the literature.[8]

The experimental studies in phase equilibria involve the following operations: (1) maintenance of constant temperature, (2) equilibration of the reaction complex, (3) separation of liquid phase from solid phase for analysis.

The equilibration cells containing reaction mixtures were immersed in a constant-temperature bath.[9,10] The bath liquid was ordinary water, and contained in a rectangular vessel (45 cm × 30 cm × 30 cm) made of brass sheet. The cells, in which the complex was equilibrated were made of Jena glass interchangeable ground glass joints. The lower part was about 14 cm long and the stopper (male joint) was 6 cm long. The cells were mounted vertically in the middle on a horizontal brass shaft (3 cm diameter) fixed to the center of the rectangular tank so that rotation of shaft will make the cells turn upside down once every revolution of the shaft. The shaft was rotated by means of worm-worm gears and electric motor, at the rate of about 12 rpm. At a time, six such cells were fixed to the shaft and these cells served as the paddle for stirring the bath liquid during equilibration. The level of the bath liquid was so adjusted that the cell is completely immersed in the bath liquid. During sampling, when the shaft is not rotating, the stirring of bath liquid was affected by circulating bath liquid by an external pump. The variation of temperature in various parts of the bath liquid was checked by using a Beckmann thermometer and was found to be less than ±0.05 °C of the control temperature.

Table I. Strontium Chloride-Formic Acid-Water

temp, °C	liquid compn, g/100 g of water		solid phase(s)
	solvent	salt	
25	61	62.3	$SrCl_2 \cdot 6H_2O$
25	132	74.3	$SrCl_2 \cdot 6H_2O$
25	146	78.5	$SrCl_2 \cdot 6H_2O$
25	156	80.7	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
25	179	83.6	$SrCl_2 \cdot 2H_2O$
25	211	84.6	$SrCl_2 \cdot 2H_2O$
25	230	86.7	$SrCl_2 \cdot 2H_2O$
25	263	89.1	$SrCl_2 \cdot 2H_2O$
25	326	97.2	$SrCl_2 \cdot 2H_2O$
25	415	113.5	$SrCl_2 \cdot 2H_2O$
25	521	131.2	$SrCl_2 \cdot 2H_2O$
25	720	173.2	$SrCl_2 \cdot 2H_2O$
50	49	81.6	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
50	65	82.0	$SrCl_2 \cdot 2H_2O$
50	167	85.9	$SrCl_2 \cdot 2H_2O$
50	220	90.1	$SrCl_2 \cdot 2H_2O$
50	300	100.0	$SrCl_2 \cdot 2H_2O$
50	342	104.0	$SrCl_2 \cdot 2H_2O$
50	433	121.0	$SrCl_2 \cdot 2H_2O$
50	546	143.0	$SrCl_2 \cdot 2H_2O$
50	630	167.0	$SrCl_2 \cdot 2H_2O$
50	655	165.0	$SrCl_2 \cdot 2H_2O$
50	680	172.3	$SrCl_2 \cdot 2H_2O$
70	126	87.3	$SrCl_2 \cdot 2H_2O$
70	277	103.0	$SrCl_2 \cdot 2H_2O$
70	374	120.0	$SrCl_2 \cdot 2H_2O$
70	430	128.0	$SrCl_2 \cdot 2H_2O$
70	490	142.0	$SrCl_2 \cdot 2H_2O$
70	508	146.0	$SrCl_2 \cdot 2H_2O + SrCl_2 \cdot 2H_2O$
70	526	147.0	$SrCl_2 \cdot H_2O$
70	565	153.5	$SrCl_2 \cdot H_2O$
70	577	156.5	$SrCl_2 \cdot H_2O$

For removal of liquid phase in equilibrium with solid phase, a simple jacketed pipet was used. The bath liquid was circulated in the outer jacket of the pipet in order to obviate any difficulty that may be caused by separation of crystals from the saturated solution during removal and transfer of the solution in the sampling bottle. After removal of the sample of liquid phase for analysis, most of the remaining liquid phase in the cell was removed by suction and the wet solid phase was taken for analyses.

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