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ON THE SOLUBILITY OF PRUSSIC ACID FOR WATER.

By

Juro HORIUTI and Kozo TANABE.

1) Introduction

It has been shown that the synthesis of prussic acid in the presence of sulphuric acid catalyst promoted by thoria proceeded practically according to the formula,[1]

$$2CO + NH_3 = HCN + CO_2 + H_2$$

In case of the commercial production of prussic acid by means of the above reaction, however, caustic soda would be wasted, if prussic acid is fixed straight forward from the resultant gas in the form of sodium cyanide owing to the coexistence of equimolecular carbon dioxide. The alternative method using potassium ferrocyanide, although not associated with such difficulty and is sometimes commercially utilized, is rather complicated and the recovery of absorbed prussic acid is only incomplete. It is hence desirable to separate prussic acid from carbon dioxide more simply and completely.

We proceeded to separate the acid from carbon dioxide in the resultant gas, after the residual ammonia is removed, by means of extraction with water before fixing it with caustic soda, taking advantage of the fact that the OSTWALD's solubility* of prussic acid for water is as large 200~300 at 18°C, whereas that of carbon dioxide is about 1 under the same condition.

Since prussic acid in resultant gas amounts only 6% at the optimum condition of reaction, however, its molarity in aqueous solution at 18°C would be 0.7 Mol/L at most.* The volatile prussic acid might better be

1) KINOSHITA, YANO and SATO; "THE CATALYST" 5, (1949) 60. 7, (1951) 1. (in Japanese).

*) OSTWALD's solubility is defined as the ratio of the concentration in liquid to that in gas at equilibrium.

*) The concentration in gas is now $\frac{1}{22.4 \times \frac{291}{273}} \times 0.06 = 2.5 \times 10^{-3}$ mol/l at 18°C and 760 mmHg total pressure, for which that in liquid amounts to $270 \times 2.5 \times 10^{-3} = 0.68$ mol/l., assuming the solubility 270.

concentrated by the fract[illegible]on, as regards the heat economy before neutralization by e[illegible]or preparing solid sodium cyanide rather than to proceed rev[illegible]

The precent work is de[illegible]o fill up the defect of the solubility data of prussic acid in wate[illegible]er the temperature range 0°C to 70°C which are required for designing the fractional distillation.

The manipulation of measurement has been plotted as simple as possible as described below in order to avoid the danger of the poison, preferably shifting the complicacy, if any, to the table work of analysing the experimental data.

The variation of hydrogen cyanide concentration by passing a known amount of air throu a series of bottles (I) and (II), each containing initially hydrogen cyanide solution of known concentration and pure water, was thus observed and the result analysed to determine the solubility.

The material used, the procedure and the results are described below

2) Preparation of prussic acid.[2]

Potassium cyanide solution (1.2 parts in 1 part water) was carefully dropped into the mixture of 1 part sulphuric acid, 0.4 water and 0.02 ferric sulphate kept at 90°C. The gas evolved was cooled to ca. 50°C, passed throu sulphuric acid and calcium chloride kept at 50°C, successively and condensed in a bottle cooled by freezing mixture of ice and common salt. The anhydrous prussic acid thus obtained was diluted with distilled water at use.

3) The procedure and the results.

The apparatus used is shown in Fig. 1. (S), (I) and (II) are the bottles of 200 cc capacity each, combined in series, containing 150 cc pure water, 150 cc prussic acid solution of known concentration below 1% and 150 cc pure water respectively. The whole series is put in a thermostat of temperature at which the solubility is to be determined.

Air is, after being dried by D[illegible]nd warmed up to the temperature of thermostat by the preheater P, [illegible]assed throu the series at a constant

2) Alfons Klemenc; Die Behandlung und [illegible]indarstellung von Gasen. 149.
K. H. Slotta; Ber. Deutsch. Chem. Ges. [illegible]7, (1934), 1030.
Liebig's Annalen der Chemie. 357, (1907), [illegible]8.

rate controlled by means of a flow-meter F by suction of an aspirator A. The difference between outside and inside the series is determined by manometers M_1 and M_2 attached to the series as shown in the figure.

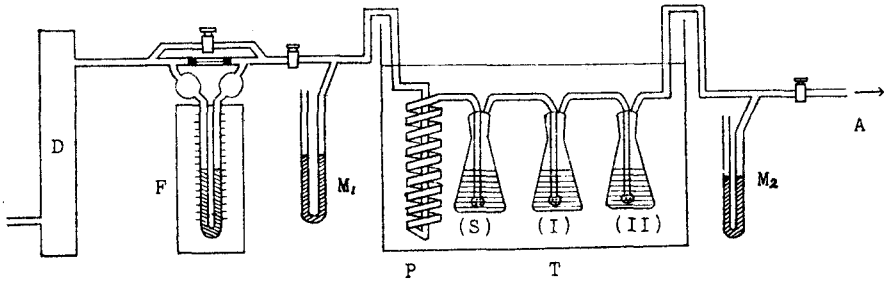

Fig. 1. Apparatus used.

D; soda lime tube. F; flowmeter, T; thermostat,
M_1, M_2; manometer, A; aspirator, P; preheater.

After a recorded time, the airation is stopped, (I) and (II) are taken out from the thermostat and dipped into ice water in order to fix the prussic acid in the liquid phase and then individually weighed for the variation of respective liquid quantities inside.

Each solution is now analysed for prussic acid concentration by pipetting out a known portion and titrating it with N/10—N/20 silver nitrate solution according to the LIEBIG's method.[3]

The experimental results thus obtained are shown in Table 1. The "Rate" is that determined by F, "Time" the recorded time of airation and "Total Volume" the product of the latter two quantities. The following three columns show the molarity of prussic acid in (I) before and after the airation and that in (II) after airation respectively. "Weight of Solution" shows those determined by weighing (I) and (II) before and after the airation. The "M_1" and "M_2" are respectively the readings of manometers M_1 and M_2 which show the excess of the barometric pressure over that inside at the respective part of series where M_1 and M_2 are attached.

The γ^{I} and γ^{II} are the upper aud the lower limit of the OSTWALD's solubility respectively obtained directly by analysing the observed data as described below and γ the true value arrived at by analysing the data kinetically, taking the rate of dissolution into account.

The limits of error given in the table are the mean error derived

3) I. M. KOLTHOFF and E. B. SANDELL; Text book of quantitative inorganic analysis. 456, 545.
I. M. KOLTHOFF; Die Massanalyse. 248.

TABLE

The Experimental

No. of Experiment	Temperatur (°C)	Airation			Molarity of Prussic Acid (mol/l)			Welght of Solution + Bottle	
					(I)		(II)	(I)	
		Rate (cc/min)	Time (min)	Total Volume (cc)	before airation $C_{L0}^{I'}$	after airation $C_{L}^{I'}$	after airation $C_{L}^{II'}$	before airation	after airation
1	18.05 ± 0.05	233.0	50.0	11650 ± 88	0.1213 ±0.0003	0.0889 ±0.0003	0.0265 ±0.0003	246.9	246.7
2	"	163.0	50.0	8150 ± 82	0.1213 ±0.0003	0.0971 ±0.0003	0.0213 ±0.0003	246.6	246.5
3	"	68.0	51.0	3468 ± 78	0.1178 ±0.0003	0.1071 ±0.0003	0.0099 ±0.0003	246.8	246.6
4	"	163.0	70.0	11410 ± 110	0.1199 ±0.0003	0.0891 ±0.0003	0.0255 ±0.0003	246.9	246.7
5	"	167.0	76.0	12692 ± 119	0.3460 ±0.0005	0.2460 ±0.0005	0.0800 ±0.0005	246.5	246.2
6	"	167.0	54.0	9018 ± 88	0.2330 ±0.0005	0.1820 ±0.0005	0.0435 ±0.0005	247.1	246.7
7	20.15 ± 0.05	163.0	50.0	8150 ± 82	0.0244 ±0.0002	0.0193 ±0.0002	0.0045 ±0.0002	246.9	246.8
8	"	"	"	"	0.0847 ±0.0002	0.0672 ±0.0002	0.0151 ±0.0002	246.9	246.9
9	"	"	"	"	0.3042 ±0.0005	0.2408 ±0.0005	0.0540 ±0.0005	246.6	246.4
10	30.20 ± 0.05	166.5	57.5	9574 ± 93	0.1355 ±0.0005	0.0907 ±0.0005	0.0358 ±0.0005	246.9	246.8
11	30.05 ± 0.05	72.0	50.0	3650 ± 76	0.0973 ±0.0003	0.0845 ±0.0003	0.0118 ±0.0003	246.8	246 5
12	40.2 ± 0.1	166.5	58.5	9740 ± 94	0.1349 ±0.0005	0.0762 ±0.0005	0.0420 ±0.0005	246.8	246.5
13	50.0 ± 0.1	162.5	61.0	9913 ± 97	0.1349 ±0.0005	0.0570 ±0.0005	0.0470 ±0.0005	247.0	247.0
14	"	73.0	50.0	3650 ± 76	0.0786 ±0.0003	0.0569 ±0.0003	0.0180 ±0.0003	246.8	246.5
15	60.0 ± 0.5	161.0	60.0	9660 ± 96	0.1349 ±0.0005	0.0407 ±0.0005	0.0446 ±0.0005	246.9	246.7
16	70.0 ± 1.0	73.0	50.0	3650 ± 76	0.0777 ±0.0003	0.0399 ±0.0003	0.0270 ±0.0003	246.8	246.5
17	0.0 ± 0.1	163.5	60.0	9810 ± 96	0.1324 ±0.0005	0.1157 ±0.0005	0.0153 ±0.0005	246.8	246.8
18	"	163.5	60.0	9810 ± 96	0.1324 ±0.0005	0.1155 ±0.0005	0.0154 ±0.0005	246 9	246.8
19	10.7 ± 0.1	163.0	50.0	8150 ± 82	0.0967 ±0.0005	0.0821 ±0.0005	0.0131 ±0.0005	246.7	246.6
		± 1.5	±0.2					± 0.2	± 0.2

1.

Results.

(gm)		Pressure (mmHg)			r^{I}	r^{II}	r	
(II)		Barometric Pressure (P_B)	"M_1"	"M_2"				Average
before airation	after airation							
237.4	237.7	755.5	68	74	258± 4	233± 8	251±10	252±11
237.4	237.5	756.0	100	105	251± 5	233± 8	250±10	
237.2	237.4	757.0	25	31	250±11	235±15	247±15	
237.3	237.4	757.0	50	56	264± 5	240±15	258±15	
237.1	237.4	760.0	52	58	261± 3	230±10	255±10	
237.4	237.8	761.0	50	56	254± 4	230±10	250±12	
237.2	237.3	756.5	50	56	239±14	220±15	235±15	238±12
237.2	237.3	755.0	50	56	243± 5	225±10	238±10	
237.2	237.4	755.0	48	54	246± 4	228±10	240±10	
237.2	237.3	760.0	52	60	169± 3	160± 5	168± 5	172± 7
237.4	237.8	757.5	29	35	178± 4	160± 8	175± 8	
237.2	237.5	760.0	52	59	126± 2	120± 4	125± 4	125± 4
237.5	237.6	760.0	52	60	90± 2	86± 2	89± 2	88± 3
237.2	237.5	758.5	40	46	88± 3	84± 3	87± 3	
237.4	237.9	762.0	52	58	70± 1	67± 2	69± 2	69± 2
237.2	237.5	758.0	45	56	58± 1	56± 2	57± 2	57± 2
237.3	237.4	759.0	50	56	491±22	440±30	485±33	482±33
237.3	237.4	759.0	50	56	485±22	430±30	478±33	
237.4	237.6	758.0	52	56	337±16	300±30	330±30	330±30
± 0.2	± 0.2	± 0.5	± 2.0	± 2.0				

from those of direct observation by means of the theory of errors.

The observed data are analysed as described in the next section.

4) The analysis of experimental data.

(A) The number of mols of prussic acid carried away from (I) within the time interval dt during the airation is given by,

$$\frac{v_0 C C_G^{\mathrm{I}} dt}{C^{\mathrm{I}} - C_W - C_G^{\mathrm{I}}}$$

where v_0 or C is the rate of flow or the total concentration of dry air respectively, C^{I} the total concentration of gas mixture corresponding the pressure prevailing in the gas phase of (I), C_W that of water vapor and C_G^{I} that of prussic acid, so that $\frac{v_0 C}{C^{\mathrm{I}} - C_W - C_G^{\mathrm{I}}}$ is the actual rate of gas flow and hence $\frac{v_0 C C_G^{\mathrm{I}}}{C^{\mathrm{I}} - C_W - C_G^{\mathrm{I}}}$ the rate of flow of prussic acid out from (I).

Equating the latter to the amount of decrease of prussic acid in (I) expressed by $-d(V_L^{\mathrm{I}} C_L^{\mathrm{I}} + V_G^{\mathrm{I}} C_G^{\mathrm{I}})$, where V_G^{I} and V_L^{I} are the respective volumes of gas and liquid phase in (I) and C_L^{I} the prussic acid concentration in the liquid, we have,

$$-\frac{v_0 C C_G^{\mathrm{I}} dt}{C^{\mathrm{I}} - C_W - C_G^{\mathrm{I}}} = d(V_L^{\mathrm{I}} C_L^{\mathrm{I}} + V_G^{\mathrm{I}} C_G^{\mathrm{I}}) \quad \cdots\cdots\cdots\cdots \quad (1)$$

Putting now,

$$\gamma^{\mathrm{I}} = \frac{C_L^{\mathrm{I}}}{C_G^{\mathrm{I}}} \quad \cdots\cdots\cdots\cdots \quad (2)$$

which gives the upper limit of OSTWALD's solutbility, inasmuch as the evaporation of prussic acid from the liquid into the gas does not necessarily attain the equilibrium during the passage, we have, by integration,

$(C^{\mathrm{I}} - C_W)(V_G^{\mathrm{I}} + \gamma^{\mathrm{I}} V_L^{\mathrm{I}}) \log \frac{V_L^{\mathrm{I}} C_{L0}^{\mathrm{I}} + V_G^{\mathrm{I}} C_{G0}^{\mathrm{I}}}{V_L^{\mathrm{I}} C_L^{\mathrm{I}} + V_G^{\mathrm{I}} C_G^{\mathrm{I}}}$

$= v_0 ct + V_L^{\mathrm{I}} C_{L0}^{\mathrm{I}} + V_G^{\mathrm{I}} C_{G0}^{\mathrm{I}} - V_L^{\mathrm{I}} C_L^{\mathrm{I}} - V_G^{\mathrm{I}} C_G^{\mathrm{I}}$ assuming $C^{\mathrm{I}} - C_W$, V_G^{I}, V_L^{I} and γ^{I} respectively constant. The C_{G0}^{I} and C_{L0}^{I} denote the respective concentration at $t=0$, i. e., at the beginning of the airation.

Assuming further that prussic acid is practically fixed in the liquid, when cooled at 0°C, or that,

$$V_L^{\mathrm{I}} C_{L0}^{\mathrm{I}} + V_G^{\mathrm{I}} C_{G0}^{\mathrm{I}} = V_L^{\mathrm{I}} C_{L0}^{\mathrm{I}\prime} \quad \cdots\cdots\cdots\cdots \quad (3, \mathrm{a})$$

$$V_L^{\mathrm{I}} C_L^{\mathrm{I}} + V_G^{\mathrm{I}} C_G^{\mathrm{I}} = V_L^{\mathrm{I}} C_L^{\mathrm{I}\prime} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (3, \mathrm{b})$$

where C_{L0}^{I} and C_L^{I} are the concentration respectively before and after the airation, as determined by analysis described in the foregoing section, we have,

$$\gamma^{\mathrm{I}} = \frac{v_0 ct + V_L^{\mathrm{I}} (C_{L0}^{\mathrm{I}\prime} - C_L^{\mathrm{I}\prime})}{(C^{\mathrm{I}} - C_W) V_L^{\mathrm{I}} \log C_{L0}^{\mathrm{I}\prime}/C_L^{\mathrm{I}\prime}} - \frac{V_G^{\mathrm{I}}}{V_L^{\mathrm{I}}} \quad \cdots\cdots\cdots\cdots \quad (4)$$

The C and C^{I} were calculated from the observation according to the formula,

$$C = \frac{P_B - \mathrm{M}_1}{RT}, \qquad C^{\mathrm{I}} = \frac{P_B - \{\mathrm{M}_1 + \frac{2}{3}(\mathrm{M}_2 - \mathrm{M}_1)\}}{RT}$$

regarding that the difference between M_1 and M_2 is caused by the hydrostatical pressure in (S), (I) and (II) which may be taken of equal amount because of the same geometry of the bottles and the same amount of liquids inside. The C_W is taken the vapor pressure of pure water. R is the gas constant $\frac{22.4 \times 760}{273}$ Lit.mmHg./°K and T the absolute temperature.

The γ^{I} thus calculated according to (4) is shown in Table 1.

(B) As regards (II) the amount $\frac{C C_G^{\mathrm{II}} v_0 dt}{C^{\mathrm{II}} - C_W - C_G^{\mathrm{II}}}$ of prussic acid leaving (II) or the whole series within the time interval dt during the airation expressed similarly as in the case of (I) may be equated to the over all decrease of prussic acid in the series as that,

$$-\frac{v_0 C C_G^{\mathrm{II}} dt}{C^{\mathrm{II}} - C_W - C_G^{\mathrm{II}}} = d(V_L^{\mathrm{I}} C_L^{\mathrm{I}} + V_G^{\mathrm{I}} C_G^{\mathrm{I}}) + d(V_L^{\mathrm{II}} C_L^{\mathrm{II}} + V_G^{\mathrm{II}} C_G^{\mathrm{II}}) \cdots \quad (5)$$

where C^{II} is the total concentration in the gas phase in (II).

Assuming V_L^{I}, V_L^{II} and V_G^{II} constant, we have now according to (3, b) that,

$$\frac{C_L^{\mathrm{II}} dx}{\gamma^{\mathrm{II}} (C^{\mathrm{II}} - C_W - C_G^{\mathrm{II}})} = -V_L^{\mathrm{I}} dC_L^{\mathrm{I}\prime} - (V_L^{\mathrm{II}} + V_G^{\mathrm{II}}/\gamma^{\mathrm{II}}) dC_L^{\mathrm{II}} \quad \cdots \quad (6)$$

or,

$$\frac{C_L^{\mathrm{II}} dx}{\gamma^{\mathrm{II}} (C^{\mathrm{II}} - C_W - C_G^{\mathrm{II}})} = -V_L^{\mathrm{I}} F(x) dx - (V_L^{\mathrm{II}} + V_G^{\mathrm{II}}/\gamma^{\mathrm{II}}) dC_L^{\mathrm{II}} \quad (6)'$$

where

$$F(x) = \frac{dC_L^{\mathrm{I}\prime}}{dx}, \quad \cdots\cdots \quad (7) \qquad x = Cv_0 t \quad \cdots\cdots\cdots \quad (8)$$

and

$$\gamma^{\mathrm{II}} = \frac{C_L^{\mathrm{II}}}{C_G^{\mathrm{II}}} \qquad \cdots\cdots (9)$$

is the lower limit of the OSTWALD's solubility inasmuch as the dissolution of prussic acid vapor from a bubble into the solution in (II) does not necessarily attain the equilibrium during the passage.

Eq. (4) may now be written according to (8) in the form,

$$C_L^{\mathrm{I}\prime} = C_{L0}^{\mathrm{I}\prime} e^{-\alpha x + \beta(C_L^{\mathrm{I}\prime} - C_{L0}^{\mathrm{I}\prime})} \qquad \cdots\cdots (10)$$

giving the implicit function $C_L^{\mathrm{I}\prime}(x)$ of x, where,

$$\alpha = \frac{1}{\left(\gamma^{\mathrm{I}} + \frac{V_G^{\mathrm{I}}}{V_L^{\mathrm{I}}}\right)(C^{\mathrm{I}} - C_W)V_L^{\mathrm{I}}}, \qquad \beta = V_L^{\mathrm{I}}\alpha$$

Expanding $C_L^{\mathrm{I}\prime} \cdot e^{\alpha x}$ according to the MACLAURIN's theorem in the power series of x, remembering that,

$$C_L^{\mathrm{I}\prime} = C_{L0}^{\mathrm{I}\prime} \quad \text{at} \quad x = 0$$

and neglecting the terms of higher than the first power with respect to x, we have that,

$$C_L^{\mathrm{I}\prime} e^{\alpha x} = C_{L0}^{\mathrm{I}\prime}\left(1 + \alpha x + \frac{\alpha x}{C_{L0}^{\mathrm{I}\prime}\beta - 1}\right) \qquad \cdots\cdots (11)$$

which gives $V_L^{\mathrm{I}} C_L^{\mathrm{I}} + V_G^{\mathrm{I}} C_G^{\mathrm{I}}$ or $C_L^{\mathrm{I}\prime}$ according to (2) and (3) as the explicit function of x as that,

$$V_G^{\mathrm{I}} C_G^{\mathrm{I}}\left(1 + \frac{V_L^{\mathrm{I}}}{V_G^{\mathrm{I}}}\gamma^{\mathrm{I}}\right) = V_G^{\mathrm{I}} C_G^{\mathrm{I}} + V_L^{\mathrm{I}} C_L^{\mathrm{I}} = V_L^{\mathrm{I}} C_L^{\mathrm{I}\prime} = V_L^{\mathrm{I}} C_{L0}^{\mathrm{I}\prime} e^{-\alpha x}\left(1 + \alpha x + \frac{\alpha x}{C_{L0}^{\mathrm{I}\prime}\beta - 1}\right)$$
$$\cdots\cdots (11)'$$

It was found by an actual calculation that (11) reproduces four significant figure of $C_L^{\mathrm{I}\prime}$ as given by the exact relation (10) as the function of x.

We have now according to (6)′ and (11) that,

$$\frac{dC_L^{\mathrm{II}}}{dx} + \frac{C_L^{\mathrm{II}}}{(V_L^{\mathrm{II}} + V_G^{\mathrm{II}}/\gamma^{\mathrm{II}})\gamma^{\mathrm{II}}(C^{\mathrm{II}} - C_W - C_G^{\mathrm{II}})} + \frac{V_L^{\mathrm{I}} C_{L0}^{\mathrm{I}\prime}\alpha e^{-\alpha x}}{(V_L^{\mathrm{II}} + V_G^{\mathrm{II}}/\gamma^{\mathrm{II}})}\left(\frac{1-\alpha x}{C_{L0}^{\mathrm{I}\prime}\beta - 1} - \alpha x\right) = 0 \qquad \cdots\cdots (12)$$

Integrating the above linear differential equation treating C_G^{II} as if

it were given as a known function of x and assuming as in the case of (I) that,

$$V_L^{II}C_L^{II} + V_G^{II}C_G^{II} = V_L^{II}C_L^{II\prime} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (13)$$

we have according to (9) that,

$$C_L^{II\prime} = C_L^{II}\left(1+\frac{V_G^{II}}{\gamma^{II}V_L^{II}}\right) = C_{L0}^{I\prime}\alpha e^{-\int_0^x H\gamma^{II}(C^{II}-C_W-C_G^{II})\,dx} \times\int_0^x e^{-\alpha x}\left(\alpha x+\frac{\alpha x-1}{C_{L0}^{I\prime}\beta-1}\right)e^{\int_0^x H\gamma^{II}(C^{II}-C_W-C_G^{II})\,dx}\,dx \quad (14)$$

where,

$$H = V_L^{II} + V_G^{II}/\gamma^{II},$$

The γ^{II} is now determined by fitting it to the observed $C_L^{II\prime}$ at relevant x according to (14) by means of a successive approximation; i. e., the integration in (14) is evaluated first by neglecting C_G^{II} as that,

$$C_L^{II\prime} = C_L^{II}\left(1+\frac{V_G^{II}}{\gamma^{II}V_L^{II}}\right) = \frac{C_{L0}^{I\prime}\alpha}{\delta}\,e^{-H\gamma^{II}(C^{II}-C_W)x} \times\left\{e^{\delta x}\left(\alpha x+\frac{\alpha x-1}{C_{L0}^{I\prime}\beta-1}\right)+\frac{1}{C_{L0}^{I\prime}\beta-1}+\frac{\alpha}{\delta}\left(1+\frac{1}{C_{L0}^{I\prime}\beta-1}\right)\left(1-e^{\delta x}\right)\right\} \quad (15)$$

where,

$$\delta = -\alpha+\frac{1}{H\gamma^{II}(C^{II}-C_W)},$$

and by means of the equation γ^{II} is fitted to the observation for the first approximation. The γ^{II} thus found gives now C_L^{II} according to (15) or according to (9) C_G^{II} as the function of x. The latter function $C_G^{II}(x)$ is now substituted into C_G^{II} in (14) and the integration numerically evaluated thus giving a relation of the second approximation to fit γ^{II} to the observed values. Constant value of γ^{II} given in Table 1. is attained by two or three times of the above successive approximation.

The C^{II} in the above calculation is taken

$$\frac{P_B - M_2}{RT}$$

or the total gas concentration corresponding the pressure at the part of series at which manometer M_2 is attached.

(C) The upper and the lower limit γ^{I} and γ^{II} determined as above are almost coincident with each other within the experimental errors at higher temperatures, but not quite at lower temperatures. Since we have no fair reason to take the mean of γ^{I} and γ^{II} the most provable value of γ at lower temperatures, although it may be due at higher temperatures, the present authors proceeded to find the latter by analysing the experimental data kinetically as follows.

We observe at first the dissolution or evaporation of the solute during the process of a bubble going up throu the solution. Assuming the rate of the dissolution or evaporation proportional respectively to the concentration in gas or in liquid phase, we have,

$$\frac{dC_G}{dt} = \vec{k}C_L - \overleftarrow{k}C_G \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (16)$$

where $\vec{k}$ and $\overleftarrow{k}$ are proportionality constants.

Since at equilibrium, $0 = \vec{k}C_L - \overleftarrow{k}C_G$ and hence $\frac{C_L}{C_G} = \frac{\overleftarrow{k}}{\vec{k}} = \gamma$,

It follows that, $\overleftarrow{k} = \vec{k}\gamma$

Eq. (16) is thus expressed in the form,

$$\frac{dC_G}{dt} = \vec{k}(C_L - C_G\gamma)$$

Or by integration, assuming that C_L is practically constant during the observed time interval t, that,

$$-\log(C_L - C_G\gamma) = \gamma\vec{k}_1 t + \text{const.}, \quad \text{when} \quad C_L > C_G\gamma \quad \cdots \quad (17, \text{a})$$

or

$$-\log(C_G\gamma - C_L) = \gamma\vec{k}_2 t + \text{const.}, \quad \text{when} \quad C_G\gamma > C_L \quad \cdots \quad (17, \text{b})$$

Determining the integration constant with regard to (I) according to the condition that $C_G^{I} = 0$, when $t = 0$, we have on one hand that,

$$-\log\frac{C_L^{I} - C_G^{I}\gamma}{C_L^{I}} = \gamma\vec{k}_1 t \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (18)$$

and with regard to (II) according the condition that $C_G^{II} = C_G^{I}$ at $t = 0$, on the other hand that,

$$\log\frac{C_G^{II}\gamma - C_L^{II}}{C_G^{I}\gamma - C_L^{II}} = -\gamma\vec{k}_2 t \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (19)$$

Practically, however, the solute may dissolve into or evaporate from the solution throu the horizontal surface even after the gas in the

bubble have joined the gas phase but this would only effectively lengthen the time of contact t so far as the above assumption of the proportionality of the rate to the concentration is valid. The effective time of contact t in (I) and (II) on one hand and also $\vec{k}_1$ and $\vec{k}_2$ on the other hand may respectively be identified by virtue of the same structure and size of the system both in the bottles. We have hence identifying $\vec{k}_1 t$ with $\vec{k}_2 t$ that,

$$\frac{C_L^{\mathrm{I}} - C_G^{\mathrm{I}}\gamma}{C_L^{\mathrm{I}}} = \frac{C_G^{\mathrm{II}}\gamma - C_L^{\mathrm{II}}}{C_G^{\mathrm{I}}\gamma - C_L^{\mathrm{II}}}$$

or that, $K = \dfrac{\gamma' - \gamma}{\gamma'} = \dfrac{C_G^{\mathrm{II}}\gamma - C_L^{\mathrm{II}}}{C_G^{\mathrm{I}}\gamma - C_L^{\mathrm{II}}}$ ..... (20)

And in consequence, according to (20) that,

$$C_G^{\mathrm{II}} = \frac{(1-K)\,C_L^{\mathrm{II}} + KC_G^{\mathrm{I}}\gamma}{\gamma} \quad \text{..... (21, a)}$$

or that,

$$dC_G^{\mathrm{II}} = \frac{(1-K)\,dC_L^{\mathrm{II}} + K\gamma dC_G^{\mathrm{I}}}{\gamma} \quad \text{..... (21, b)}$$

Assuming again V_L^{I}, V_L^{II} and V_G^{II} constant, we have by substituting C_G^{II} and dC_G^{II} from (21) into (5) and remembering (7), that,

$$-V_L^{\mathrm{I}}F(x)dx - \frac{\dfrac{(1-K)\,C_L^{\mathrm{II}} + K\gamma C_G^{\mathrm{I}}}{\gamma}}{C^{\mathrm{II}} - C_w - \dfrac{(1-K)\,C_L^{\mathrm{II}} + K\gamma C_G^{\mathrm{I}}}{\gamma}}\,dx = V_L^{\mathrm{II}}dC_L^{\mathrm{II}} + \frac{V_G^{\mathrm{II}}}{\gamma}\left\{(1-K)\,dC_L^{\mathrm{II}} + K\gamma dC_G^{\mathrm{I}}\right\}$$

or that,

$$-V_L^{\mathrm{I}}F(x)\,dx - \frac{C_L^{\mathrm{II}}(1-K)}{\gamma\left(C^{\mathrm{II}} - C_w - C_L^{\mathrm{II}}\dfrac{1-K}{\gamma} - KC_G^{\mathrm{I}}\right)}dx - \frac{KC_G^{\mathrm{I}}}{C^{\mathrm{II}} - C_w - C_L^{\mathrm{II}}\dfrac{1-K}{\gamma} - KC_G^{\mathrm{I}}}\,dx = dC_L^{\mathrm{II}}\left\{V_L^{\mathrm{II}} + \frac{V_G^{\mathrm{II}}}{\gamma}(1-K)\right\} + KV_G^{\mathrm{II}}dC_G^{\mathrm{I}}$$

Substituting further C_G^{I} in the above equation from (11)′, we now obtain that,

$$\left\{-V_L^{\mathrm{I}}C_{L0}^{\mathrm{I}\prime}\alpha e^{-\alpha x}\left(\frac{1-\alpha x}{C_{L0}^{\mathrm{I}\prime}\beta-1}-\alpha x\right)-\frac{KV_G^{\mathrm{II}}C_{L0}^{\mathrm{I}\prime}\alpha}{\gamma^{\mathrm{I}}}\ e^{-\alpha x}\left(\frac{1-\alpha x}{C_{L0}^{\mathrm{I}\prime}\beta-1}-\alpha x\right)\right.$$
$$\left.-\frac{P(x)}{C^{\mathrm{II}}-C_W-C_L^{\mathrm{II}}\dfrac{1-K}{\gamma}-P(x)}\right\}dx-\frac{C_L^{\mathrm{II}}(1-K)}{\gamma\left(C^{\mathrm{II}}-C_W-C_L^{\mathrm{II}}\dfrac{1-K}{\gamma}-P(x)\right)}dx$$
$$=dC_L^{\mathrm{II}}\left(V_L^{\mathrm{II}}+\frac{V_G^{\mathrm{II}}}{\gamma}(1-K)\right)\cdots\cdots\cdots\cdots\quad(22)$$

where, $$P(x)=\frac{KC_{L0}^{\mathrm{I}\prime}}{\gamma^{\mathrm{I}}}e^{-\alpha x}\left(1+\alpha x+\frac{\alpha x}{C_{L0}^{\mathrm{I}\prime}\beta-1}\right),$$

The (22)is linear differential equation with respect to C_L^{II} provided that $C_L^{\mathrm{II}}\dfrac{1-K}{\gamma}$ in the denominator is neglected.

Proceeding with the successive approximation similarly as in the case of γ^{II}, neglecting $C_L^{\mathrm{II}}\dfrac{1-K}{\gamma}$ in the denominator we integrate the resulting linear differential equation remembering the relation (13) as that,

$$\frac{C_L^{\mathrm{II}\prime}}{\left(1+\dfrac{V_G^{\mathrm{II}}}{\gamma^{\mathrm{II}}V_L^{\mathrm{II}}}\right)}=C_L^{\mathrm{II}}=\frac{C_{L0}^{\mathrm{I}\prime}\alpha}{H'}\ e^{-\int_0^x\frac{(1-K)\,dx}{H'\gamma(C^{\mathrm{II}}-C_W-\mathrm{P}(x))}}$$
$$\times\int_0^x\left\{e^{-\alpha x}\left(\frac{\alpha x-1}{C_{L0}^{\mathrm{I}\prime}\beta-1}+\alpha x\right)\left(V_L^{\mathrm{I}}+\frac{KV_G^{\mathrm{II}}}{\gamma^{\mathrm{I}}}\right)-\frac{P(x)}{C^{\mathrm{II}}-C_W-P(x)}\right\}e^{\int_0^x\frac{(1-K)\,dx}{H'\gamma(C^{\mathrm{II}}-C_W-P(x))}}dx$$
$$\cdots\cdots\cdots\cdots\quad(23)$$

where, $$H'=V_L^{\mathrm{II}}+V_G^{\mathrm{II}}\frac{1-K}{\gamma},$$

The γ is now fitted to the obserbed values of $C_L^{\mathrm{II}\prime}$ and x according to (23) by trial and error, known values of γ^{I} and γ^{II} being put into it. Tne $C_L^{\mathrm{II}\prime}$ thus expressed by (23) as a function of x with this values of γ is now put into the denominator of (23) and the resulting linear differential equation integrated as that,

$$\frac{C_L^{\mathrm{II}\prime}}{\left(1+\dfrac{C_G^{\mathrm{II}}}{\gamma^{\mathrm{II}}V_L^{\mathrm{II}}}\right)}=C_L^{\mathrm{II}}=\frac{C_{L0}^{\mathrm{I}\prime}\alpha}{H'}\ e^{-\int_0^x\frac{(1-K)\,dx}{H'\gamma\left(C^{\mathrm{II}}-C_W-C_L^{\mathrm{II}}\frac{1-K}{\gamma}-P(x)\right)}}$$

$$\times \int_0^x \left\{ e^{-\alpha x} \left(\frac{\alpha x - 1}{C_{L0}' \beta - 1} + \alpha x \right) \left(V_L^{\mathrm{I}} + \frac{K V_G^{\mathrm{II}}}{\gamma^{\mathrm{I}}} \right) - \frac{P(x)}{C^{\mathrm{II}} - C_W - C_L^{\mathrm{II}} \dfrac{1-K}{\gamma} - P(x)} \right\}$$

$$e^{\int_0^x \frac{(1-K)\,dx}{H'\gamma \left(C^{\mathrm{II}} - C_W - C_L^{\mathrm{II}} \frac{1-K}{\gamma} - P(x) \right)}} dx \cdots\cdots \quad (24)$$

The successive approximation is thus carried out similarly as in the case of γ^{II}.

Fig. 2 shows γ thus determined which lies between γ^{I} and γ^{II} as expected.

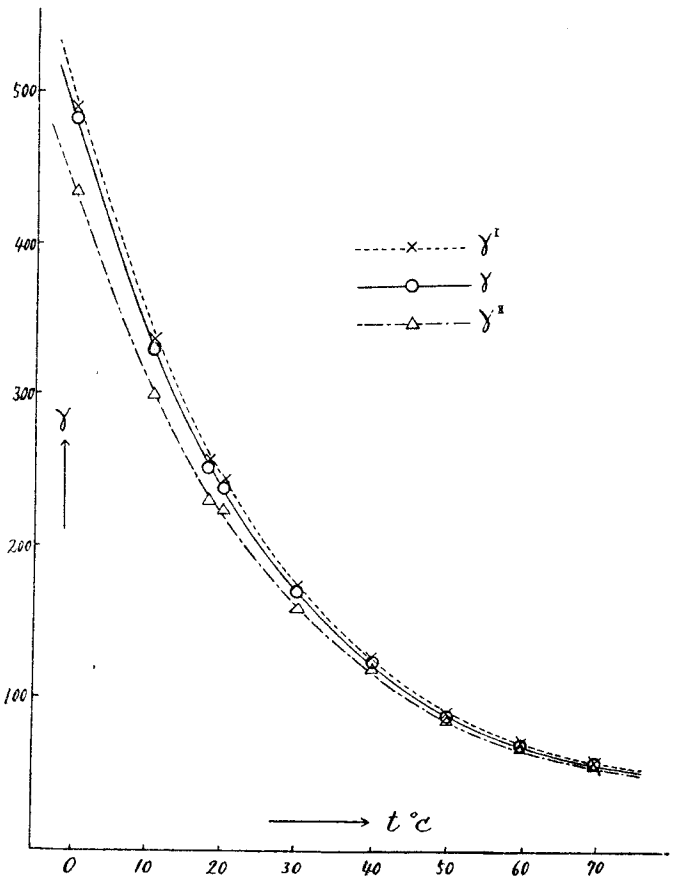

Fig. 2. Solubility of Prussic Acid for Water.
($\gamma - t$ curve)

Plotting $\log_{10}\gamma$ against 1/T, we obtain, as shown in Fig. 3, a straight line over the range of observation from 0°C to 70°C. Obserbing that $\gamma = 1$ at critical temperature of the solvent, we may interpolate the solubility at temperatures above those of measurement by combining the observed straight line properly with the point $\gamma = 1$ at the critical temperature as shown in Fig 3.

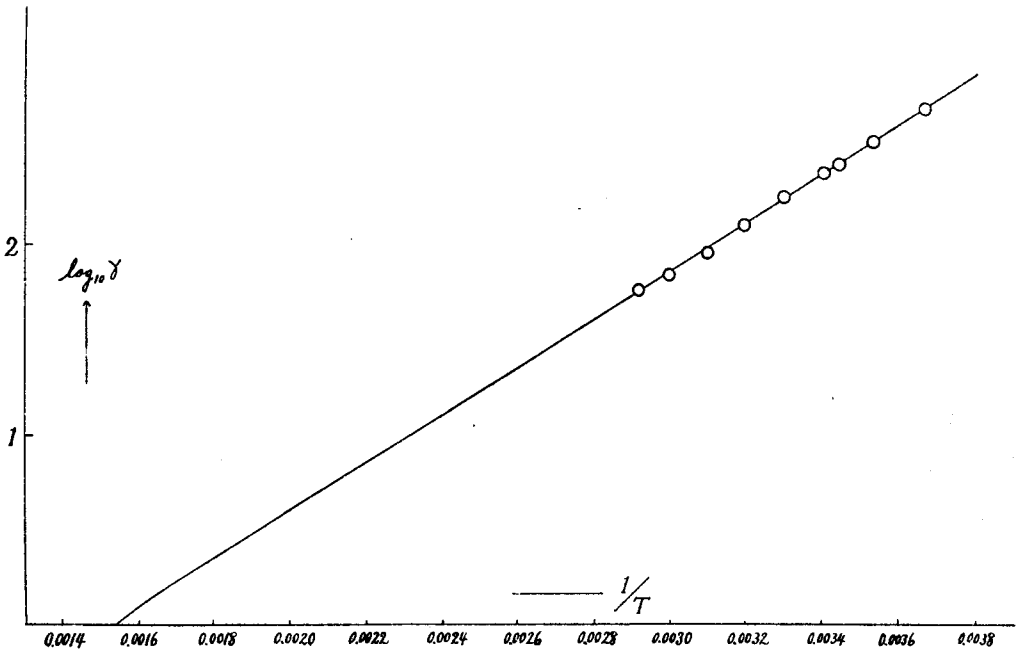

Fig. 3. Solubility of Prussic Acid for Water.
($\log_{10}\gamma - 1/T$)

The observed straight line gives, on the other hand, the heat of dissolution according to the relation,

$$Q_S^{*)} = -RT^2 \frac{\partial \log \gamma}{\partial T} - RT^2\alpha + RT \quad (= 5.1 \pm 0.4)$$

where α denotes the expansion coefficient of solvent.

The value $\gamma_{18°C} = 252$ among the above result may be compared with

*) The Q_S gives the heat evolved per mol of the solute transferred from the gas into the liquid phase at constant pressure or the difference of the partial molal enthalpy of the solute in the gas and the liquid phase.

that $\gamma_{18°C} = 270$ derived*) from the vapor pressure measurement by G. BREDIG and M. SHIRADO, both the values seeming satisfactorily coincident.

5) Summary

1) A simple procedure of measurement of solubility was devised and the upper and the lower limit of the solubility were first determined over the temperatures ranging from 0°C to 70°C.

2) Both the limits were found practically coincident at higher temperatures but not quite at lower temperatures.

3) In order to arrive at reasonable value γ of solubility even at lower temperatures, the experimental data was kinetically analysed the result being that,

t °C	0.0	10.7	18.1	20.2	30.2	40.2	50.0	60.0	70.0
γ	482	330	252	238	172	125	88	69	57

4) The heat of dissolution derived from the observed solubility is 5.1 $\pm$ 0.4 Kcal.

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*) OSTWALD's solubility may be expressed as that,

$$\gamma = \frac{C_L}{C_G} = \frac{x/V_L}{p/RT'} = \frac{RT}{V_L}\,\frac{x}{p}$$

where p denotes the partial pressure of solute and x the molfraction of solute in liquid. And hence γ at $x = 0$ is determined by extrapolating observed x/p (Landolt-Börnstein Erg. ii, 1340) to $x = 0$.