ON THE SATURATION OF NON-VOLATILE SUBSTANCES IN AQUEOUS SOLUTIONS.*

By Taizo Kume.

The solubility of a solute in a solvent is considered to be one of the characteristic physico-chemical properties of the solute from the fact that it is of a definite quality under such conditions as the temperature and the pressure. Nevertheless, the relation between the solubility of a solute and its other properties has not been elucidated yet, and theories concerning the saturation of a solute still remain within the scope of thermodynamics.

Prof. S. Horiba discussed the relation between the molecular volumes of substances slightly soluble in water and their solubilities[1]. This, however, is not applicable to a substance having a large solubility, such as salts. Under Prof. S. Horiba's guidance the present author studied comprehensively the influence of non-volatile substances on the vapour pressures of their aqueous solutions[2] and found that each solute had a characteristic constant to show its solubility, which he named "Saturation coefficient". The results obtained are reported below.

Experiments and Experimental Results.

The principal part of the apparatus used consists of a Pyrex spring manometer (pressure indicator) soldered with a copper tube, a thermostat, a mercury-manometer, a Precision-manometer of metal, a gas-tank of high pressure and regulating valves. A glass valve which held pure water free from any gas or air and a given amount of the sample (salt) were sealed in vacuum at the bottom of the spring manometer, and the glass valve was made to break due to the freezing of water. As for the thermostat, it consists of an oil-bath with a special apparatus and is kept constant for a long time in the temperature range between 50° and 350°C. The unit of the reading pressure was 1/5 mm. below 3–4 atmospheres, the mercury manometer being employed, and 7 mm. above these atmospheres, the Metal-manometer being employed. The samples (salts) used were absolutely pure $HgCl_2$, $NaNO_3$ KNO_3, and $CaCl_2$ of Kahlbaum and Merck.

The experimental results are shown in Figs. 1, 2, 3 and 4, being summarized.[3]

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* This is the English translation of the paper which appeared in *Rev. Phys. Chem. Japan*.

1) S. Horiba, *Trans. Farad. Soc.*, 15, 178 (1920).

2) This *Journal*, 10, 74 (1936).

3) As to the detailed report, see this *Journal* 10, 75; 311 (1936).
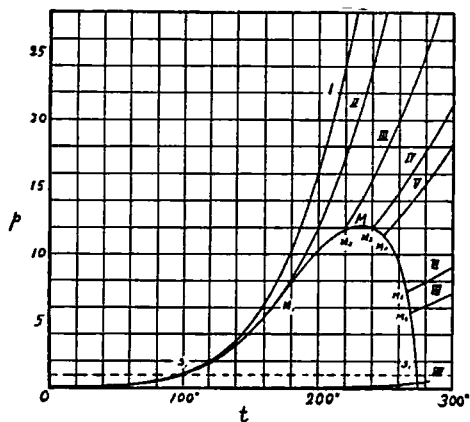
Fig. 1.

Vapour Pressure of Concentrated aqueous
Solution of HgCl₂.

Fig. 2.
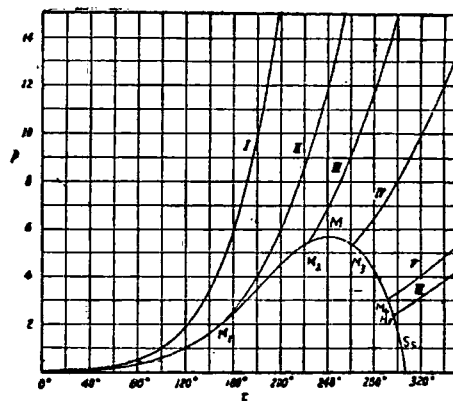
Vapour Pressure of Concentrated aqueous
Solution of NaNO₃.

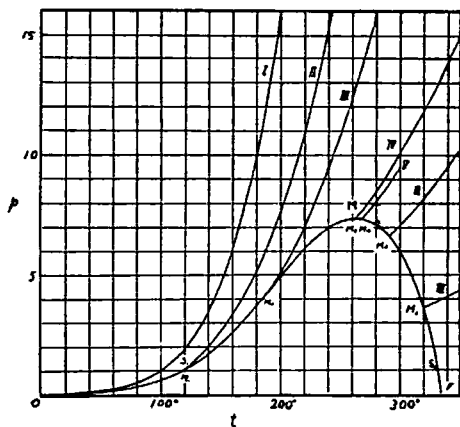
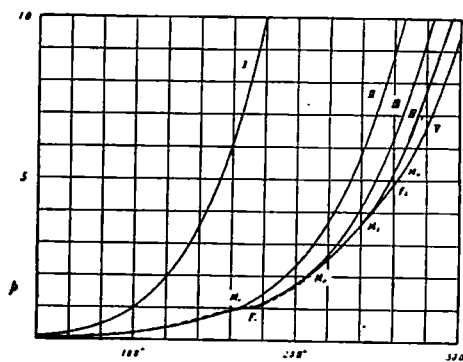Fig. 3.

Vapour Pressure of Concentrated aqueous
Solution of KNO₃.

Fig. 4.

Vapour Pressure of Concentrated aqueous
Solution of CaCl₂.

Theoretical Consideration.

The relation that the binary solution of a non-volatile solute and its vapour phase are in equilibrium is thermodynamically expressed by

$$-\frac{Q_0}{T}dT+(v_0'-v_0)dp-n_0\frac{\partial\varphi}{\partial n_0}\,d\left(\frac{n}{n_0}\right)=0 \qquad (1)$$

where Q_0 is the heat of vapourisation of a solvent, v_0' and v_0 the molecular volumes of the solvent in the vapour and liquid phases respectively, n and n_0 the numbers of mols of the solute and the solvent in the solution respectively and φ the chemical potential of the solute.

The relation that a solution and its " Bodenkörper " are in equilibrium is expressed by

$$-\frac{L}{T}dt+(v''-v)dp+\frac{n_0^2}{n}\frac{\partial\varphi}{\partial n_0}d\left(\frac{n}{n_0}\right)=0\,,\qquad(2)$$

where L is the heat of solution of a solute, v'' and v the molecular volumes of the solutes in the solid and solution phases respectively.

Vapour Pressure and Temperature.

Saturated Solution.

In the saturated solution of a solute whose solubility increases with the rise of temperature, the vapour pressure increases with the rise of temperature, reaching the maximum particular to the solute, and will decrease sharply toward the the melting point of the solute and then disappear. This phenomenon was deduced by Roozeboom from his experiment on the hydrate of $CaCl_2$ and theoretical discussions were made by van der Waals[5], Smits[6] and others. Jellinek has lately derived the theoretical formula of this from the activity of a solution[7].

Let us examine this relation from the above mentioned general relation. In a saturated solution, the vapourisation of a solvent is accompanied by the crystallisation of a solute. This requires the relations (1) and (2) to hold simultaneously :

$$\frac{Q_0-xL}{T}\,dT-\left\{(v_0'-v_0)+(v''-v)x\right\}dp=0\,.\quad\left(x=\frac{n}{n_0}\right)$$

Therefore,

$$\frac{dp}{dT}=\frac{Q_0-xL}{T\{(v_0'-v_0)+(v''-v)x\}}\,.$$

In this equation, v_0 and $(v''-v)x$ are negligibly small. So assuming that vapour obeys the gas law, we have

$$\frac{d\ln p}{dT}=\frac{Q_0-xL}{RT^2}\,.\qquad(3)$$

This equation expresses the relation between the vapour pressure and the temperature of a saturated solution. While the solubility x is small and $Q_0-xL>0$, the vapour pressure increases with the rise of temperature. When the solubility becomes remarkably large with the rise of temperature, Q_0-xL becomes 0 and here the vapour pressure reaches the maximum. At higher temperatures,

4) H. W. B. Roozeboom, *Rec. trav.*, **8**, 1 (1889) ; *Z. physik. Chem.*, **2**, 146 (1888) ; **4**, 31 (1889).

5) Van der Waals, *Lehrb. d. Thermodynamik*, II. 370, 521 (1912).

6) A. Smits, *Z. physik. Chem.*, **78**, 708 (1912).

7) K. Jellinek, *Lehrb. d. physik. Chemie*, IV. 736 (1933).

$Q_0 - xL$ becomes less than 0, and the vapour pressure falls with the rise of temperature. When the solubility x increases infinitely with the rise of temperature, the vapour pressure of the solution is to approach 0 towards the melting point of the solute. So far as the author knows, however, these phenomena have not been experimentally verified yet.

The present experimental results show, as seen from the curves OS_1MS_2F in Figs. 1, 2 and 3, that the vapour pressure of a saturated solution presents the first boiling point at S_1, reaches the maximum at M and decreases sharply towards the melting point of its solute F, presenting the second boiling point at S_2. The observed values are as follows:

	$HgCl_2$	$NaNO_3$	KNO_3
S_1	101°C.	120°C.	115°C.
M	234°C. (12.15 atm.)	242°C. (5.6 atm.)	265°C. (7.5 atm.)
S_2	274.5°C.	304°C.	333°C.

These results justify the van der Waals-Roozeboom theory.

Unsaturated Solution.

The relation between the vapour pressure of an unsaturated solution and the temperature has generally been discussed by the Clausius-Clapeyron theory, but the question whether this theory is applicable to a concentrated solution or not has not yet been experimentally demonstrated.

Assuming that the concentration is constant, equation (1) becomes Clausius-Clapeyron's formula. Taking C to be the integration constant, the equation may be rerwitten as

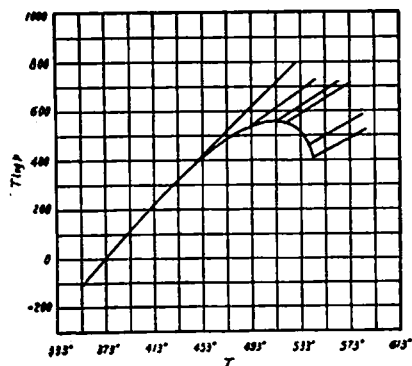$$T \log p = \frac{Q_0}{4.573} + CT. \qquad\qquad (4)$$

Fig. 5.

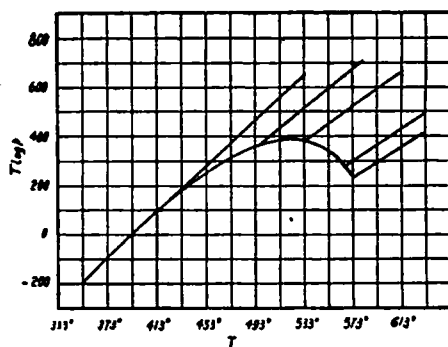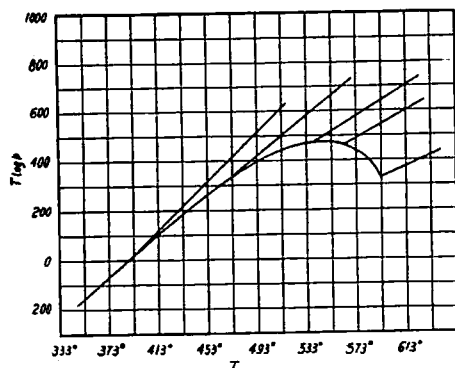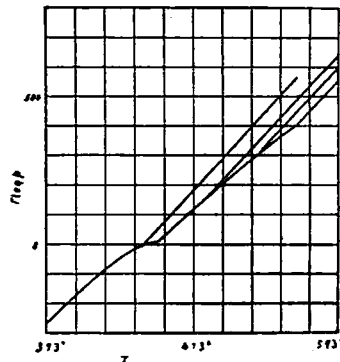Fig. 6.

Fig. 7.

Fig. 8.

The vapour pressures of an unsaturated solution which has lost "Bodenkörper" at M_1, M_2, M_3, etc. are shown by the curves M_1II, M_2III, M_3IV, etc. in Figs. 1, 2, 3 and 4 respectively.   As for these parts, $T \log p$ plotted for T are shown in Figs. 5, 6, 7 and 8.   As seen in these figures, the linear relation holds between $T \log p$ and T.   This proves the applicability of the Clausius-Clapeyron theory to a concentrated solution, however high the temperature and the concentration, so long as the solution is in the unsaturated state.

Solubility.

The measurement of the solubility of a solvent at the temperatures near the boiling point, especially at temperatures higher than the point being
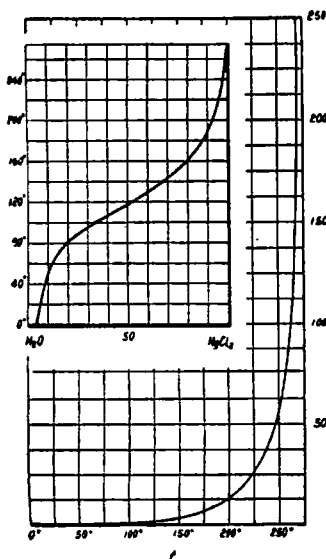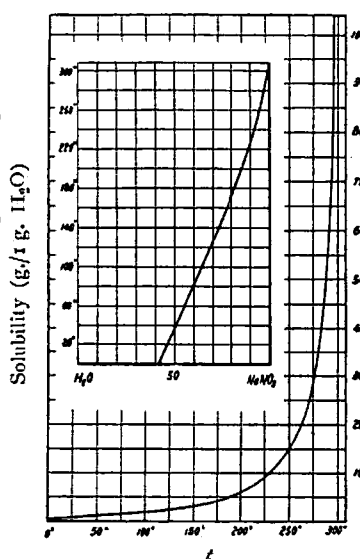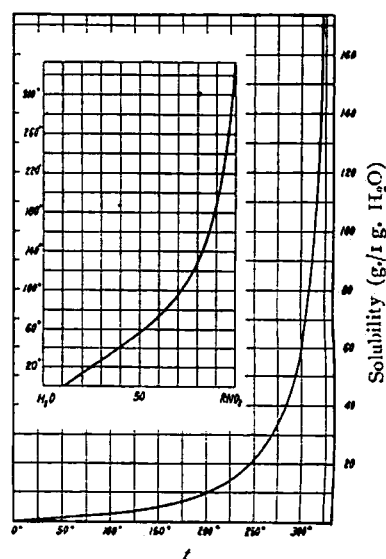

Fig. 9.

Fig. 10.

Fig. 11.

hard to make, the solubilities of these salts at high temperatures had not been determined before. The author, however, could determine the solubilities by the ratios of the solutes to their solvents in the mixtures and the angular points of the vapour pressure curves of the solutions, that is, the transition points from the saturated states to the unsaturated ones (for example, M_1, M_2, M_3, etc. in Figs. 1, 2, 3 and 4). The results thus determined are shown in Figs. 9, 10 and 11, and the solubility curves thus obtained above 100°C. continue smoothly to those already obtained below the temperature. This fact justifies the determination of the solubility by this method.

Vapour Pressure and Concentration of a Concentrated Solution.

Raoult's law concerning the depression in the vapour pressure of a solution by its non-volatile solute is applicable only to dilute solutions and not to any other solutions, especially to concentrated solutions. This deviation has been explained from the molecular depression of the vapour pressure, or with van't Hoff's coefficient, or by a kinetic theory, and yet there is no satisfactory explanation made.

From the experimental results, the author derived the following empirical formula concerning the vapour pressure and concentration of a concentrated aqueous solution :

$$\frac{p_0-p}{p} = \frac{kn}{n_0} = kx , \qquad \left(\frac{n}{n_0}=x\right) \qquad (5)$$

or

$$\frac{p_0}{p} = \frac{kn+n_0}{n_0} = kx+1 , \qquad (5)'$$

where p_0 and p are the vapour pressures of pure water and of an aqueous solution respectively, n_0 and n the numbers of mols of water and of a solute in the solution respectively. As for k, it is a coefficient characteristic of a given solute and is constant, so long as the solution is in the saturated state, being always independent of the temperature and the concentration, but it varies according to the concentration while the solution is in the unsaturated state. As will be mentioned later, this coefficient is a characteristic coefficient.

In a solution, both the solute and the solvent are in some particular molecular states. Accordingly, it is considered that the solute has a value or effect k times as large as its own number of mols; in other words, the solvent has a value or effect $\mu(=1/k)$ times as large. Therefore, the actual effects of the solute and the solvent in a solution as concentrations will be as follows ;

$$\frac{kn}{kn+n_0}=\frac{n}{n+\mu n_0}\ , \quad \text{for solute}$$

$$\frac{n_0}{kn+n_0}=\frac{\mu n_0}{n+\mu n_0}\ , \quad \text{for solvent}$$

$$\left(\mu=\frac{1}{k}\right) \quad (6)$$

The author has named these values the "effective concentrations" in an aqueous solution.

Then the above-mentioned relation (5) or (5)' may be interpreted as follows. The vapour pressure of a concentrated aqueous solution of a non-volatile solute is proportional to the effective concentration of the solvent in the solution, that is, of water. This is an experimentally obtained relation common to the solutions of non-volatile solutes. In the case of an ideal solution which does not make ionisation or a dilute solution approximate to it, the value of k approaches 1, and its effective concentration becomes the ordinary concentration or the molar fraction; hence equation (5) becomes Raoult's equation.

In equation (1), assuming that the temperature is constant, v_0 is negligible for v_0' and the vapour obeys the gas law, we have

$$\frac{d\ln p}{dx}=\frac{n_0}{RT}\frac{\partial \varphi}{\partial n_0}\ . \qquad \left(x=\frac{n}{n_0}\right) \qquad (7)$$

This is the general equation expressing the relation between the vapour pressure and the concentration of a solution of a non-volatile solute. The function $\frac{\partial \varphi}{\partial n_0}$, however, is unknown, because the inner state of a solution has not been made clear. Therefore, the equation can not be integrated.

In the case of an ideal solution the chemical potential of a solute is expressed by

$$\varphi=\overline{\varphi}+RT\ln N, \qquad\qquad (8)$$

where $\overline{\varphi}$ is the function only for the temperature and the pressure and N is the molar fraction of the solute. Accordingly, equation (7) being integrated, it becomes

$$\ln p= -\ln(x+1)+C, \qquad\qquad (9)$$

or

$$\frac{p}{p_0}=\frac{1}{x+1}\ . \qquad\qquad (9)'$$

This is precisely Raoult's law and shows that the vapour pressure of a solution is proportional to the concentration or the molar fraction of the solvent in the solution.

As this relation can not be applied to the general case, let us consider Lewis'

activity for the actual solution, then the chemical potential of the solute will be as follows:

$$\varphi = \bar{\varphi} + RT \ln a = \bar{\varphi} + RT \ln N + RT \ln f, \qquad (10)$$

where a and f are activity and the activity coefficient of the solute respectively. Accordingly, from equation (7), we have

$$\ln p = -\ln (x+1) - \int x \frac{d \ln f}{dx} dx + C.$$

Now, let a_0 and f_0 represent the activity and the activity coefficient of the solvent respectively, then we have

$$\ln f_0 = -\int x \frac{d \ln f}{dx} dx .$$

Therefore,

$$\ln p = -\ln (x+1) + \ln f_0 + \ln p_0 , \qquad (11)$$

or

$$\frac{p}{f_0} = \frac{f_0}{x+1} = a_0 . \qquad (11)'$$

Here we have the said relation that the vapour pressure of a solution is proportional to the activity of the solvent.

In the case of a concentrated solution of non-volatile solute, it is evident from equations $(9)'$ and $(11)'$ that the vapour pressure is proportional experimentally to the effective concentration of a solvent and theoretically to the activity of the solvent. When those two relations are considered to be of the same nature, the relations between the effective concentration and the activity of a solution can be obtained thus: for the solvent,

$$a_0 = \frac{1}{kx+1} = \frac{n_0}{kn+n_0} . \qquad (12)$$

and for the solute,

$$\ln a = -\int \frac{1}{x} \frac{d \ln a_0}{dx} dx = \int \frac{1}{x} \frac{1}{kx+1} \frac{d(kx)}{dx} dx .$$

Therefore, $\qquad \ln a = k \ln \frac{kx}{kx+1} - \int \ln \frac{kx}{kx+1} \frac{dk}{dx} \cdot dx . \qquad (13)$

These expressions, however, can not be integrated, for the relation between k and x is unknown. In the case of a saturated solution k is constant, irrespective of the concentration. Therefore, let a_s represent the activity of the solute in this case, then

$$\ln a_s = k \ln \frac{kx}{kx+1}, \tag{14}$$

or

$$a_s = \left(\frac{kx}{kx+1}\right)^k. \tag{14}'$$

This relation shows that the activity of the solute is equivalent to the k'th order of the effective concentration, when k is a constant in the saturated state.

Saturation of Aqueous Solution : Saturation Coefficient.

First, let us examine the coefficient k which shows the effective concentration. In the case where a solution is in the saturated state, the coefficient is constant, irrespective of the temperature and the concentration.   This is seen in Tables I, II and III.

Table I.

Saturation Coefficient k of Saturated aqueous Solutions of $HgCl_2$.

$t\,^{\circ}C$	Solubility $x=\frac{n}{n_0}$	Vapour pressure (atm.)				$\frac{f_0-f_{H_2O}}{f_{H_2O}}$	k
		f_0	f	f_{HgCl_2}	f_{H_2O}		
80	0.016071	0.467	0.4625		0.4625	0.009730	0.6054
100	0.035883	1.000	0.9795		0.9795	0.020929	0.5833
120	0.077890	1.960	1.874		1.874	0.045890	0.5892
140	0.14100	3.567	3.316		3.316	0.075693	0.5368
160	0.26540	6.10	5.350		5.350	0.14018	0.5281
180	0.46446	9.90	7.813	0.01	7.803	0.26874	0.5786
200	0.85521	15.34	10.204	0.031	10.173	0.50791	0.5939
220	1.4767	22.89	11.810	0.071	11.739	0.94990	0.6432
240	2.7417	33.03	12.072	0.151	11.921	1.7701	0.6459
260	6.5689	46.31	9.553	0.310	9.243	4.0102	0.6105
						mean	0.5946

Table II.

Saturation Coefficient k of Saturated aqueous Solutions of $NaNO_3$.

$t\,^{\circ}C$	$\frac{n}{n_0}$	f_0 (mm. & atm.)	f (mm. & atm.)	$\frac{f_0-f}{f}$	k	Observer
10	0.1706	9.21	7.13	0.29172	1.710	Adams and Merz.[8]
30	0.2036	31.84	23.07	0.38015	1.867	,,
50	0.2589	92.51	62.21	0.48705	1.881	,,
100	0.3836	1.000	0.560	0.78571	2.048	T. Kume
140	0.5788	3.567	1.631	1.1870	2.051	,,
180	0.9982	9.90	3.404	1.9083	1.912	,,
220	1.7505	22.89	5.281	3.3344	1.905	,,
260	4.027	46.31	5.349	7.6577	1.902	,,
300	30.062	84.80	2.561	32.112	1.068	,,
				mean	1.904	

8) J. R. Adams and A. R. Merz, *Ind. Eng. Chem.*, 21, 305 (1929).

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Table III.

Saturation Coefficient k of Saturated aqueous Solutions of KNO_3.

t °C	$\dfrac{n}{n_0}$	$\dfrac{f_0}{}$ (mm. & atm.)	$\dfrac{p}{}$ (mm. & atm.)	$\dfrac{f_0-f}{p}$	k	Observer
10	0.0368	9.21	8.87	0.038331	1.042	Adams, Merz.[8]
30	0.0821	31.84	28.84	0.10402	1.267	,,
60	0.1969	149.4	122.5	0.21959	1.115	Pawlowitsch[9]
90	0.3634	525.8	367.5	0.43075	1.185	,,
100	0.4384	1.000	0.666	0.50150	1.144	T. Kume
140	0.8411	3.567	1.774	1.0107	1.202	,,
180	1.3900	9.90	3.720	1.6613	1.195	,,
220	2.406	22.84	6.025	2.7909	1.160	,,
260	4.598	46.31	7.316	5.3299	1.159	,,
300	11.492	84.80	5.930	13.3002	1.157	,,
320	26.035	111.46	3.601	29.952	1.151	,,
				mean	1.169	

As seen from these tables, over a very wide temperature range such as from low temperatures up to the melting point of each salt and also over a wide concentration range such as $n/n_0 = 0.01 - 30.0$, each salt always has its particular constant value. This fact is observed without exception in all the results of experiments on saturated solutions, which have already been reported by many investigators. The values of k of various kinds of salts thus obtained are given in Table IV.

When a solution is in the unsaturated state, k varies according to the temperature or concentration of the solution. But in case the degree of saturation of the solution is taken into consideration, k becomes independent of the temperature.

Let x and x_s represent a given concentration of a solution and its solubility at the same temperature respectively, then the value of the ratio, $S = \dfrac{x}{x_s}$, is always $0 \sim 1$. The author calls S "the degree of saturation" of the solution. From the experimental results of the author and other investigators, for unsaturated solutions such results were obtained as shown in Figs. 12, 13, etc., k being plotted for the degree of saturation S instead of the concentration x.

It is apparent from these figures that the values of k plotted for S at different temperatures lie on a smooth curve and that the change of k for S is independent of the temperature.
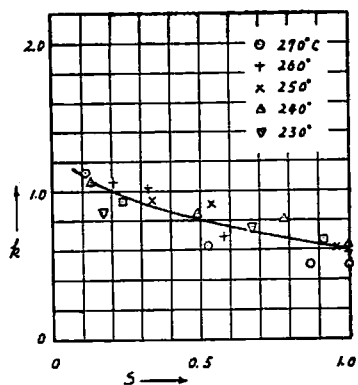
9) P. Pawlowitsch, *Z. physik. Chem.*, 84, 170 (1913).

Fig. 12.

Relation between k and Degree of Saturation S
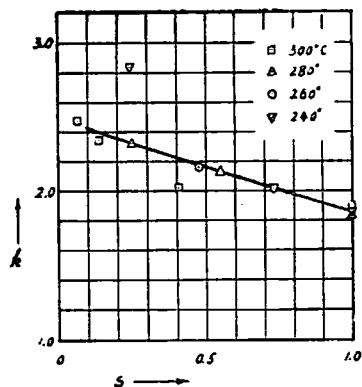of Unsaturated Aqueous Solutions of $HgCl_2$.

Fig. 13.

Relation between k and Degree of Saturation S
of Unsaturated Aqueous Solutions of $NaNO_3$.

Fig. 14.

Relation between k and Degree of Saturation S
of Unsaturated Aqueous Solutions of KNO_3.

Fig. 15.

Relation between k and Degree of Saturation S
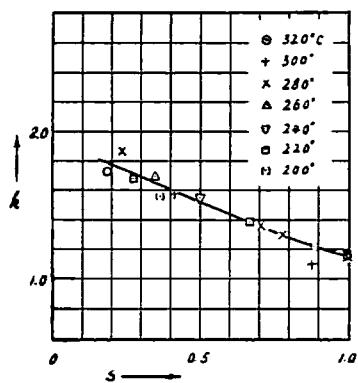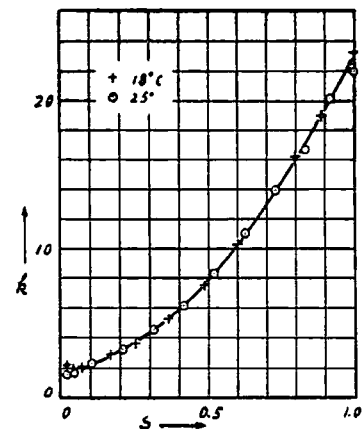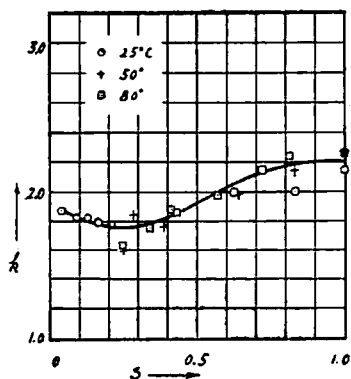of Unsaturated Aqueous Solutions of $LiCl$.

Fig. 16.

Relation between k and Degree of Saturation S
of Unsaturated Aqueous Solutions of KCl.
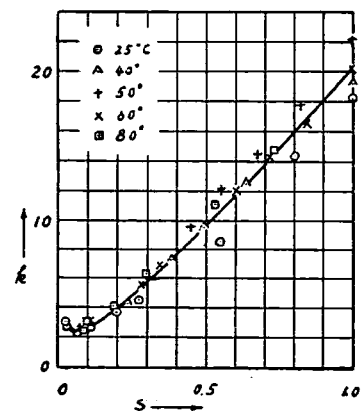
Fig. 17.

Relation between k and Degree of Saturation S
of Unsaturated Aqueous Solutions of $CaCl_2$.

From these results it is clear that the coefficient k has a close connection to the degree of saturation of the solution and is a constant characteristic of the

Table IV.
Saturation Coefficients of various Salts including their Hydrates.

Salt	k values					Salt	k values		
$LiCl \cdot 2H_2O$	21.88	22.71				NH_4Cl	2.05	2.26	2.27
$LiBr \cdot 2H_2O$	38.15					NH_4Br	2.84		
$LiJ \cdot 3H_2O$	19.20					$NH_4NO_3 \cdot \beta$	1.11		
$LiNO_3 \cdot 3H_2O$	5.49					—— $\cdot \alpha$	1.37		
						$(NH_4)_2SO_4$	2.10	2.24	2.43
NaF	1.93					$(NH_4)H_3PO_4$	1.17	1.30	
$NaCl$	2.82	2.87	2.85	2.90	2.93				
	2.95	2.95	2.97	3.01		$CuCl_2 \cdot 2H_2O$	4.55		
$NaBr$	4.62					$CuSO_4 \cdot 5H_2O$	1.61	1.72	
—— $\cdot 2H_2O$	4.22								
NaJ	7.79					$AgNO_3$	1.02		
—— $\cdot 2H_2O$	7.66								
$NaNO_3$	1.77	1.79	1.90	2.04	2.18	$MgCl_2 \cdot 6H_2O$	21.02		
$NaClO_3$	2.46					$MgSO_4 \cdot H_2O$	2.80		
$Na_2CO_3 \cdot H_2O$	3.00	3.02				—— $\cdot 6H_2O$	2.42		
Na_2SO_3	2.48					—— $\cdot 7H_2O$	1.62		
—— $\cdot 7H_2O$	4.56								
Na_2SO_4	2.06	2.08	2.11						
KF	7.22					$CaCl_2 \cdot H_2O$	15.19	15.19	
—— $\cdot 2H_2O$	8.71					—— $\cdot 2H_2O$	14.67	16.03	
KCl	2.05	2.11	2.13	2.13	2.14	—— $\cdot 4H_2O \cdot \alpha$	22.49		
	2.15	2.25	2.28	2.48	2.50	—— $\cdot$ —— $\cdot \beta$	24.25		
KBr	2.22	2.60	2.79			—— $\cdot 6H_2O$	16.08		
KJ	2.70	2.80	3.40	3.46	3.63				
KNO_3	1.11	1.12	1.22	1.22		$SrCl_2 \cdot 6H_2O$	6.35		
$KClO_3$	1.62	1.65	1.83						
K_2SO_4	2.00	2.37	2.52	2.54	2.65	$BaCl_2 \cdot 2H_2O$	3.31		
$K_2Cr_2O_7$	2.51					$Ba(NO_3)_2$	2.11		
$RbF \cdot H_2O$	21.37					$ZnSO_4 \cdot 6H_2O$	1.50		
$RbCl$	2.14								
$RbBr$	2.10					$CdCl_2 \cdot 6H_2O$	2.08		
RbJ	2.03					$CdBr_2 \cdot 4H_2O$	1.96		
						CdJ_2	1.58		
$CsF \cdot H_2O$	66.34					$CdSO_4 \cdot \frac{8}{3}H_2O$	0.80		
$CsCl$	2.39								
$CsBr$	1.78								
CsJ	1.62					$HgCl_2$	0.595		

Each value of this table is the mean value obtained for the results of the same investigators. Some deviation in the value of k for same salt is ascribed to large influence of the experimental error in the measurement of vapour pressure or solubility upon the value of k.

solute which is to decide the solubility, being independent of both the temperature and the concentration. The coefficient, therefore, is named "Saturation coefficient" of the solute in an aqueous solution. It is apparent that it is affected by the inner state, for example, the ionic dissociation, association or hydration of the solute, or the depolymerisation of the solvent in an aqueous solution. As is seen in Table IV, the large the radius of the ion, the value of k is small for the cation, and vice versa for the anion. The value of k, however, varies even in the same salt if the molecular state of the salt as "Bodenkörper" differs, as seen in Table V.

Table V.
Saturation coefficients k of Saturated aqueous Solutions of various Salts.

t °C	p_0(mm)	p(mm)	$\frac{n_0}{n}$	Bodenkörper		k	k (mean)
	CaCl$_2$.				Roozeboom[10]		
o	4.579	1.944	10.37	(A)	CaCl$_2 \cdot 6H_2O$	14.056	
10	9.209	3.456	9.49		,,	15.797	
20	17.535	5.616	8.28		,,	17.573	
25	23.756	6.696	7.52		,,	16.90	
28.5	29.189	7.02	6.81		,,	(21.501)	16.082
29.5	30.923	6.91	6.46	(C)	CaCl$_2 \cdot 6H_2O$ schm.	22.449	
30.2	32.191	6.696	6.00		,,	22.845	
29.6	31.102	5.83	6.70		,,	24.708	
29.2	30.392	5.67	5.41	(E)	$\left(\begin{array}{c}CaCl_2 \cdot 6H_2O \\ CaCl_2 \cdot 4H_2O \cdot \beta\end{array}\right)$	23.588	23.398
20	17.535	4.744	6.78	(C'	CaCl$_2 \cdot 4H_2O \cdot \alpha$	(18.280)	
25	23.756	5.724	6.42		,,	20.224	
29.8	31.461	6.80	6.10	(C)	,,	22.122	
35.0	42.175	8.64	5.75		,,	22.318	
40.0	55.324	10.37	5.35		,,	23.192	
45.3	72.99	11.77	4.73	(D)	$\left(\begin{array}{c}CaCl_2 \cdot 4H_2O \cdot \alpha \\ CaCl_2 \cdot 2H_2O\end{array}\right)$	24.603	22.492
20	17.535	3.564	5.90	(D')	CaCl$_2 \cdot 4H_2O \cdot \beta$	23.128	
25	23.756	4.644	5.66		,,	23.292	
29.2	30.392	5.67	5.41	(E)	,,	23.588	
30	31.842	5.83	5.40		,,	24.093	
35	42.175	7.128	5.04		,,	24.781	
38.4	50.774	7.803	4.83	(E')	$\left(\begin{array}{c}CaCl_2 \cdot 4H_2O \cdot \beta \\ CaCl_2 \cdot 2H_2O\end{array}\right)$	26.599	24.247
50	92.51	15.5	4.66		CaCl$_2 \cdot 2H_2O$	(23.157)	
70	233.7	43.0	4.37		,,	(19.381)	
90	525.76	100.0	4.08		,,	(17.373)	
110	1.414	0.268	3.72		,,	(15.907)	
135	3.089	0.572	3.33		,,	14.652	
155	5.363	0.895	2.88		,,	14.378	
170	7.82	1.097	2.42		,,	14.831	14.671

10) H. W. B. Roozeboom, Z. physik. Chem., 4, 42 (1889).

180	9.90	1.197	2.05	$CaCl_2 \cdot H_2O$	14.905	
190	12.39	1.466	2.02	,,	15.052	
200	15.34	1.782	1.98	,,	15.064	15.193

Na_2SO_3					K. Arii[11]	
20	17.535	16.24	0.018876	$Na_2SO_3 \cdot 7H_2O$	4.224	
25	23.756	21.61	0.021824	,,	4.550	
30	31.842	28.38	0.024841	,,	4.911	4.561
35	42.08	37.01	0.05641	Na_2SO_3	2.480	
45	71.88	63.74	0.05152	,,	2.478	
50	92.51	82.39	0.04930	,,	2.491	2.483

NH_4NO_3					Adams a. Merz.[12]	
10	9.21	6.88	0.3587	NH_4NO_3 rhomb. a	0.9440	
20	17.54	11.74	0.4388	,,	1.125	
30	31.84	18.93	0.5379	,,	1.268	1.112
40	55.32	29.11	0.6541	NH_4NO_3 rhomb. β	1.377	
50	92.51	44.71	0.7797	,,	1.371	1.374

In the table, the irregularity of the value of k both in the neighbourhood of the transition point of " Bodenkörper " and in the temperature range between 50°–100°C. seems to be due to the facts that the " Bodenkörper " is not homogeneous and that some unstable hydrate of higher order coexists.

It should be noted that even in the same salt the value of k varies according to the stage of hydration—anhydrate, hydrate and the intermediate, and that the difference of the crystal structure as " Bodenkörper " causes variation in the value of k as in the case of NH_4NO_3.

Conclusion.

The results of the experiments on the vapour pressure of a concentrated aqueous solution carried out over very wide temperature and concentration ranges proved that in both the saturated and the unsaturated states the relation between the vapour pressure and the temperature was quite in agreement with what was obtained from the thermodynamical theory.

In the relation between the vapour pressure and the concentration, however, there was found a remarkable deviation from what was required by the thermo-dynamical theory, and the deviation can be represented by a new coefficient having a close relation to the saturation of a solution. The very coefficient is what the author has named " Saturation coefficient ". In the saturated state of a

11) K. Arii, *Bull. Inst. phys. chem. Research* (*Tokyo*), 7, 891 ; *Eng. Ed.*, 1, 83, (1928).

12) Adams and Merz, *Ind. En. chem.*, 21, 305 (1929).

solution it has always a constant value particular to each solute, being independent of the temperature and the concentration.   In the unsaturated state it is related only to the degree of saturation and makes a change particular to each solute, being independent of the temperature.   Therefore, the coefficient is a characteristic coefficient of an aqueous solution to decide the state of saturation of the solution.

The physical meaning of this coefficient can not be elucidated yet, but the above-mentioned facts show that in case the degrees of saturation in aqueous solutions of a salt are the same the inner states of the solutions are always the same, being independent of the temperature and the concentration.   Furthermore, they show that even in the case of the same salt the difference of the molecular state of the "Bodenkörper",—an anhydrate, a hydrate, a degree of hydration or a crystal structure—leads to the difference of the molecular state in each aqueous solution and hence the difference of the state of saturation.

Further research on the subject is in progress.

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