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THE SYSTEM Na_2CO_3—$NaHCO_3$—CO_2—H_2O AT TEMPERATURES UP TO 200°

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ABSTRACT. The equilibrium conditions in the system above were obtained by a differential vapor pressure method and the results up to 200° are reported.

From measurements of the differences in vapor pressure between pure water and a salt solution it is possible in principle to obtain activity coefficients for the ions in solution. The vapor pressures of sodium chloride and sodium carbonate solutions up to 200° are given, but it was not possible to obtain results of sufficient accuracy to derive activity coefficients.

INTRODUCTION

Information on the system Na_2CO_3—$NaHCO_3$—CO_2—H_2O is required in understanding many problems which involve carbonate deposition in nature.

Results giving the equilibrium conditions were reported by Walker, Bray, and Johnston (1927) at 25° and 37°, and more recently by Mai and Babb (1955) at temperatures up to 65°C. Both workers used a wide range of concentrations, and the agreement between the two sets of results is satisfactory.

A sensitive method of measuring small differences in the vapor pressures over two liquids is often required in the investigation of two phase aqueous solutions at high temperatures (e.g. equilibria involving a second gas, accurate determination of the vapor pressure of salt solutions). Results from the present investigation showed that the mercury-in-glass manometer could be used to record small pressure differences up to at least 250°. The limiting factor in measuring small differences in water vapor pressure is the minimum temperature difference that can be maintained between the two containers. The behavior of a suitable differential pressure apparatus was tested on the carbonate system and in determining the vapor pressure of salt solutions.

THEORY

In this paper carbonic acid refers to the molecule H_2CO_3 and not to the mixture ($H_2O + CO_2$) often called by this name. At 25°, 0.259 percent of the total carbon dioxide in a pure water solution consists of H_2CO_3 (Wissbrun, French, and Patterson, 1954).

For the liquid-vapor equilibrium of carbon dioxide the following equation holds.

$$(CO_2) = B.\, f_{CO_2} \tag{1}$$

where B is an inverse Henry's Law coefficient, (CO_2) is the activity of molecular carbon dioxide in solution, and f_{CO_2} its fugacity in the vapor. In this paper rounded brackets indicate activities of species, and square brackets concentrations.

For the first and second ionization constants of carbonic acid at constant temperature and pressure the following relationships exist.

$$(H^+)\,(HCO_3'')/(H_2CO_3) = K_1 \tag{2}$$

$$(H^+)\,(CO_3'')/(HCO_3') = K_2 \tag{3}$$

The hydration of carbon dioxide in solution to carbonic acid is given by the equilibrium constant

$$K_s = (H_2CO_3)/f_{H_2O}.\ (CO_2) \tag{4}$$

where f_{H_2O} is the fugacity of water vapor. For the ionic reaction

$$2HCO_3'(\text{soln.}) \rightarrow CO_3''(\text{soln.}) + H_2O(\text{gas}) + CO_2(\text{gas})$$

the equilibrium constant K is equivalent to

$$K = (CO_3'').\ f_{H_2O}.\ f_{CO_2}./(HCO_3')^2$$

By substitution from equation (1) to (4) it can be shown that

$$K = K_2/K_1.\ B.\ K_s$$

The quantities determined directly from the experiments are the concentrations of sodium carbonate and bicarbonate in solution and the partial pressures of water and carbon dioxide.

Let $[Na_2CO_3].\ p_{CO_2}.\ p_{H_2O}/[NaHCO_3]^2 = k,$

$$(HCO_3') = \gamma_1\ [NaHCO_3],$$

and

$$(CO_3'') = \gamma_2\ [Na_2CO_3]\ .$$

γ_1 and γ_2 are the respective ion activity coefficients for the HCO_3' and CO_3'' ions. k may then be related to K.

$$k = K.\ \gamma_1^2/\gamma_2.\alpha_1.\alpha_2 = \frac{K_2}{K_1.K_s.\ B} \cdot \frac{\gamma_1^2}{\gamma_2.\alpha_1.\alpha_2}$$

α_1 and α_2 are the fugacity coefficients of CO_2 and H_2O in the vapor phase.

The apparent acid dissociation constant of the mixture $(CO_2 + H_2O)$ is labelled K_1'.

$$\begin{aligned} K_1' &= (H^+)\ (HCO_3')/(H_2CO_3 + CO_2) \\ &= (H^+)\ (HCO_3')/(CO_2)\ (1 + K_s.f_{H_2O}) \\ &= K_1.K_s.\ f_{H_2O}/(1 + K_s.\ f_{H_2O}) \\ &\cong K_1.K_s.\ f_{H_2O} \end{aligned}$$

The error involved in the last approximation is equal to the percentage of total carbon dioxide present in solution as carbonic acid. This is unlikely to be greater than 1 percent in the temperature range examined.

THE PRESENT EXPERIMENTAL METHOD

The present study of the system Na_2CO_3—$NaHCO_3$—CO_2—H_2O, was made by a differential pressure technique. Figure 1 is a diagrammatic outline of the apparatus. In a 3 inch stainless steel block two holes were drilled; the large one had a volume of approximately 105 cc and the other one held approximately 5 cc. In the experiments the small chamber contained pure water, and the large one a carbonate solution of known initial composition. The difference in pressure, as indicated by a thick-walled glass manometer, was equal to the partial pressure of carbon dioxide above the carbonate solution less the lowering of water vapor pressure by the salts in solution. The glass manometer was shielded by heavy metal gauze in case of an explosion.

The technique was as follows: the high pressure lines (capillary stainless steel tubing) were removed from the top of the glass-metal connection and connected to dead-end pieces. The bombs and all the lines at this stage were completely dry. Known quantities of sodium bicarbonate and carbonate were placed in the large chamber, and both heads placed on the bomb.

With all valves open the system was quickly evacuated to better than 1

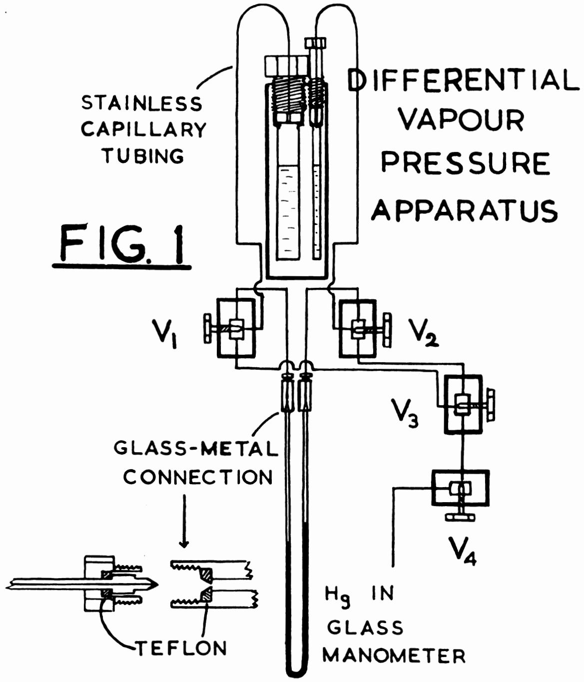

Fig. 1. Apparatus for measuring small differences between the vapor pressure of two solutions.

mm vacuum by a rotary oil pump. This was found not to affect appreciably the dry $NaHCO_3$. The evacuation was through valve 4 which was also connected to a source of degassed water through a T piece.

The degassed water was prepared by boiling water under reflux for 2-3 hours under a partial vacuum in an apparatus of the type described by Law (1949). With valve 2 closed, approximately 70 cc of water was let into the large chamber and valve 1 closed. Valve 2 was temporarily opened to admit a few cc of water into the small chamber. At this stage all the lines were filled with degassed water at atmospheric pressure. The manometer was always filled with water from the mercury surface up to the top of the glass-metal connection. With the latter overflowing with water the lines were again connected to it with valves 3 and 4 closed.

The bomb was heated in an 18 inch diameter 10 gallon bath of oil which was surrounded by a foot thickness packing of diatomaceous earth. A thermostat controlled the temperature to about ± 0.1° and the bath was vigorously stirred. The fact that the two chambers were in the one massive piece of metal damped out temperature variations in the bath. With pure water in both cavities the differences in pressure registered at 200° were of the order of ± 0.3 cm. As at 200° the change of vapor pressure is about 24 cm for a degree temperature difference, the difference in temperature between the two chambers was less than 0.01°.

After the apparatus had been at the temperature of observation for about an hour, valves 1 and 2 were opened and the values of Δp read on the manometer until they remained constant. This usually required less than an hour. With a little experience the manometer could be pre-set to about the value of Δp expected so that there was no appreciable transfer of water into either the solution or the small chamber when the mercury moved.

The weight of solution in the bomb was measured after the experiments and the concentrations estimated. In the calculations, corrections were made for the water transferred by changes in the mercury level, the water in the vapor space, the depression of the water vapor pressure by the salt in solution, the carbonate in the bicarbonate used, and the change in the original carbonate-bicarbonate ratio by the reaction to form carbon dioxide in the vapor and liquid.

The only correction which was very appreciable was the depression of the water vapor pressure by the salts in solution. Values for this correction were taken from experiments reported below with the assumption that the osmotic effect of NaCl equalled that of $NaHCO_3$.

The lines from the bomb were arranged symmetrically about the manometer and the heads of the two chambers were at the same level. The values of Δp were corrected to pressures in centimetres of mercury by taking the effective density of the manometer liquid as 12.55 g/cc.

RESULTS

Three series of experiments were completed at ionic strengths equal to 0.2, 0.5, and 1.0. A typical experimental result is calculated in detail.

Ionic strength (μ) = 1 T = 162°C
Bomb volume 105.4 cc The $NaHCO_3$ used contained 0.0034 moles Na_2CO_3/mole $NaHCO_3$.
Na_2CO_3 added = 0.01063 moles
$NaHCO_3$ added = 0.0385 moles
Weight of water in solution = 67.9 g
v.p. pure water, 162° = 487.7 cm Hg
Correction for salts = 11.6 cm Hg
v.p. water over solution = 476.1 cm Hg
Δp = 12.9 cm Hg
Partial pressure of CO_2 (p_{CO_2}) = 24.5 cm Hg
Volume of solution (162°) = 76.6 cc
Volume of gas = 28.8 cc
Total moles of CO_2 in system = 0.00048
Corrected moles $NaHCO_3$ = 0.03755
Corrected mole Na_2CO_3 = 0.01111
$NaHCO_3$ concentration $[NaHCO_3] = 0.553$ moles/1000 g water
Na_2CO_3 concentration $[Na_2CO_3] = 0.162$ moles/1000 g water
$k = p_{H_2O} \cdot p_{CO_2} \cdot [Na_2CO_3]/[NaHCO_3]^2$ = 1.08 at.^{2} kg.mole^{-1}

The total quantity of carbon dioxide in the system was calculated from the partial pressure of the gas, the volumes of gas and liquid, and the solubility of carbon dioxide reported in the first paper of this series (Ellis, 1959).

TABLE 1

T°C	Wt.H_2O (g)	p_{H_2O} corrected (cm Hg)	ΔP (cm Hg)	p_{CO_2} (cm Hg)	Moles CO_2 in system $\times 10^4$	Corrected $NaHCO_3$ moles per 1000g H_2O $\times 10$	Corrected Na_2CO_3 moles per 1000g H_2O $\times 10^2$	Volume Soln. T° (cc)	k (at.^{2} kg. moles^{-1})
	$\mu = 0.2$								
133.5	72.6	237.1	3.9	5.0	1.0	1.32	2.11	78.4	0.24
162.5	72.6	488.8	5.2	7.4	1.4	1.31	2.16	80.7	0.79
190.5	72.6	948.0	5.2	9.2	1.5	1.31	2.18	83.3	1.91
126	72.8	178.6	9.8	10.7	2.3	1.57	1.33	78.0	0.18
163	72.8	497.4	11.6	14.2	2.7	1.56	1.39	81.0	0.69
193	72.8	999.4	13.7	19.0	3.2	1.55	1.46	83.8	2.00
119	70.8	143.6	2.5	3.2	0.7	1.22	2.61	75.4	0.18
147	70.8	327.9	3.3	4.8	1.0	1.23	2.66	77.3	0.48
172	70.8	620.8	2.6	5.2	1.0	1.21	2.66	79.4	1.02
194	70.8	1022.4	2.3	6.4	1.1	1.23	2.67	81.4	2.00
	$\mu = 0.5$								
125.5	49.8	158.1	25.2	27.9	6.6	3.83	4.44	53.9	0.231
165	49.8	518.3	25.6	32.9	8.0	3.78	4.72	56.6	0.98
120	49.8	146.6	20.5	22.8	5.5	3.88	4.21	53.5	0.162
180	49.8	742.5	28.0	37.5	8.8	3.75	4.87	56.9	1.69
124	58.5	166.6	10.9	13.1	3.3	2.88	4.95	62.6	0.226
163.5	58.5	499.8	8.1	14.6	3.3	2.88	4.95	65.1	0.754
180	58.5	743.5	12.0	20.5	4.4	2.84	5.14	66.3	1.68
127	66.5	182.3	38.4	41.2	9.1	4.36	3.62	72.4	0.247
158	66.5	434.0	45.6	52.1	10.5	4.32	3.83	74.7	0.79
197	66.5	1079.6	47.0	61.9	11.1	4.30	3.92	78.0	2.45
125	75.3	170.0	4.1	6.2	1.3	2.41	7.61	80.8	0.239
162	75.3	484.9	2.0	7.6	1.4	2.38	7.62	83.8	0.85
190	75.3	939.2	2.1	9.5	1.5	2.38	7.64	86.4	2.08
	$\mu = 1$								
124	83.6	164.0	45.8	50.6	9.3	6.38	7.20	90.7	0.254
157	83.6	417.5	53.3	65.1	10.0	6.38	7.28	93.5	0.842
187	83.6	859.0	59.8	81.7	11.7	6.33	7.49	96.7	2.27
125.5	69.3	172.8	12.8	16.8	3.7	5.45	15.9	75.2	0.269
160.5	69.3	458.2	14.0	25.4	4.9	5.42	16.2	77.9	1.11
191	69.3	941.0	10.9	31.9	5.5	5.40	17.0	80.6	3.03
126.5	67.9	177.5	11.5	15.6	3.4	5.57	16.2	73.9	0.25
162	67.9	476.1	12.9	24.5	4.8	5.53	16.4	76.6	1.08
192	67.9	961.7	11.3	32.7	5.8	5.52	16.5	79.2	3.30
126.5	71.3	177.7	27.5	32.6	6.9	6.68	13.1	77.3	0.294
163	71.3	487.1	35.1	48.0	8.9	6.62	13.4	80.3	1.24
192	71.3	959.8	37.1	60.4	10.2	6.59	13.6	82.0	3.14
127	67.4	180.2	20.7	25.6	5.7	6.48	15.6	73.5	0.296
165	67.4	513.0	24.9	37.5	7.3	6.43	15.8	76.4	1.27
195	67.4	1025.8	25.5	48.6	8.6	6.39	16.0	79.2	3.38

The results from the experiments are given in table 1 and the values of log k are plotted against 1/T° K in figure 2.

It was shown that $K = k.\ \gamma_2.\alpha_1.\alpha_2/\gamma_1^2$
where K is the thermodynamic equilibrium constant for the reaction

$$2HCO_3{}' \text{ (soln.)} \rightarrow CO_3{}'' \text{ (soln.)} + H_2O\text{(gas)} + CO_2\text{(gas)}$$

At constant pressure and composition

$$\frac{\partial \ln K}{\partial T} = \frac{\partial \ln k}{\partial T} + \frac{\partial \ln(\gamma_2.\alpha_1.\alpha_2/\gamma_1^2)}{\partial t}$$

$$\Delta H^\circ = \Delta H + \Delta h$$

where ΔH° is the standard increment in heat content for the reaction and Δh incorporates the overall change in relative partial molal heat contents of ions in solution and gases in the vapor. Table 2 gives values of ΔH obtained from the experiments.

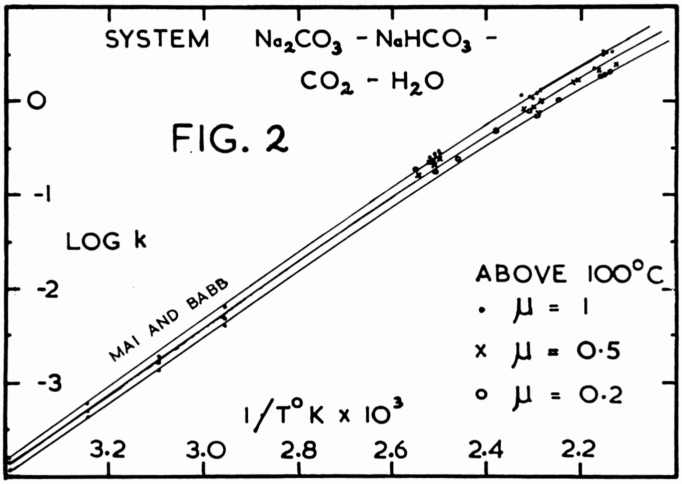

Fig. 2. The results obtained for k at various temperatures
($k = [Na_2CO_3].\ p_{CO_2}.\ p_{H_2O}/[NaHCO_3]$).

TABLE 2

T°C	25	50	100	150	200
$\Delta H(\mu = 1)$	16400	16400	15800	14600	13000 cals./mole
$\Delta H(\mu = 0.2)$	15900	15900	15500	14200	12500 cals./mole
ΔH_{H_2O}(vapzn.)	10480	10230	9697	9074	8348 cals./mole
$\Delta H^*(\mu = 0.2)$	5700	5670	5800	5130	4150 cals./mole

ΔH_{H_2O} (vapzn.) is the latent heat of vaporization for pure water (Keenan and Keyes, 1936), and assuming that this heat of vaporization is the same for a solution of ionic strength $\mu = 0.2$, $\Delta H^* = \Delta H - \Delta H_{H_2O}$ (vapzn.) is the experimental increment in heat content if the reference state of water is taken as the liquid rather than the gas.

For the reaction

$$2NaHCO_3\text{(soln.)} \rightarrow Na_2CO_3\text{(soln.)} + H_2O(1) + CO_2(g)$$

ΔCp^* is very small at temperatures below 100° (ΔH^* is constant within experimental error). At higher temperatures ΔH for vaporization of CO_2 from solution decreases rapidly (see first paper of this series) and this will be a major factor in the decrease of ΔH^*.

If as an approximation in the equation

$$k = \frac{K_2}{K_1.K_s.B} \cdot \frac{\gamma_1^2}{\gamma_2.\alpha_1.\alpha_2}$$

, it is assumed that the fugacity coefficients α_1 and α_2 are unity, and that $K_1' = K_1.K_2.f_{H_2O}$,

$$\text{then } k = \frac{K_2.p_{H_2O}.\ \gamma_1^2}{K_1'.B.\ \gamma_2} = k' \,.\, \frac{\gamma_1^2}{\gamma_2}$$

Approximate values of k′ are calculated in table 3 from known experimental data (K_1' up to 50°, Harned and Davis, 1943; K_2 up to 50°, Harned and Scholes, 1941; and up to 90°, Cuta and Stráfelda, 1954). Values of K_1' and K_2 are extrapolated to higher temperatures by means of equations of the type used by Pitzer (1937). Values of B were obtained from the solubility results reported earlier.

Mean ionic activity coefficients $\gamma_\pm$ determined by experiment are related to the individual ion activity coefficients by the equation

$$\gamma_\pm^{\,n+m} = \gamma^n_+ . \gamma^m_- \quad \text{(Harned and Owen, 1950, p. 10)}$$

where n and m are the number of positive and negative ions respectively produced by a salt.

TABLE 3

T°C	K_2 × 10^{11}	K_1' × 10^7	B × 10^2 (mol. at.$^{-1}$kg^{-1})	p_{H_2O} (at.)	k′	k (μ=1.0)	γ_1^2/γ_2 (μ=1.0)
25	4.69	4.45	3.43	0.0313	9.6×10^{-5}	2.6×10^{-4}	2.7
50	6.73	5.16	1.89	0.1217	8.4×10^{-4}	2.1×10^{-3}	2.5
100	7.3	5.8	1.18	1.00	1.1×10^{-2}	6.3×10^{-2}	5.7
150	5.6	4.7	1.14	4.70	4.4×10^{-2}	0.74	17
200	3.8	2.8	1.27	15.3	0.16	4.3	27

$$\text{Therefore} \qquad \frac{\gamma_1^2}{\gamma_2} = \frac{\gamma_\pm^{4}\ (\text{NaHCO}_3\ \text{soln.})}{\gamma_\pm^{3}\ (\text{Na}_2\text{CO}_3\ \text{soln.})}$$

$$\cong \frac{\gamma_\pm^{4}\ (\text{NaCl soln.})}{\gamma_\pm^{3}\ (\text{Na}_2\text{CO}_3\ \text{soln.})}$$

Values of $\gamma_\pm$ are reported by Harned and Owen (1950) p. 557, for NaCl solutions up to 100°, and for Na_2CO_3 solutions up to 95° by Taylor (1955). For solutions in the series $\mu = 1.0$, $[Na_2CO_3]$ and $[NaHCO_3]$ equal approximately 0.1 m and 0.75 m respectively. Values of the ratio,

$$\gamma_\pm^{4}\ (\text{NaCl soln.})\ /\ \gamma_\pm^{3}\ (\text{Na}_2\text{CO}_3\ \text{soln.}) \cong \gamma_1^2/\gamma_2\,,$$

at these concentrations are given in table 4.

TABLE 4

T°C	25	50	75	100	125
$\gamma\pm$ (0.75m NaCl)	0.666	0.665	0.643	0.626	0.600
$\gamma\pm$ (0.1m Na_2CO_3)	0.465	0.524	0.505	0.430	0.30
Calc. Ratio γ_1^2/γ_2	1.95	1.4	1.3	1.9	4.8

The calculated values of γ_1^2/γ_2 in table 4 are intended only as a qualitative illustration and cannot be expected to equal the experimental values in table 3. The mean activity coefficients for 0.1m Na_2CO_3 in a 0.75m $NaHCO_3$ solution, will be different, and probably lower than $\gamma_\pm$ (Na_2CO_3) in a pure 0.1m solution.

However, the figures show that the rapid increase in γ_1^2/γ_2 at higher temperatures is caused mainly by the decrease in the mean activity coefficient of sodium carbonate. This would indicate that this substance is only slightly dissociated in high temperature water. Its decrease in solubility to almost zero at the critical temperature of water is therefore not unexpected.

VAPOR PRESSURES OF NaCl and Na_2CO_3 SOLUTIONS

The water vapor pressures over solutions of sodium chloride and sodium carbonate were determined up to 200° using the differential pressure apparatus.

The procedure used was to dry and evacuate the bomb and lines, and with valve 1 closed, to allow degassed water to enter the small chamber. Valve 2 and valve 4 were then closed. The solution to be studied was also degassed in the reflux apparatus and approximately 70 cc of degassed solution was allowed to enter the large chamber through valve 1, valve 3 and valve 4. All valves were then closed and the manometer connections made as before. The manometer was pre-set to the approximate level expected in the experiment.

The concentration and weight of the solution was obtained after the experiment, and where appropriate, corrections were made as before. The practical osmotic coefficient ϕ is defined by the equation

$$\mu_{H_2O} = \mu^{o}_{H_2O} - \phi RT \frac{t.m}{55.51}$$

or $\ln a_{H_2O} = - \phi\ t.m/55.51$ (Harned and Owen, 1950, p. 13). The activity of water $a_{H_2O} = f_{H_2O} / f^{o}_{H_2O}$ where f_{H_2O} and $f^{o}_{H_2O}$ are the fugacities of water over the solution, and over pure water. If it is assumed that the fugacity ratio can be replaced by $p_{H_2O} / p^{o}_{H_2O}$, i.e., the fugacity coefficients are the same

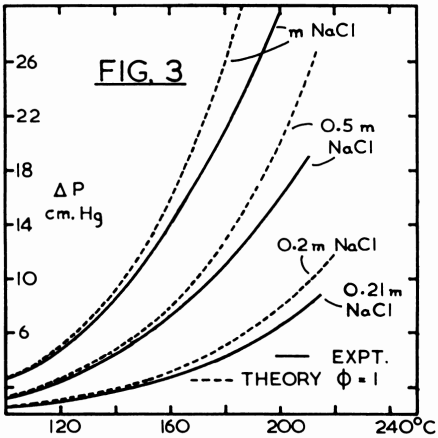

Fig. 3. The difference between the vapor pressure of sodium chloride solutions, and pure water at various temperatures.

for water vapor over the solution and over pure water, then

$$\phi = \frac{55.51}{t.m} \ln \frac{p_{H_2O}}{p^{o}_{H_2O}}$$

where t is the number of ions formed by the salt, m its molality, p_{H_2O} the water vapor pressure over the solution, and $p^{o}_{H_2O}$ that over pure water.

The results of the determinations are given in figures 3 and 4. Lines for various concentrations, obtained by giving ϕ a value of unity, are also shown.

Harned and Owen (1950, p. 363) tabulate osmotic coefficients for sodium chloride solutions up to 100°. Table 5 gives some of their values for ϕ and the values obtained with sodium chloride in this work above 100°.

Within experimental error the present results follow on smoothly from the previous values.

TABLE 5

Values of ϕ for NaCl Solutions

T°C m	60	80	100	120	140	160	180	200
0.2	0.9210	0.9178	0.9135	—	—	—	0.82	0.80
0.5	0.9234	0.9195	0.9145	0.91	0.91	0.88	0.82	0.77
1.0	0.9442	0.9402	0.9345	0.91	0.88	0.86	0.785	0.705

It was planned originally to obtain mean activity coefficients for ions of various salts from the vapor pressure measurements by the standard process (Taylor, 1955) of applying an integrated form of the Gibbs-Duhem equation.

$$\log \frac{\gamma_{\pm}\ (m)}{\gamma_{\pm}\ (m_r)} = -\int_{a_1,\ \text{at}\ m_r}^{a_1,\ \text{at}\ m} \frac{55.51}{t.m}\, d \log a_1 - \log m/m_r$$

where m_r is a reference molality at low salt concentrations below which values of the activity coefficients can be extrapolated to infinite dilutions by the Debye-Hückel theory, and a_1 is the activity of water.

To derive useful values for $\gamma_{\pm}$ (m) it would be necessary to obtain values

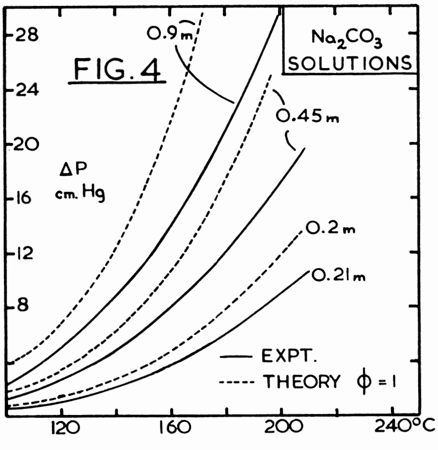

Fig. 4. The difference between the vapor pressure of sodium carbonate solutions, and pure water at various temperatures.

of Δp for solutions down to about 0.1m with an accuracy of the order of 1 percent. It is unlikely that the present results are better than ± 3mm in Δp over most of the range. Even at 200° this would amount to an error of almost ± 10 percent in activity coefficients at concentrations of 0.1m.

The results are therefore left in terms of pressure differences and osmotic coefficients, and as such should be useful in calculating water vapor pressures over hydrothermal solutions.

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