[AMERICAN JOURNAL OF SCIENCE, VOL. 257, MARCH 1959, P. 217-234]

THE SOLUBILITY OF CARBON DIOXIDE IN WATER AT HIGH TEMPERATURES

A. J. ELLIS*

Chemistry Dept., University of Otago, Dunedin, New Zealand

ABSTRACT. There are few results available in the literature for the solubilities of gases in water over 100°C, and for the geologically important gas carbon dioxide there is no information. In this paper the presentation and interpretation of high temperature gas solubilities is discussed, and values are reported for the solubility of carbon dioxide in water up to 350°C. The anomalous behavior of water compared with other liquids as a solvent for gases is reviewed briefly.

Extrapolation of solubility data from low temperatures can be completely misleading unless it is realized that gas solubility coefficients pass through minimum values, usually in the temperature range 70° to 200°C.

INTRODUCTION

In the investigation of many natural hydrothermal processes, a knowledge is required of the solubility of carbon dioxide in water above 100°C. The pH of many hydrothermal solutions is controlled by the buffer system bicarbonate-carbon dioxide, and the conditions for the deposition of many minerals, especially carbonates and sulphides, are defined in turn by the pH of the solutions.

Detailed information on the system $CaCO_3$—CO_2—H_2O was given by Miller (1952), but his experiments were terminated at 100° because information was not available on the system CO_2—H_2O at higher temperatures. Results are given below for the solubility of carbon dioxide in water up to 350°C. In two further papers, the equilibrium condition in the system Na_2CO_3—$NaHCO_3$—CO_2—H_2O up to 220°, and the solubility of calcite in carbon dioxide solutions up to 300° will be reported.

RESULTS REPORTED FOR OTHER GASES

There has been little work on the solubilities of gases in water over 100°C. Before 1952, results available were for ammonia up to 150° at partial pressures of gas from 0.01 to 10 atmospheres (Clifford and Hunter, 1933), for nitrogen up to 240°C at pressures of 100, 200 and 300 atmospheres (Saddington and Krase, 1934), and for hydrogen up to 220° at 31 to 116 atmospheres (Ipatieff and Teodorovich, 1934).

Pray, Schweickert and Minnich (1952) reported the solubilities of O_2, H_2, N_2, He and A up to about 340° with partial pressures of gas approximately equal to that of water vapor. Henry's Law was obeyed within the accuracy of their experiments (about $\pm 5\%$) to at least 35 atmospheres for the gases examined.

The Henry's Law coefficient does not remain constant at high gas pressures of the order of hundreds of atmospheres, but an improvement is noticed at higher temperatures (Saddington and Krase, 1934). These workers found an almost linear relationship between the partial pressure of nitrogen, p_{N2}, and its mole fraction in solution, x_{N2}, up to 300 atmospheres at 240°.

* Present address: Dominion Laboratory, Dept. of Scientific & Industrial Research, Wellington, New Zealand.

METHODS OF EXPRESSING GAS SOLUBILITY

The results from gas solubility or distribution measurements at constant temperature are usually expressed by means of one of the following coefficients. β (mean Bunsen absorption coefficient) is the volume of gas (measured at N.T.P.) dissolved in one volume of solvent, when free of gas, divided by the partial pressure of the gas in atmospheres.

λ (Ostwald coefficient) is the fraction

$$\frac{\text{grams gas/cc. liquid phase}}{\text{grams gas/cc. vapor phase}}$$ (as defined by Saddington and Krase).

$K = p_g/x$ (Henry's Law coefficient). p_g is the partial pressure of the gas, and x is the ratio of the moles of gas to the sum of moles of gas and water in solution.

The coefficient β was designed originally for interpreting solubilities at room temperatures where the concentration of water in the gas phase is small. In the presence of a steam phase of moderate density it is often convenient to use distribution coefficients of the Ostwald type. In the present work two other distribution coefficients are used. These are defined below.

(1) $A = \dfrac{n^l_a/n^l_{H_2O}}{n^v_a/n^v_{H_2O}}$, where n_a is the number of moles of gas (a), and n_{H_2O} the number of moles of water in the liquid (l) and vapor (v) phases.

(2) $D = x^l_a/x^v_a$, where $x_a = n_a/(n_a + n_{H_2O})$ in the liquid and vapor phases.

(3) It can be shown that $D = A\,[1 + (n^v_a/n^v_{H_2O})(1 - D)]$ where the value of $(1 - D)$ is close to unity, except at temperatures approaching the critical point. When p_a is very much less than p_{H_2O}, D is approximately equal to A.

β and K relate the *amount* of gas dissolved in the liquid to the partial pressure (or better, the fugacity) of the gas in the vapor phase, while λ, A, and D express the *distribution* of the gas between two phases.

The Henry's Law coefficient is equivalent to $K = p_a/x_a = P/D$, where P is the total pressure of the system, water + gas. The partial pressure of a gas is defined by the equation $p_a = P.x_a$. This will not be the actual pressure exerted by molecular species (a) unless the gas mixture is ideal. To obtain the chemical potential μ of (a) from the equation

$$\mu_a = \mu_a^o(T) + RT \ln p_a\alpha_a$$

the fugacity coefficient α_a must be evaluated. α_a incorporates all the deviations from ideal behavior caused by gas imperfections and interactions.

The coefficients A and D are useful for showing the distribution of small amounts of gas between water and steam phases. This situation is often met with in geological systems. Along with the Ostwald coefficient they have the advantage of becoming equal to unity at the critical temperature of the mixture, but they become insensitive as an indication of gas distribution at high gas pressures.

$$D = \frac{P}{K} = \frac{p_{H_2O} + p_a}{K}$$

If K is assumed to remain constant with variations in pressure, when p_a is very much greater than p_{H_2O}, D becomes approximately proportional to the pressure of the gas and therefore of little value.

The relationship of A to β is given by the equation

$$A = \frac{\beta . M_{H_2O} . p_{H_2O} . \rho^0_a .}{M_a . f_{H_2O} . \rho^1}$$

M_a and M_{H_2O} are the molecular weights of (a) and water, ρ^1 the density of the liquid phase, ρ^0_a the density of the gas (a) at 0°C and 1 atmosphere, and f_{H_2O} the weight fraction of water in the liquid solution.

The coefficients β and λ show minima for many gases at temperatures in the vicinity of 100°. An example is the solubility of nitrogen at 100 atmospheres pressure (Saddington and Krase, 1934). The actual temperature of maximum solubility depends on the solubility coefficient used.

TABLE 1

T°C	50	65	80	125	180
100β	1.10	0.96	0.95	1.13	1.45

The Henry's Law coefficient K for each gas shows a maximum with increasing temperature. At the critical temperature of the mixture, K = P (total pressure).

Weight distribution coefficients such as A or D do not show minimum values with increasing temperature, but increase continuously up to the critical point distribution of unity. The distribution of gas between liquid and vapor changes rapidly just below the critical region due to rapid changes in the structure of water.

If the values of the solubility or distribution coefficients are extrapolated to zero gas pressure, constants (e.g. K^0, A^0, or D^0) are obtained for a gas at each temperature. It is considered that the constants at zero gas pressure provide the best measure of the solubility of a gas in a liquid, or its distribution between two phases. Values at high gas pressures emphasize factors arising from imperfect gas behavior. At zero gas pressure the coefficients A and D become equivalent.

In figure 1 (from Ellis and Fyfe, 1957) a plot of log D^0 versus log (ρ^v / ρ^1) is given for various gases for which experimental data are at present available. Lines of slight curvature from room temperatures up to the critical temperature are obtained. The density of a phase seems to be the factor controlling most vapor-liquid distributions. Styrikovich, Khaibullin, and Tshvirashvili (1955) found that the coefficient, A, for the distribtuion of SiO_2 NaCl, $CaCl_2$, and Na_2SO_4 between vapor and liquid water phases was related to the density, ρ, by the following relationship

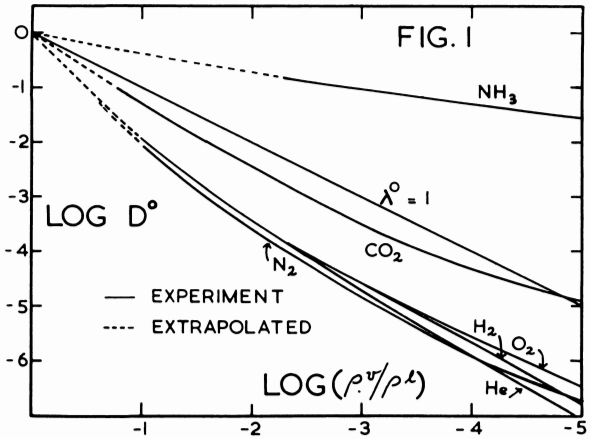

Fig. 1. Distribution of various gases between liquid and vapor phases of water up to the critical point.

$$A = \left(\frac{\rho^v}{\rho^l} \right)^m$$, where m is a constant for each substance.

From this type of graph it is possible to predict the approximate high temperature solubilities of gases from values below 100°C. In figure 1, $\lambda^\circ = 1$ is given as a line of reference. Along this line the mass of gas is the same in unit volumes of both liquid and vapor.

CO_2 SOLUBILITY AT LOWER TEMPERATURES

The two most important sets of results are those of Zel'venskii (1937) and Wiebe and Gaddy (1939, 1940). These workers reported values for carbon dioxide solubilities up to 100° at gas pressures ranging from 25 to 700 atmospheres. In table 2 the values reported have been extrapolated to zero gas pressures and values of K°, and A° or D° obtained. The agreement between

TABLE 2

T°C	Source*	K° (at.) (Henry's Law)	D° or A° $\times 10^6$	$P = p_{H_2O}$(at.)
0	Z	680	8.9	0.00603
18	W	1450	14.0	0.0203
25	Z	1640	19.0	0.0312
31	W	2000	22	0.0442
50	Z	2870	42	0.121
50	W	2980	41	0.121
75	Z	3900	98	0.380
75	W	4230	90	0.380
100	W	5270	190	1
100	Z	5150	195	1

* Z = Zel'venskii, W = Wiebe and Gaddy.

the solubility values reported by the two workers is usually better than ± 5 percent. Wiebe and Gaddy's results were obtained by a rather more satisfactory technique.

An abstract of Zel'venskii's paper stated that a "corrected thermodynamic form of Henry's Law" was obeyed to 30 atmospheres at 25°, 55 atmospheres at 50°, and 95 atmospheres at 100°C. The original was not available but this presumably refers to Henry's Law applied to the un-ionized fraction of carbon dioxide in solution.

APPARATUS AND PROCEDURE

Saddington and Krase (1934) analyzed both the liquid and vapor phases in equilibrium with a continuous stream of high pressure gas. Wiebe and Gaddy (1939), and also Pray, Schweickert and Minnich (1952) analyzed the liquid phase only and recorded the total pressure of gas + water vapor. This is satisfactory only at high gas pressures. Wiebe and Gaddy (1941) later determined the solubility relationships in the vapor phase of the system CO_2—H_2O.

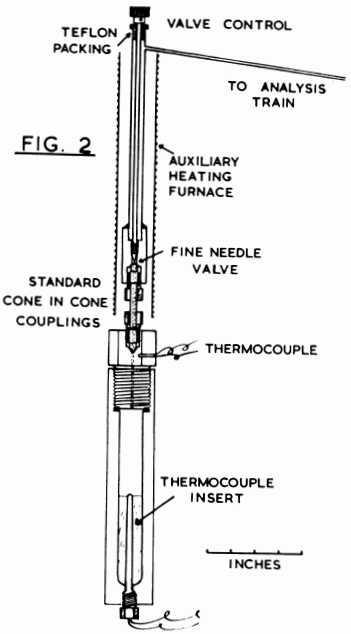

Fig. 2. Bomb with sampling valve.

In the present investigation the apparatus shown in figure 2 was used. A system of known composition was contained in a stainless steel bomb of approximately 100 cc capacity. The liquid volume was approximately half to two-thirds of the total bomb volume at the temperature of the experiment. The whole assembly up to the lead-off tube to the analysis train was heated in a 3" diameter electric tube furnace. The temperature gradient between the thermocouple inserted in the liquid and the one in the bomb head was usually about

2-3°, the top being hotter. Stainless steel was used for all parts except the lead-off tube which was silver.

The vapor phase was sampled through a needle valve capable of fine control. It was necessary to maintain the sampling valve assembly at a higher temperature than the bomb (about 10-20°) by means of an auxiliary furnace to prevent condensation of the steam sample. The valve chamber was sealed and vacuum tight.

A known mixture of carbon dioxide and water was generated in the bomb by the reaction of sodium bicarbonate with hydrochloric acid. Known amounts of water and bicarbonate were placed in the bomb, and standard hydrochloric acid placed in a thin-walled 7 cc stainless steel tube which was too wide to fall below the top of the thermocouple insert. The bomb-head and valve were connected, the bomb quickly evacuated, and the assembly was then inverted and agitated to ensure complete mixing of the acid and bicarbonate solutions.

Preliminary experiments showed that if the apparatus was maintained at a temperature overnight this was sufficient time for equilibrium to be established between the liquid and gas phases.

A fraction of the vapor phase (about 10 percent of the phase) was then sampled. The sampling train is shown in figure 3. With valve 2 closed and the remaining valves open, the sampling train and the valve chamber were evacu-

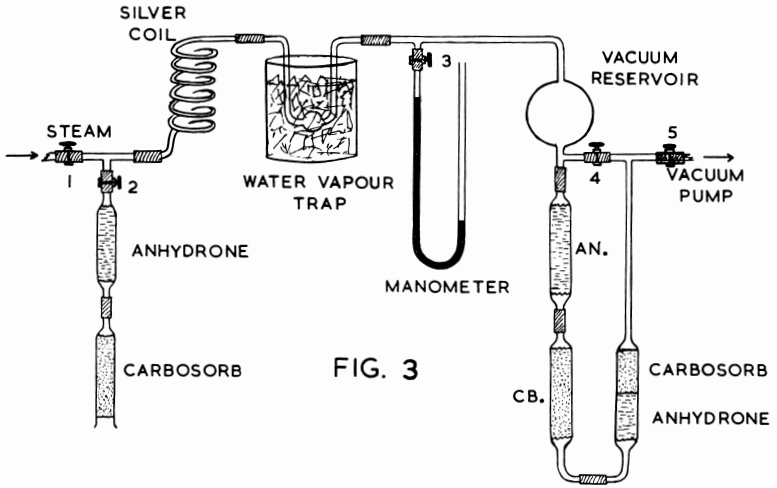

FIG. 3

Fig. 3. Train for analysis of steam phase.

ated. Valves 3, 4 and 5 were then closed, and a sample of steam allowed to escape from the bomb in a single burst lasting only about a second. The water-vapor trap in an ice-salt mixture, and the silver coil which was also cooled, collected almost all the condensed steam. Condensation did not occur until the steam reached the silver coil as the lead-off tube was short and was kept at about 100° until after valve 1. Valve 5 was opened and the system again evacuated, thus pulling most of the carbon dioxide through the Carbosorb tube (CB). Valves 1 and 5 were then closed and valve 2 opened slowly. With valve 5 opened slightly, air purified from water and carbon dioxide was pulled

through the apparatus through valve 2 for about 30 minutes to ensure that all the carbon dioxide from the sample was collected in the Carbosorb. The water in the traps and Anhydrone tube (AN), and the carbon dioxide in the tube (CB) were then weighed. In this way the weight ratio of carbon dioxide to water in the steam phase was obtained.

Sufficient acid was added to react with rather less than half the bicarbonate present. It was found that a solution of carbon dioxide and sodium chloride caused appreciable corrosion in the bomb, whereas with an approximately equimolar mixture of bicarbonate and carbon dioxide corrosion was negligible. A small correction was necessary for the dissociation of the bicarbonate remaining in solution by the reaction

$$2HCO'_3 \rightarrow CO_3'' + H_2O + CO_2$$

Information on this reaction is reported in the second paper of this series.

Allowance was made for the increase in volume of the bomb due to thermal expansion. The bomb volume was 97.3 cc, measured at 20°C with the tube for HCl in place. The volume was estimated for other temperatures by taking the coefficient of linear thermal expansion of stainless steel as equal to 1.0×10^{-5} deg. $^{-1}$

The volume of the solution at a temperature was obtained from its volume at 20° by multiplying by the density (ρ) ratio for liquid water $\rho^{20}{}_{H_2O} / \rho^{T}{}_{H_2O}$ obtained from the steam tables of Keenan and Keyes (1936).

A typical experiment is worked through in detail below.

T = 257°C NaHCO$_3$ added	= 1.680 g
(purity 99.7% remainder assumed Na$_2$CO$_3$)	= 0.0200 moles
HCl added	= 0.00797 moles
Volume solution 20°	= 52.75 cc
Volume solution 20° corrected for H_2O in steam	= 52.04 cc
Volume solution 257°	= 65.9 cc
Volume bomb 257°	= 98.0 cc
Volume steam phase	= 32.1 cc
Wt. water in steam sample	= 0.0629 g
Wt. CO_2 in steam sample	= 0.0174 g
Ratio $n^{v}{}_{CO_2} / n^{v}{}_{H_2O}$	= 0.1131
Density of pure sat. steam, 257°	= 0.0225 g/cc
Density of sat. steam over solution (lowering of vapor pressure by ions)	= 0.0222 g/cc
Wt. water in vapor phase	= 0.713 g
Moles water in vapor phase	= 0.0396
Moles CO_2 in vapor phase	= 0.00448
Moles CO_2 due to acid	= 0.00797
Total CO_2 corrected for HCO'_3 decomposition	= 0.00805
Moles CO_2 in liquid	= 0.00357
Moles water in liquid phase	= 2.850
$n^{l}{}_{CO_2} / n^{l}{}_{H_2O}$	= 0.001253
$A = 0.001253/0.1131$	= 0.0111
$D = A\,[1 + (n^{v}{}_{CO_2} / n^{v}{}_{H_2O})(1 - D)]$	= 0.0123

The bicarbonate used was B.D.H. Analar which was exposed to an atmosphere of carbon dioxide in a desiccator for some weeks before use. The water and CO_2 samples were weighed to the nearest 0.1 mg on a semi-micro balance. The lowering of vapor density due to ions in solution was estimated from experimental results reported in the second paper of this series. It was

assumed in calculating values of A that the vapor density of saturated steam over the ionic solution was the same in the presence of about 10 percent (mole) of carbon dioxide, as over the solution with no other volatile present.

The experiments of Pollitzer and Strebel (1924) show that this is a safe assumption. These workers determined the concentration of water in the saturated vapor phase in the presence of various pressures of carbon dioxide. Table 3 shows approximate interpolations of their results at 50° and 70°C given as the ratio x, where x = grams of water per liter of vapor/grams water per liter of pure saturated water vapor.

TABLE 3

p_{CO_2}	5	10	20	30
x (50°)	1.10	1.15	1.35	1.6
x (70°)	1.05	1.10	1.15	1.4

The interaction of gaseous CO_2 and H_2O molecules becomes less at higher temperatures. As the pressures, p_{CO_2}, in the present experiments were usually under 5 atmospheres, it is unlikely that the assumption above introduces more than 1-2 percent error into the values of A or D.

To obtain values of $K = D/P$ the total pressure P is required. It is assumed that $P = p'_{H_2O}[1 + (n^v_{CO_2} / n^v_{H_2O})]$ where p'_{H_2O} is the saturated water vapor pressure above the solution at the temperature, corrected for the salts in solution. The correction for dissolved carbon dioxide is small and is neglected.

In the example taken, at 257°, $p^o_{H_2O} = 44.08$ at., where $p^o_{H_2O}$ is the vapor pressure of pure water, and $p'_{H_2O} = 43.6$ at.

Therefore $P = 48.5$ at.,

and $K = P/D = 3940$ at.

This assumption is examined again below.

RESULTS

Two series of experiments were completed.

Series A.—Materials added were, 0.02 moles $NaHCO_3$, 2 cc of a solution containing 0.00797 moles HCl, and either 40 cc or 50 cc of water (20°).

Series B.—Materials added were, 0.007 moles $NaHCO_3$, 50 cc water (20°), and 5 cc of a solution containing 0.00302 moles HCl.

Tables 4 and 5 give the results obtained from Series A and B respectively.

It was found in Series B that the results obtained with the first sample of steam from a bomb filling were not so consistent as those from second or third samples taken after time was allowed for equilibrium to be re-established. This effect did not appear to be important in Series A, and no simple explanation can be offered. The results from the first samples of steam from each bomb

TABLE 4

T°C	Steam Wt. H_2O (g)	Sample Wt. CO_2 (g)	CO_2 system moles × 10^3 (Uncorrected)	Vol. Soln. 20° (cc)	p'_{H_2O} (at.)	g H_2O per cc vapor × 100	A × 100	D × 100	1 – D	P (at.)	K = P/D
114	0.0066	0.0347	7.38	42.75	1.59	0.0920	0.0333	0.105	0.999	5.00	4800
128	0.0091	0.0317	7.43	42.70	2.47	0.139	0.0531	0.129	0.999	6.00	4640
147	0.0186	0.0389	7.37	42.75	4.45	0.232	0.0900	0.167	0.099	8.25	4940
175	0.0335	0.0395	7.97	42.75	8.68	0.462	0.175	0.259	0.997	12.85	4960
182	0.0300	0.0277	7.37	42.76	10.21	0.531	0.219	0.301	0.997	14.1	4680
192	0.0252	0.0191	7.11	52.75	12.77	0.658	0.328	0.429	0.996	16.7	3890
195	0.0467	0.0320	6.75	52.70	13.63	0.701	0.338	0.432	0.996	17.5	4040
208	0.0182	0.0102	7.97	42.75	17.86	0.910	0.474	0.582	0.994	22.0	3770
227	0.0308	0.0131	7.45	52.75	25.65	1.30	0.628	0.737	0.993	30.1	4080
228	0.0397	0.0163	7.28	52.80	26.3	1.33	0.632	0.738	0.993	30.7	4160
228	0.0397	0.0148	7.67	42.65	26.3	1.33	0.701	0.807	0.992	30.3	3750
231	0.0479	0.0177	7.97	42.75	28.1	1.41	0.732	0.842	0.992	32.3	3840
232	0.0262	0.0097	7.97	42.75	28.3	1.43	0.711	0.818	0.992	32.6	3980
255	0.0441	0.0127	7.97	52.80	42.2	2.15	1.04	1.16	0.988	47.1	4060
257	0.0629	0.0174	7.97	52.75	43.6	2.22	1.10	1.22	0.988	48.5	3980
291	0.0954	0.0150	7.97	52.80	73.7	3.94	2.34	2.49	0.975	78.4	3150
298	0.1870	0.0249	7.97	52.80	81.5	4.36	3.03	3.19	0.968	85.9	2690
305	0.0796	0.0099	7.97	52.80	89.9	5.03	3.24	3.40	0.966	94.5	2780
314	0.1413	0.0131	7.97	52.80	101.9	5.79	5.03	5.21	0.948	105.8	2030
322	0.1658	0.0144	7.76	52.65	113.1	6.63	5.02	5.19	0.948	117.1	2250
343	0.0989	0.0068	7.97	52.80	148.1	9.75	7.9	8.1	0.919	152.3	1870
348	0.0598	0.0040	7.83	51.75	157.6	10.8	8.5	8.7	0.913	161.9	1860

TABLE 5

T°C	Steam Wt. H_2O (g)	Sample Wt. CO_2 (g)	CO_2 in system moles $\times 10^3$ (Uncorrected)	Vol. Soln. 20° (cc)	p'_{H_2O} (at.)	g H_2O per cc vapor $\times 100$	A $\times$ 100	D $\times$ 100	1 – D	P (at.)	K = P/D
163	0.0239	0.0117	2.24	55.25	6.54	0.346	0.138	0.166	0.998	7.85	4730
179	0.0485	0.0202	2.80	55.25	9.61	0.502	0.212	0.248	0.998	11.25	4530
197.5	0.0612	0.0180	2.83	55.31	13.15	0.743	0.312	0.349	0.997	14.7	4220
199	0.0454	0.0103	2.45	55.25	14.93	0.766	0.397	0.434	0.996	16.3	3760
222	0.0717	0.0121	2.81	55.25	23.62	1.20	0.647	0.692	0.993	25.2	3640
224	0.1020	0.0154	2.53	55.25	24.53	1.24	0.630	0.669	0.993	26.0	3890
227	0.1088	0.0156	2.61	55.22	25.94	1.32	0.711	0.752	0.992	27.5	3900
233	0.1048	0.0126	2.44	55.17	28.96	1.47	0.815	0.855	0.991	30.4	3550
242.5	0.1350	0.0164	2.81	55.27	34.3	1.74	0.920	0.965	0.990	36.0	3730
244	0.1112	0.0120	2.62	55.20	35.2	1.79	1.00	1.04	0.990	36.8	3530
287	0.0968	0.0060	2.85	55.20	69.8	3.72	2.11	2.16	0.978	71.6	3310
288	0.0908	0.0054	2.78	55.15	70.8	3.76	2.18	2.23	0.978	72.5	3250
317	0.1722	0.0070	2.97	55.29	105.0	6.10	4.05	4.11	0.959	106.7	2600
319	0.2264	0.0092	2.98	55.20	109.3	6.32	4.07	4.14	0.959	111.1	2680

filling in Series B are not reported. The quantity given in column 4 of the tables is the CO_2 which was present in the bomb at the time the sample was taken. This value does not include the correction for the decomposition of bicarbonate.

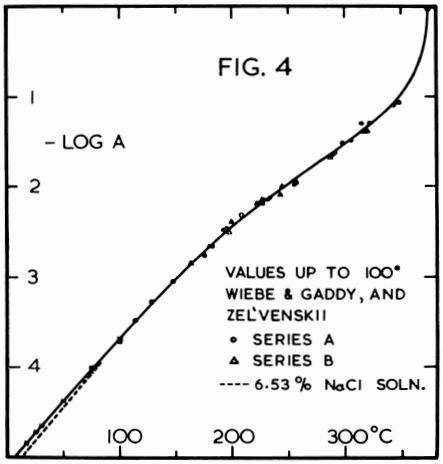

Fig. 4. Variation with temperature of the distribution coefficient A for carbon dioxide.

Figure 4 shows the values of log A at various temperatures and figure 6 the values of Henry's Law coefficient K at various temperatures. The results for A and K in Series A can be compared directly with those in Series B if it is assumed that Henry's Law is applicable. This is likely to be the case at partial pressure of CO_2 of the order of 5 atmospheres, especially as the ionization of H_2CO_3 in solution is repressed by the presence of excess HCO'_3 ions.

$$K = P/D = \frac{P}{A[1 + (n^v_{CO_2}/n^v_{H_2O})(1 - D)]}$$

$$= \frac{p'_{H_2O}\ [1 + (n^v_{CO_2}/n^v_{H_2O})]}{A[1 + (n^v_{CO_2}/n^v_{H_2O})(1 - D)]}$$

$$= p'_{H_2O} \cdot B/A$$

$$\approx p'_{H_2O}/A$$

$B \approx 1$, as at low temperatures $(1 - D) \approx 1$, and at higher temperatures $n^v_{CO_2}/n^v_{H_2O}$ becomes small compared with unity. Writing $B = 1$ does not introduce more than 0.3 percent error into any of the results. This is not significant.

p'_{H_2O} at constant temperature is an average of 0.5–.7 percent higher in Series B than in Series A because of the smaller electrolyte concentration. It cannot be expected that this will be reflected in the values of A given as it is doubtful whether they are more accurate than about $\pm$ 5 percent.

The results at temperatures from 100-200° provide a test of the assumption $P = p'_{H_2O}\ [1 + (n^v_{CO_2} / n^v_{H_2O})]$. In Series A the ratio $n^v_{CO_2} / n^v_{H_2O}$ ranges from 0.28 at 195° up to 2.15 at 114°. In Series B the ratio is 0.12 at 197° and 0.20 at 163°. If the assumption was not reasonable the values of A and K from Series A should show a definite trend away from Series B. This is not apparent.

Even if a complex of type $CO_2.nH_2O$ was formed in the vapor (Pollitzer and Strebel's results at 50° can be explained by a complex $H_2O.CO_2$) the total pressure may not be affected greatly. The total pressure, which is assumed to be the sum of $p_{CO_2} + p'_{H_2O}$, may actually be due to $p_{(CO_2.nH_2O)} + p'_{H_2O}$ where $p_{CO_2} = p_{(CO_2.nH_2O)}$.

SALTING-OUT OF GASES BY ELECTROLYTES

The solubilities of carbon dioxide reported in tables 4 and 5 are for solutions containing both $NaHCO_3$ and NaCl. The difference between the solubility of CO_2 in these solutions and that which could be expected in pure water is now examined.

The fraction of carbon dioxide ionized in a pure water solution is given approximately by

$x = (K^1_a/m.\ \gamma^2_{\pm})^{1/2}$ where K^1_a is the apparent first acid dissociation constant of carbonic acid, m the molality of the solution, and $\gamma_{\pm}$ the mean molal activity coefficient of the ions. K^1_a is not likely to rise above 7×10^{-7} (Ellis and Fyfe, 1957). m in the present experiments was not less than 0.02 moles/1000 g, and $\gamma^2_{\pm}$ at this concentration is approximately 0.96 at 25° (Harned and Owen, 1950, p. 547) and is unlikely to change by more than a few percent in liquid water at higher temperatures (Leitzke, 1955). The value of x is not likely to exceed 0.006 at the temperatures and pressures of gas used.

As the presence of excess HCO'_3 ions represses the ionization of H_2CO_3, the solubility of carbon dioxide in the bicarbonate solutions will be not less than 0.994 of the solubility in pure water (ignoring salting-out effects). This difference between unity and 0.994 is not considered further.

The solubility of a non-electrolyte in a solvent is changed by the addition of an electrolyte. The empirical Setschenow equation is often used to relate the ratio of solubility (β) at salt concentration, m, to the solubility in the pure solvent (β_0).

$$\log_{10} \frac{\beta_0}{\beta} = k.m$$

An example of the magnitude of the effect is given by the results of Morrison and Billett (1952) for the salting-out of n-butane from water solution.

The salting-out coefficient decreases with increasing temperature, and except for a few anomalous cases this behavior is general.

Electrostatic theories such as that due to Debye and McAulay (1925) consider that salting-out arises from the solution component of highest dielec-

tric constant being concentrated around the ions by their electric field, and the component of lower dielectric thereby being concentrated in the remaining solution. As the dielectric constant of water is usually higher than the solute, the latter is "salted-out" of solution.

TABLE 6

Values of k in Setschenow Eqn. (m in moles salt/1000 g H_2O)

Salt	NaCl	KCl	HCl
T°C			
12.5	0.243	0.200	0.080
30	0.217	0.182	0.049
49.5	0.194	0.164	0.031
71.5	0.176	0.144	0.028

McDevit and Long (1952) suggested that salting-out might be related to the volume change when the electrolyte is dissolved in water, or to the related "effective pressure" of the electrolyte as derived by compressibility measurements.

Neither the electrostatic theories nor the internal pressure theory are generally valid, although each can be applied with success to a limited number of systems (Morrison and Johnstone, 1955).

Salting-out is a rather complex phenomenon. It depends on the size of the added ions, their charge, the nature of the non-electrolyte, the salt concentration, and the temperature. The simple theories mentioned do not take into account specific interaction between ions, solute molecules and solvent molecules.

Although there is no satisfactory detailed quantitative theory to predict the change in salting-out with temperatures much above room temperatures, qualitatively it can be predicted to decrease. The effect is related to the solvation of the ions and solute molecules in solution, and to changes in the structure of water in the presence of ions (Frank and Evans, 1945). The average number of water molecules associated with the solvation sheath about an ion decreases with increasing temperature, while at the same time water tends to a random arrangement of molecules.

The solubility of CO_2 in a 6.53 percent solution of sodium chloride is given by Seidell (1940). The values of the Bunsen coefficient β and the coefficient A are given in table 7 for pure water and the salt solution.

The figures are probably not of great accuracy but they show the marked decrease in salting-out between 0 and 60°. From these figures it appears that at 100° the ratio of solubility in water to that in a 4-5 percent salt solution is about 1.05. The trend of solubility in a 6.53 percent NaCl solution is shown with the present results in figure 4.

The solubilities reported for Series A are possibly 5 percent low about 100°, but over about 150° it can be anticipated that the solubilities will equal those in pure water within the reproducibility of the present experiments. The

TABLE 7

T°C	β_0	β 6.53% NaCl	$A_0 \times 10^5$	$A_{(6.53\ NaCl)} \times 10^5$	Ratio $\frac{A\ (water)}{A\ (NaCl\ soln.)}$
0	1.713	1.234	0.835	0.614	1.36
10	1.194	0.875	1.17	0.877	1.33
20	0.878	0.664	1.64	1.27	1.29
30	0.665	0.517	2.26	1.79	1.26
40	0.530	0.414	3.14	2.51	1.25
50	0.436	0.370	4.34	3.76	1.15
60	0.359	0.305	5.81	5.04	1.15

solubilities from Series B can be taken as equal to solubilities in water within the significance of the results.

DISCUSSION OF CARBON DIOXIDE SOLUBILITY

The solution of gases in water compared with solution in organic solvents is unusual in many respects.

The temperature coefficients of gas solubility in water are negative at low temperatures, and the rate of change of solubility with temperature is very high, i.e. the partial molal heat capacity $\bar{C}_p$ of the gases in solution is very large. Eley (1939, 1944), and Frank and Evans (1945) pointed out that at room temperatures the entropy change, ΔS_s, associated with the solution of a given gas is 10-12 e.u. more negative for water than for organic solvents. At room temperatures the partial molal volume of the dissolved gas is smaller in water than in organic solvents.

It is convenient to consider the energy of solution of a gas in a liquid as the sum of two terms (Eley, 1939, 1944).

$$\Delta E_s = \Delta E_C + \Delta E_A$$

ΔE_C is the energy of creating a cavity of a sufficient size in the liquid to contain the gas molecule, and ΔE_A is the energy associated with placing the gas molecule in the cavity. ΔS_s can be divided in the same manner.

$$\Delta S_s = \Delta S_C + \Delta S_A$$

Eley showed that ΔE_A and ΔS_A for the solution of an inert gas do not differ greatly for organic solvents and water. The differences between solvents arise mainly from the terms ΔE_C and ΔS_C. At low temperatures in water Eley concluded that ΔE_C was very small, and that solution of gas occurred into interstitial positions in the open structure of water. This would also explain the low values of the partial molal volume, $\bar{V}$, for gases in water.

$\Delta E_C = T.\ \bar{V}.\ \alpha/\beta$, where α is the thermal expansion coefficient of the solvent, and β its compressibility. The rapid increase in α with temperature causes a similar increase in ΔE_C.

At low temperatures in water $\Delta E_C < -\Delta E_A$ and the temperature coefficient of solubility in the liquid is negative. With increasing temperature, as ΔE_C becomes equal to and then greater than $-\Delta E_A$, the temperature coefficient passes through zero and then becomes positive.

In organic liquids and high temperature water a dissolved gas molecule occupies one of the quasi-lattice sites in the close-packed structures. The energy ΔE_C of forming a cavity on this site is greater than $-\Delta E_A$ and therefore the temperature coefficient of solubility is positive (Eley, 1939).

There is a loss of entropy through the confinement of a gas molecule when it is dissolved in the solvent. There may be also a breaking-down of the solvent structure with a consequent gain in entropy. This is significant mainly in solvents with a close-packed structure. The large loss of entropy and the negative values of ΔH_s associated with the solution of inert gases in water at room temperatures was explained by Frank and Evans (1945) by the structure of water being modified towards greater crystallinity. They suggested that each gas molecule is surrounded by an "iceberg" or region of definite solvent structure.

In the vapor and liquid phases the chemical potential (μ_a) of a gas (a) is given by

$$\mu^v_a = \mu^\dagger_a\,(T) + RT \ln f_a \quad \text{and}$$
$$\mu^l_a = \mu^*_a\,(T) + RT \ln x_a.\gamma_a$$

where $\mu^\dagger_a$ and μ^*_a are the chemical potentials in the standard states of unit fugacity in the vapor phase and a hypothetical mole fraction of unity in the solution, f_a is the fugacity of the gas, and x_a and γ_a the mole fraction and activity coefficient of the gas molecules in solution.

At constant temperature for the solution process

$$a(\text{vapor}) \rightarrow a(\text{solution})$$

at equilibrium. $\Delta G = 0 = \mu^l_a - \mu^v_a$

$$= \mu^*_a - \mu^\dagger_a + RT \ln \frac{x_a\,\gamma_a}{f_a}$$

$$= \Delta G^0_s + RT \ln \frac{x_a\,\gamma_a}{p_a\,\alpha_a}$$

(α is the fugacity coefficient of the gas).

Where Henry's Law is obeyed $\gamma_a/\alpha_a = 1$, and $\Delta G^0_s = -RT \ln \frac{x_a}{p_a} = RT \ln K$

Figure 5 shows the relationship of RT ln K to temperature. ΔS^0_s was obtained from graphical differentiation of this type of plot, and ΔH^0_s from the equation

$$\Delta H^0_s = \Delta G^0_s + T\Delta S^0_s$$

The values of these three thermodynamic functions are given in table 8. The bracketed values are those given by Frank and Evans (1945). The values are intended mainly as an illustration, and at higher temperatures can be regarded as only semi-quantitative.

The change in heat and entropy associated with the vaporization of gas from solution decreases as the temperature rises. This can be correlated with the change in water structure from an open tetrahedral arrangement of molecules at low temperatures to a close-packed liquid at high temperatures.

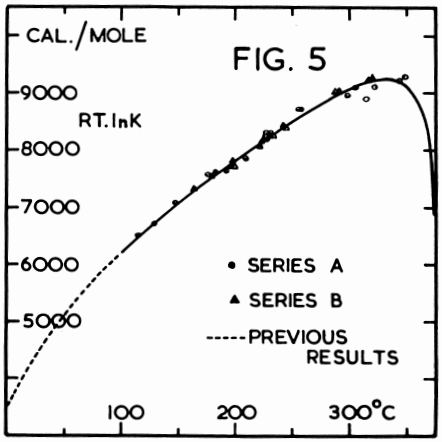

Fig. 5. Graph of the free energy of solution of carbon dioxide versus temperature.

TABLE 8

T°C	25	40	100	150	200	250	300
ΔG^{o}_{s} (cals.)	4380	4840	6270	7130	7880	8500	9030
$-\Delta S^{o}_{s}$ (e.u.)	31.5	28.5	20.5	16.0	13.5	12	8
	(30.6)	(28.2)					
ΔH^{o}_{s} (cals.)	-5010	-4090	-1380	370	1490	2200	4400
	(-4730)	(-3870)					

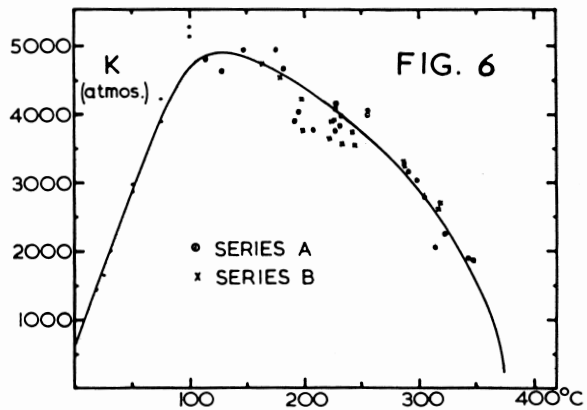

Fig. 6. The variation with temperature of the solubility of carbon dioxide represented by the Henry's Law coefficient, K. The results up to 100° are from Wiebe and Gaddy, and Zel'renskii.

About 200°, ΔS for vaporization of carbon dioxide from solution becomes approximately equal to that for vaporization of an inert gas from an organic solvent at room temperatures. For the latter process ΔS is not expected to vary greatly with temperature (Eley, 1939).

Table 9 gives for comparison the values of ΔS^{o}_{s} for solution of helium and water in methyl alcohol-water mixtures (Law, 1949). The change in

ΔS^0_s with increasing methyl alcohol content is similar to the effect of increasing temperature for pure water solutions. In both cases there is a collapse of the open structure of low temperature water.

TABLE 9

Entropy of Solution at 25° for Helium and Argon in MeOH—Water Mixtures

Mole % MeOH	0	20	40	60	80	100
$-\Delta S^0_s$ (Argon)	29.4	23.2	19.3	18.0	17.2	16.6
$-\Delta S^0_s$ (Helium)	25.1	21.0	17.7	16.2	14.8	13.9

For the carbon dioxide solutions ΔG^0_s reaches a maximum at about 340°C and ΔS^0_s becomes zero. At higher temperatures ΔS^0_s becomes increasingly positive, reaching a high value at the critical point. Near to the critical point, insertion of gas molecules into the liquid further weakens the already weak water-water adhesive forces and ultimately causes the liquid phase to become unstable with respect to a supercritical fluid. A large positive entropy change is associated with this process.

APPLICATION OF RESULTS

The present results, while not of high precision, are the only high-temperature solubility values available for carbon dioxide. They demonstrate the general solubility behavior of gases in water at high temperatures.

The principles involved in calculating conditions of equilibrium in systems containing carbon dioxide and metal carbonates have been adequately discussed by Garrels and Dreyer (1952). The methods of calculation can be used at any temperature. It is sufficient in this paper to point out the fallacy of extrapolating results from low-temperature gas solubility experiments by assuming a continuous decrease in solubility with increasing temperature. This procedure has been used in several geological and mineralogical papers. The partial pressure of a gas above a given solution does not increase continuously with temperature, but after passing through a maximum value, approaches a pressure determined by the mole fraction of the gas and the total pressure in the system.

The information summarized in figure 1 is useful in interpreting processes of liquid-vapor separation that occur in natural hydrothermal systems. At high temperatures, carbon dioxide and ammonia remain more soluble than gases such as hydrogen, oxygen, nitrogen and the rare gases, but the distribution behavior of small quantities of all gases tends to become equivalent near the critical point of water.

Information on the temperature of separation of liquid and vapor phases in hydrothermal systems can be obtained by utilizing the ratios of the more soluble gases, ammonia and carbon dioxide, to the less soluble gases such as nitrogen or hydrogen contained in the gas of the steam from fumaroles, hot-springs or drill-holes, e.g., Wilson (1955).

ACKNOWLEDGMENTS

The author wishes to thank Prof. H. N. Parton and Dr. W. S. Fyfe for a

critical reading of this paper. and Mr. V. G. Tyrrell for construction of the apparatus used. He is also indebted to the New Zealand Department of Scientific and Industrial Research for the opportunity of doing this work at the Chemistry Department of the University of Otago.

References

Clifford, I. L., and Hunter, E., 1933, The system ammonia-water at temperatures up to 150° and at pressures up to 20 atmospheres: Jour. Phys. Chem., v. 37, p. 101-118.

Debye, P., and McAulay, J., 1925, The electric field of ions and the action of neutral salts: Physik. Zeit., v. 26, p. 22-29.

Eley, D. D., 1939, Solubility of gases; I, The inert gases in water; II, Comparison of organic solvents with water: Faraday Soc. Trans., v. 35, p. 1281-1293 and p. 1421-1432.

————, 1944, Structure of water in aqueous solutions: Faraday Soc. Trans., v. 40, p. 184-194.

Ellis, A. J., and Fyfe, W. S., 1957, Hydrothermal chemistry: Rev. Pure and Applied Chem., v. 7, p. 261-316.

Frank, H. S., and Evans, M. W., 1945, Entropy in binary liquid solutions; partial molal entropy in dilute solutions; structure and thermodynamics in aqueous solutions: Jour. Chem. Phys., v. 13, p. 507-532.

Garrels, R. M., and Dreyer, R. M., 1952, Mechanism of limestone replacement at low temperatures and pressures: Geol. Soc. America Bull., v. 63, p. 325-380.

Harned, H. S., and Owen, B. B., 1950, The physical chemistry of electrolyte solutions, 2d ed.: New York, Reinhold.

Ipatieff, V. V., and Teodorovich, V. P., 1934, Solubility of hydrogen in water under pressure at elevated temperatures: Jour. Gen. Chem. (U.S.S.R.), v. 4, p. 395-399.

Keenan, J. H., and Keyes, F. G., 1936, Thermodynamic properties of steam: New York, John Wiley & Sons.

Law, J. T., 1949, The solubility of gases in water-methanol mixtures, and derived thermodynamic properties: Ph.D. Thesis, University of New Zealand.

Leitzke, M. H., 1955, The hydrogen electrode-silver chloride electrode system at high temperatures and pressures: Am. Chem. Soc. Jour., v. 77, p. 1344-1346.

McDevit, W. F., and Long, F. A., 1952, The activity coefficient of benzene in aqueous salt solutions: Am. Chem. Soc. Jour., v. 74, p. 1773-1777.

Miller, J. P., 1952, A portion of the system calcium carbonate-carbon dioxide, water: Am. Jour. Sci., v. 250, p. 161-203.

Morrison, T. J., and Billett, F., 1952, Salting-out of non electrolytes; II, The effect of variation of non-electrolyte: Chem. Soc. Jour., p. 3819-3822.

Morrison, T. J., and Johnstone, N. B., 1955, Solubilities of the inert gases in water: Chem. Soc. Jour., p. 3441-3446.

Pollitzer, F., and Strebel, E., 1924, The influence of an indifferent gas on the saturation vapor concentration of a liquid: Zeit. Physik. Chem., v. 110, p. 768-785.

Pray, H. A., Schweickert, C. E., and Minnich, B. H., 1952, Solubility of hydrogen, oxygen, nitrogen and helium in water at elevated temperatures: Indust. Eng. Chem., v. 44, p. 1146-1151.

Saddington, A. W., and Krase, N. W., 1934, Vapour-liquid equilibria in the system nitrogen-water: Am. Chem. Soc. Jour., v. 56, p. 353-361.

Seidell, A., 1940, Solubilities of inorganic and metal organic compounds: New York, D. van Nostrand Co. Ltd.

Styrikovich, M. A., Khaibullin, I.Kh., and Tskhvirashvili, D. G., 1955, Solubility of salts in high-pressures steam: Doklady Akad. Nauk S.S.S.R., v. 100, p. 1123-1126.

Wiebe, R., and Gaddy, V. L., 1939, The solubility in water of carbon dioxide at 50°, 75°, and 100° at pressures to 700 atmospheres: Am. Chem. Soc. Jour., v. 61, p. 315-318.

Wiebe, R., and Gaddy, V. L., 1940, The solubility of carbon dioxide in water at various temperatures from 12 to 40° and at pressures to 500 atmospheres: Am. Chem. Soc. Jour., v. 62, p. 815-817.

Wiebe, R., and Gaddy, V. L., 1941, Vapor-phase composition of carbon dioxide-water mixtures at various temperatures and pressures to 700 atmospheres: Am. Chem. Soc. Jour., v. 63, p. 475-477.

Wilson, S. H., 1955, Geothermal steam for power: Bull. 117, N. Z. Dept. Scientific & Industrial Research, (Edited by L. I. Grange), p. 27-42.

Zel'venskii, Ya. D., 1937, The solubility of carbon dioxide in water under pressure: Jour. Chem. Ind. (U.S.S.R.), v. 14, p. 1250-1257 (Chem. Abstracts, 1938, v. 32, p. 852).