Studies on the Equilibrium between Dilute Solution and Solute Vapour. I. Measurement of the Condensation Coefficient (α) of Solute Vapour at the Liquid Surface of Solvents.

By Ituro UHARA.

(Received July 23, 1943.)

Part I. Experimental.

(1) *Introduction.* When a solute (S) is dissolved in a solvent (L), Henry's law, $C/p = \text{constant} \equiv K$, holds between the concentration of S in solution (C mol./l.) and the partial pressure of S (p mm. Hg) when the solution is dilute. Though K is an important constant which determines solubility (for small solubility, solubility $= Kp_o$, where p_o is the vapour pressure of pure S) and the partial pressure, it is not deduced thermodynamically. In the kinetic derivation of K which will be stated later, the knowledge of the condensation coefficient (α) of S at the liquid surface of L, in other words, the fraction of dissolving S molecules which have collided with the surface must be obtained. It has been vaguely believed that, when gas or vapour is absorbed by liquid, the molecules colliding with the liquid surface are all dissolved because the dissolution of them is usually exothermic. Late Prof. S. Miyamoto⁽¹⁾, in his wide researches on the chemical absorption of gases (oxygen in sulphite solution etc.), considered that in colliding molecules, only those with more vertical velocity than a critical value can enter into liquid, instead of considering the effect of diffusion as usually believed. He obtained the value of order of 10^{-7} for α, but the gases which were used being of atomospheric pressure, perhaps the effect of diffusion cannot be neglected, and then the real value of α may be still higher.

(2) *Method of measurement of the condensation coefficient* (α). α can be determined by dividing the absorbed quantity of S which is analytically determined with the number of collisions of S molecules at the liquid surface, i.e. p (time of contact of S vapour and L) (area of interface)$/\sqrt{2\pi MRT}$ (see § 5). Ordinary methods to measure the absorption velocity, however, give nothing but the diffusion velocity at the interface. To eliminate the effect of diffusion to obtain real value of α, p must be low and the liquid surface of the known area must be always kept fresh, and for this purpose the following simple method was deviced, which proved to be considerably satisfactory (Fig. 1, 2).

(a) Source of low pressure vapour: to determine α of iodine, for example, three or four large bottles amounting 50–70 l. are connected, in which iodine was sublimed on the inner wall and the saturated solution of iodine in L is introduced. These bottles are filled with saturated

---

(1) S. Miyamoto, this Bulletin, (1927–1932).

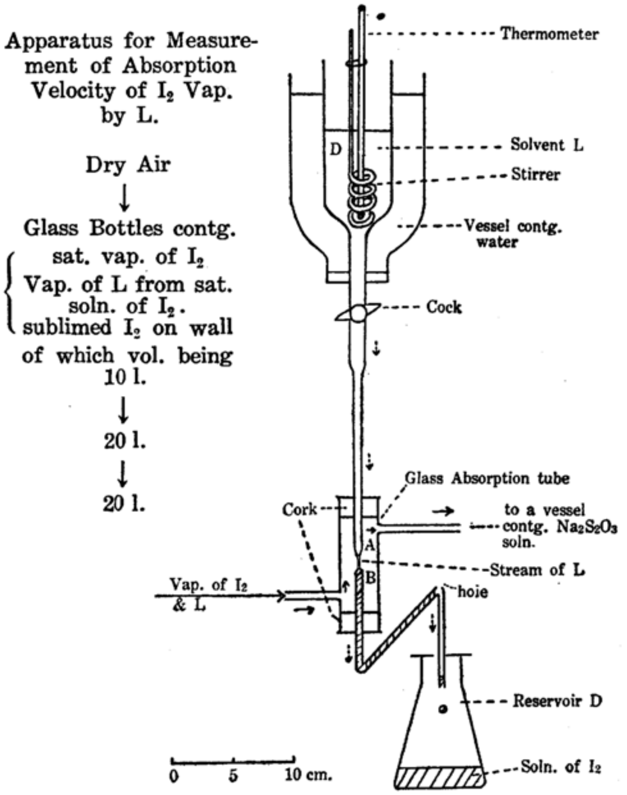


Fig. 1.

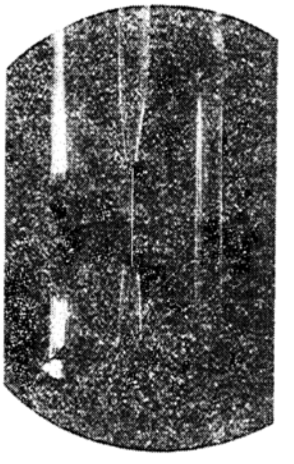


Fig. 2. Absorption tube and the stream.

vapours of iodine and L when kept in a room of almost constant T. In other cases, dilute aqueous solutions of the known vapour pressure were used. p mm.Hg used: $I_2 = 0.09$–0.6 $NH_3 = 0.8$–1.0 $HCl = 0.8$–1.2 acetone $= 0.4$–0.5 $CH_3OH = 0.8$–1.0 $C_2H_5OH = 1.5$–1.8 $C_5H_{11}OH = 4.8$–5.3.

(b) Procedure: vapour is sent at the rate of 1–2.5 l./min. and the velocity of gas flow in the absorption tube (Fig. 1, 2, diameter 2–3 cm.) is the order of 10 cm./sec. even when turbulence is neglected. On opening the cock, L in D streams down from the point (A) of thin glass tube (the out-side is paraffined when polar L is used.) and enters in B. Under the experimental conditions suitably selected, this stream between A and B (Fig. 2) is cylindrical and its surface area is calculable on photographic plate, and no bubble enters in B, liquid level being maintained at B (of which area is 1/10–1/7 of that of the surface of the stream). Diameter of stream=0.03–0.05 cm., length=0.48–1.1 cm., quantity of L streaming = 0.15 c.c./sec. or more, velocity of streaming $L=1\times10^2$cm./sec. or more, time of contact with vapour flowing in the counter direction $=0.5$–0.8×10^{-2} sec., time of streaming L=2–5 min., usually 3 min.

(c) Method of analysis: as the solution collected in the reservoir is very dilute (under 10^{-6} mol. in about 30 c.c.) measured cases are limited.

Iodine: titrated with 1/300–1/1000 N sodium thiosulphate solution with microburette (calibrated thin glass tube). Iodine in non-polar L is titrated, starch as indicator, being shaken with concentrated potassium iodide solution. Iodine in the acid solution is titrated after extracting with carbon tetrachloride. In the case of polar L which hinders the iodine-starch reaction, the end point is determined from vanishing of yellow colour after shaking in a long test tube on adding iodide. (As for higher alcohols which are only partly miscible with water, ethanol is mixed to form homogeneous liquid.) Some L (toluene, heptane, decalin and amyl alcohol etc.) contain or yield minute quantity of substance which oxidizes iodide, hence the results of titration is entirely disturbed. This cannot be removed by ordinary methods of purification, but was removed completely by shaking with magnesium amalgam and distillation.

Hydrogen chloride: determined nephelometrically as silver chloride. When dissolved in benzene, it is determined after extraction with pure alkali(2).

Ammonia: determined nephelometrically with a mixture of mercuric chloride, sodium chloride and lithium carbonate solution(3).

Acetone: determined nephelometrically with mercuric cyanide complex solution(4).

Methanol: oxidized with permanganate and the constant volume of the first distillate is collected and determined colorimetrically on adding Schiff's reagent.

Ethanol: after oxidation with chromic acid, treated analogously with methanol.

Butanol and amyl alcohol: determined with an interferometer of Rayleigh-type. As for lower alcohols, the changes of refractive index on dissolving are too minute.

(3) *Were real values of a obtained by this method?* Under the most unfavourable condition, it may be supposed, the surface of the stream may be occupied by same L molecules from A to B (Fig. 1, 2) and soon covered with mono-layer of S, which remains there in consequence of the small diffusion velocity in liquid and hinders further dissolution of vapour. The real conditions are as follows:

(a) As the most favourable case for establishment of circumstances stated above, the case of dissolution of iodine in 0.05 N aqueous solution of potassium iodide is taken, in which very high value of α 13.5×10^{-4} was obtained and the length of the stream was very long (1.1 cm.). The time of contact with vapour between A and B is 0.64×10^{-2} sec., and the total area of the stream exposed to vapour is 3.03×10^{3} sq. cm.. If iodine molecules (radius 2.23 A) form closely packed mono-layer on this area, 3.00×10^{-6} mol. must exist, whereas iodine really dissolved was 5.15×10^{-7} mol., i.e. 17% of the mono-layer. In many cases, α is 1/2–1/10 of this case.

(b) In the Brownian motion, average squared displacement is expressed as $\overline{x^2}=2$ (diffusion coefficient) × (time). The values of $\sqrt{\overline{x^2}}$ for iodine in ethanol and carbon bisulphide are 2.2×10^{-4} and 3.8×10^{-4} cm. respectively in 1/400 sec., hence dissolved iodine may not be fixed at the surface.

(c) If iodine flows down into B in an adsorbed state at the liquid surface, the quantity of iodine measured is independent of the length (h) of the stream, consequently observed α must be reversely proportional to h, but as a matter of fact α is found to be independent of h. Furthermore, the time of adsorption is

---

(2) Lamb, Carleton and Meldrum, *J. Am. Chem. Soc.*, **43**(1920), 251.

(3) Grave, *ibid.* **37**(1915), 1171.

(4) Marriott, *J. Biochem.* **16**(1913), 289.

expressed approximately by $e^{\frac{Q}{RT}}/\nu$, (Q=heat of adsorption, ν=frequency of molecular vibration at the surface) and if Q is assumed 6 kcal./mol. at common T, it is about 10^{-8} sec., accordingly S at the surface soon re-evaporates or dissolves, and the quantity which flows into B in an intermediate state is indeed negligible. As about 1000–4000 iodine molecules impacts with the surface of $(10\ \mathrm{A})^2$ width while the liquid passes between A and B in ca. 5×10^{-3} sec., (in which usually one or two molecules are dissolved) it is easily seen that the adsorption isotherm is attained very fast, and that θ in Langmuir's adsorption isotherm is under 0.01, indicating the existence of almost clear liquid surface free from S with the facts stated in (a) and (b). Another evidence is that, if iodine flows down into B in an adsorbed state at the surface, α for alkali or potassium iodine solution must be smaller than that for water, because ions do not exist at the surface and reduce α, (§ 10) whereas the facts are entirely opposite.

(d) As the flow velocity of vapour becomes lower, the diffusion velocity of S in the air near the liquid surface is less than the dissolution velocity, resulting in the decrease of α value. In our experimental condition, however, the flow velocity of vapour is far larger and the obtained value is independent of it, showing non-existence of the effect due to the diffusion in the air⁽⁵⁾.

(e) According to the Fresnel's law of reflection, if the transition between air and the medium of refractive index n is absolutely abrupt, the light is completely plane-polarized, when the angle of incidence is $\tan^{-1} n$. But if the transition is gradual, the light is elliptically polarized. As for the surface of water and various liquids, practically no or only slight ellipticity exists, showing that the transition layer is about one molecule thick, and that the interface of liquid and gas is quite sharp⁽⁶⁾. This is also concluded from the studies of surface film. In these experiments, the adsorption layer of air molecules at the surface is not found, though it is easily detectable if it really exists. That the difference of surface tension (σ) of water in vacuum and in the air is only barely observable shows the fact that the quantity of air molecules at the surface is far less than mono-layer.

(f) There is no reliable evidence for the time change of σ of the newly formed surface of a pure liquid, and considering from the frequency of molecular motion in the liquid, it is estimated that the state of surface used in our measurements (1/500–1/100 sec. old) is the same as the normal one (for the case of solution, see § 10 and 12).

It may be concluded from the facts stated above that we obtained nearly real values of α free from the effects of diffusion of S in L and air, and from the effects of the adsorption layer of S and air at the liquid surface.⁽⁷⁾

(4) *Results of measurements of α of some solutes* (S) *on various solvents* (L).

---

(5) For iodine vapour in the air, $\sqrt{\overline{x^2}}$=ca. 2×10^{-3} cm. in 1/400 sec. and mean free path=ca. 10^{-5} cm. The diffusion layer between reacting solid and liquid is ca. 10^{-3} cm. thick, and that between the stream of liquid and flowing gas may be far less than this.

(6) Rayleigh, *Phil. Mag.* **33** (1892), 1; Raman and Randas, *ibid.* **3** (1927), 220.

(7) As for the comparison with ordinary methods of gas absorption, see § 13.

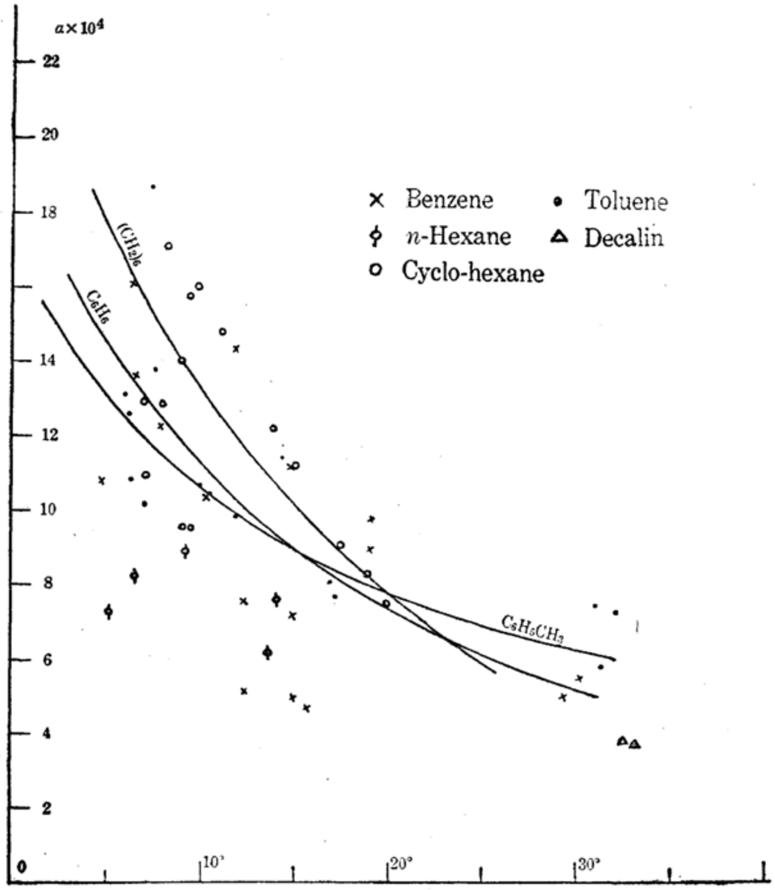
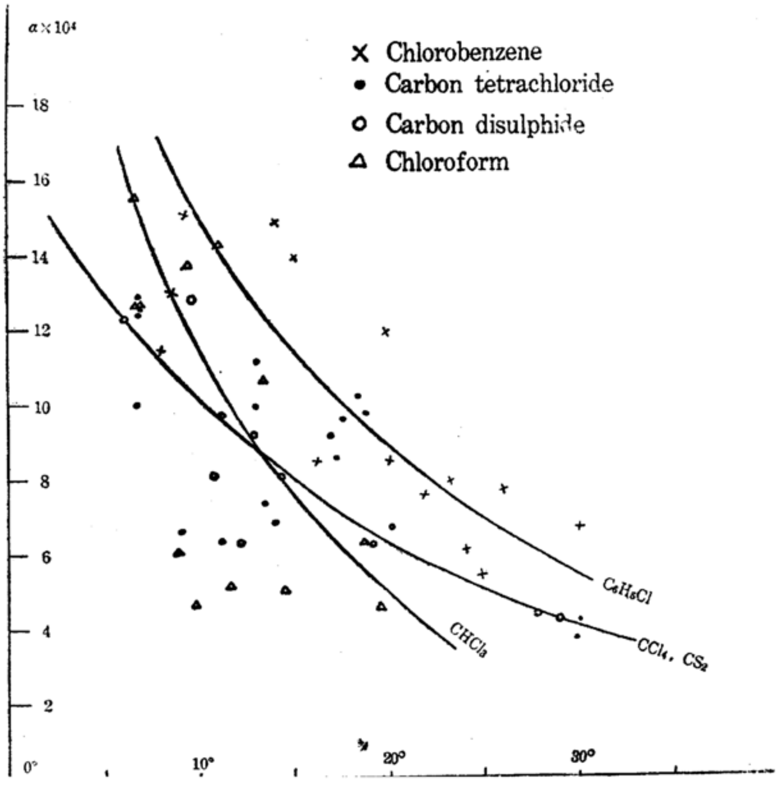


Fig. 3. α of iodine on non-polar solvents.



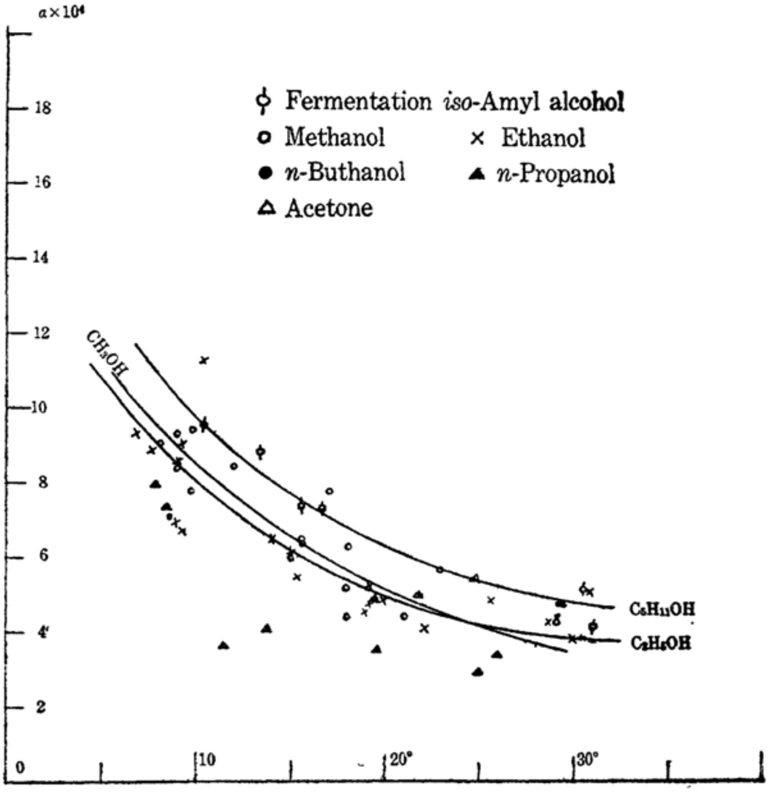
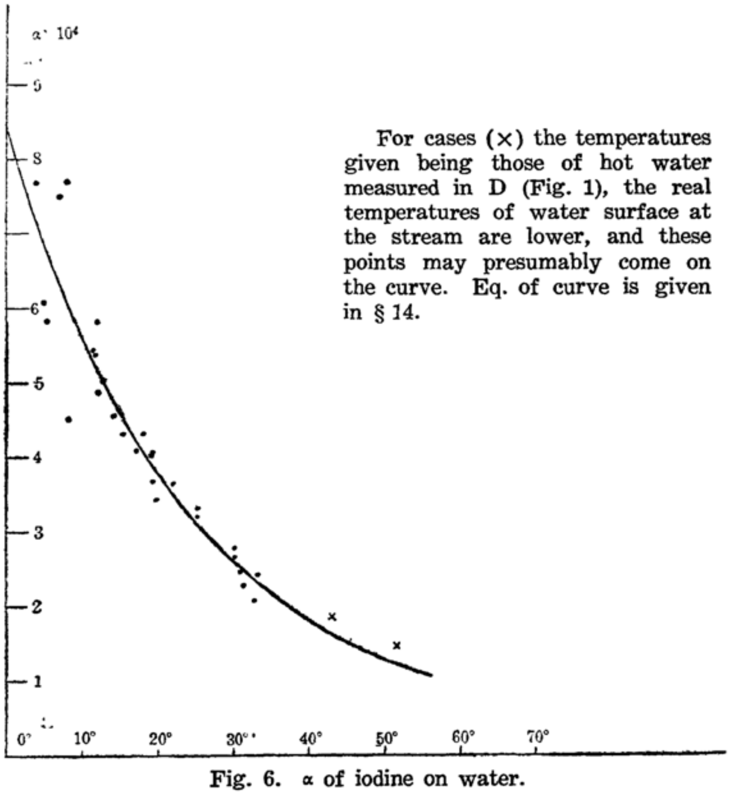


Fig. 5. α of iodine on alcohols.



For cases (×) the temperatures given being those of hot water measured in D (Fig. 1), the real temperatures of water surface at the stream are lower, and these points may presumably come on the curve. Eq. of curve is given in § 14.

Fig. 6. α of iodine on water.

Table 1. $S = I_2$. (Obtained from Fig. 3–6. For α on aqueous solution, see § 10, 11, 12, 13 and Fig. 8.)

L	$\alpha \times 10^4$							
	5°	10°	15°	20°	25°	29°	30°	
n-C_6H_{14}	—	7.2	—	—	—	—	—	
$(CH_2)_6$	—	13.2	10.1	7.8	6	—	—	
C_6H_6	—	11.2	8.9	7.3	6.1	—	—	
$C_6H_5CH_3$	—	10.6	8.9	7.7	6.8	—	—	
Decalin	—	—	—	—	—	—	—	3.8 (32.7°)
CCl_4	—	10.2	7.9	6.2	5.0	—	—	
$CHCl_3$	—	11.4	7.5	4.9	2.8	—	—	
C_6H_5Cl	—	15.0	11.3	8.8	6.9	—	—	
CS_2	—	10.2	7.9	6.2	5.0	—	—	
$(CH_3)_2CO$	—	—	—	5	—	—	—	
$C_5H_{11}OH$	—	9.7	7.7	6.3	5.3	—	4.8	
n-C_4H_9OH	—	—	—	—	—	4.5	—	
n-C_3H_7OH	—	—	—	—	3.2	—	—	
C_2H_5OH	—	8.0	6.2	5.0	4.2	—	3.8	
CH_3OH	—	8.5	6.6	5.2	4.1	—	—	
H_2O	6.85	5.60	4.56	3.75	3.11	—	2.6	1.8 (40°)

L	S = HCl					
	C_6H_6	Decalin	C_6H_5Cl	C_2H_5OH	H_2O	NaOH aq. (0.05 N)
t°	24.1	26.1	30	28.2	28.4	29
$\alpha \times 10^4$	0.10	0.32	0.20	2.45	1.89	1.67

L	$S = NH_3$					
	$C_6H_5CH_3$		Decalin	H_2O		HCl aq. (0.5 N)
t°	15.4	30.2	30.0	16	29	15.0
$\alpha \times 10^4$	0.56	0.24	0.37	46	41	49.5

L	S = Acetone			$S = CH_3OH$	$S = C_2H_5OH$
	C_6H_6	$C_6H_5CH_3$	H_2O	H_2O	H_2O
t°	27.0	27.0	26.6	15.0	15.5
$\alpha \times 10^4$	5.2	3.3	4.2	6.3	5.9

L	$S = n$-C_4H_9OH		S = fermentation iso-$C_5H_{11}OH$		
	Decalin	H_2O	C_6H_5Cl	n-C_4H_9OH	H_2O
t°	31.2	30	31.3	32.0	30.0
$\alpha \times 10^4$	2.2	4.5	4.3	8.5	4.7

Part II. Theory of Equilibrium between Dilute Solution and Vapour of Solute.

(5) *Most simple Case* (i). In the equilibrium of S vapour and its dilute solution, the dissolution velocity $= \alpha$ (the number of S molecules impacting with the liquid surface) $= \dfrac{\alpha p}{\sqrt{2\pi MRT}}$ mol./sq.cm./sec. The evaporation of S from the solution is treated gas-kinetically, as S in a dilute solution behaves like gas molecules as known from the studies on the Brownian motion and the dilute solution (discussed later). The number of S molecules with a component of velocity normal to the surface between u and $u + du$ is,

$$n_0\sqrt{\frac{M'}{2\pi RT}}\exp\left(-M'u^2/2RT\right)du/\text{c.c.}\,,$$

where n_0=the number of S molecules/c.c.$=CN_A/10^3$ and M'=molecular weight of kinetic unit containing S, e.g. that of solvate. In (i) we consider the case in which the concentration near the surface is equal to that of bulk solution. The number of molecules of this range of speed arriving at the surface upwards is,

$$n_0\sqrt{\frac{M'}{2\pi RT}}\,u\exp\left(-M'u^2/2RT\right)du/\text{sq.cm./sec.}$$

When the heat of dissolution of gaseous S in L or the heat of evaporation from the dilute solution (W) is put as follows: W kcal./mol. $= \frac{1}{2}M'u_0^2$, molecules having larger normal velocity than u_0 can evaporate, hence the evaporation velocity is,

$$\beta_1 n_0\sqrt{\frac{M'}{2\pi RT}}\int_{u_0}^{\infty}u\exp\left(-\frac{M'u^2}{2RT}\right)du$$

$$= \beta_1 n_0\sqrt{\frac{RT}{2\pi M'}}\exp\left(\frac{-W}{RT}\right) = \frac{\beta_1 C}{10^3}\sqrt{\frac{RT}{2\pi M'}}\exp\left(\frac{-W}{RT}\right)\text{mol./sq.cm./sec.}$$

(β_1 is the probability of evaporation of S molecule colliding with the surface with sufficient energy for evaporation.) By equating two velocities, we obtain,

$$\frac{\alpha p}{\sqrt{2\pi MRT}} = \frac{\beta_1 C}{10^3}\sqrt{\frac{RT}{2\pi M'}}\,e^{-W/RT} \qquad (1')$$

$$\left.\begin{array}{l}\text{and Henry's constant}\\ \qquad K = (C/p)_{C=0}\ \text{mol./l. mm. Hg} = \dfrac{10^3}{RT}\,\dfrac{\alpha}{\beta_1}\sqrt{\dfrac{M'}{M}}\,e^{W/RT},\\ \qquad R = 6.24\times10^4\ \text{c.c. mm. Hg/degree}\\ \text{Ostwald's absorption coefficient}\quad \gamma = C/C_g = \dfrac{\alpha}{\beta_1}\sqrt{\dfrac{M'}{M}}\,e^{W/RT}\end{array}\right\} \qquad (1)$$

If a solvate is not formed, $M' = M$ in (1).

K in Table 1. is calculated from solubility data by the Margules's formula, $p_0 = \chi$ (p of liquid iodine) $\exp\{b(1-\chi)^2\}$, in which p_0 is the sublimation pressure of iodine and χ is the solubility expressed in mol. fraction (a little different from solubility/p_0).

As for a concentrated solution, especially when S is surface active, α is different from that for pure L, accordingly K calculated from solubility in good solvents may give rise to some errors in further discussion, the order of which can be estimated from data given in § 10 and 12.

Table 2. Results of Calculation by Formula (1). (at 25°)

Solvent	Solute = I_2					
L	Heat of solution of [I_2] kcal./mol.	W kcal./mol.	K mol./l./mm.Hg	Solubility mol./l.	$\alpha \times 10^4$	β_1
n-C_7H_{16}	−6.77	+ 8.13	0.152	4.99×10^{-2}	ca. 5	0.18
Cyclohexane	−6.6*	8.3	0.262	8.45×10^{-2}	5.9	0.15
C_6H_6	−4.68	10.22	1.48	0.476	6.1	0.69
$C_6H_5CH_3$	−5.62*	9.28	1.56	0.593	6.8	0.15
Decaline	−5.60*	9.30	0.319	0.109	5	0.56
$CHCl_3$	−5.49	9.41	0.550	0.178	2.8	0.22
CCl_4	−5.78	9.12	0.355	0.117	5.0	0.37
C_6H_5Cl	−5.72*	9.18	0.862	0.320	6.9	0.23
CS_2	−5.24–4.8	9.66–10.1	2.62	0.814	5.0	0.12–0.26

* means 0.30

Solvent	Solute = Acetone				
L	Heat of mixing when solution is very dilute. (kcal /mol. acetone)	W	K	$\alpha \times 10^4$	β_1
C_6H_6	−0.30	7.41	0.050	5.2 (27°)	0.15
$C_6H_5CH_3$	ca. 0	7.7	0.0235	3.3 (27°)	0.33

Note: Values with asterisk were calculated from solubility data measured by the author.
Heat of sublimation of iodine at 25° = 14.9 kcal./mol.

(6) *Case* (ii) *Vibration in the solvate takes part in the evaporation of the solute.*

Table 3. S = I_2. (at 25°)

L	W	$\alpha \times 10^4$	Solubility mol./l.	K mol./l. mm.	β_1	β_2
C_2H_5OH	13.18	4.2	0.795	1.70	65	0.45
CH_3OH	12.89	4.1	0.474	0.707	94	0.67
H_2O	9.57	3.1	1.32×10^{-3}	4.29×10^{-3}	42	0.51
KI_3 aq.	13.2	4.8	—	—	220	0.76

As $\beta_1 > 1$ means that more molecules evaporate than those striking the surface with sufficient energy for evaporation, it is apparently irrational. It cannot be attributed to the concentration increase due to the surface adsorption (discussed in § 7 and 8), as is obvious from the following surface tension (σ) measurements.

L	Concentration of iodine. mol./l.	σ dyne/cm.	σ of L	t°	$\frac{d\sigma}{dC}$ $\frac{\text{dyne/cm.}}{\text{mol./l.}}$	
CH_3OH	0.50	23.44	22.58	25.6	+1.72	Dancaster(8)
C_2H_5OH	0.80	22.50	21.21	29.0	+1.61	Author

Though the change of σ in water is not observed on account of low concentration, β_1 of the same order of magnitude in spite of large difference from alcohols in W and solubility suggest this anomaly to be due to some analogous mechanism rather than adsorption.

The formation of oxonium compounds of the type $L.I_2$ between iodine and L containing oxygen and giving brown colour on dissolving iodine is confirmed by the studies of the freezing-point of the mixtures of iodine and those L in inactive L, the effect of alcohol etc. on the solubility of iodine in non-polar L and of absorption of light etc.(9) Though iodine does not form solid hydrate as chlorine or bromine, the aqueous solution gives absorption spectrum analogous to an alcoholic solution suggesting compound formation.

We consider that upward translational energy of solvate molecules as a whole and vibrational energy of two bonds between O and two I in

is utilized for the evaporation of iodine.

The number of molecules which come to the surface with sufficient energy for evaporation is as follows:

(a) Those for which $\frac{1}{2}M'u^2 > \frac{1}{2}M'u_0^2$.

$$n_0\sqrt{\frac{M'}{2\pi RT}}\int_{u_0}^{\infty} u \exp\left(\frac{-M'u^2}{2RT}\right)du = n_0\sqrt{\frac{RT}{2\pi M'}}\exp\left(-\frac{W}{RT}\right) \qquad (2a)$$

(b) Those for which $\frac{1}{2}M'u^2 < \frac{1}{2}M'u_0^2$ and $\left(\frac{1}{2}M'u^2 + \text{either of two vibrational energies}\right) > \frac{1}{2}M'u_0^2$.

$$2n_0\int_0^{u_0} u\sqrt{\frac{M'}{2\pi RT}}\exp\left(-\frac{M'u^2}{2RT}\right)du.\ \exp\left(-\frac{W-\frac{1}{2}M'u^2}{RT}\right)$$

$$= 2n_0\sqrt{\frac{RT}{2\pi M'}}\cdot\frac{W}{RT}\exp\left(-\frac{W}{RT}\right). \qquad (2b)$$

---

(8) Dancaster, *J. Chem. Soc.*, **125** (1924), 2036.

(9) Gmelin, "Handbuch der anorganische Chemie", Jod. System-Nr. 8, p. 125.

(c) Those for which $\left(\frac{1}{2}M'u^2+\text{either of two vibrational energies}\right)<\frac{1}{2}M'u_0^2$ and $\left(\frac{1}{2}M'u_2+\text{sum of two vibrational energies}\right)>\frac{1}{2}M'u_0^2$

$$n_0\int_0^{u_0}\left\{\sqrt{\frac{M'}{2\pi RT}}\,u\exp\left(-\frac{M'u^2}{2RT}\right)\int_0^{W-\frac{M'u^2}{2}}\frac{1}{RT}\exp\left(-\frac{E_1}{RT}\right)dE_1\right.$$

$$\left.\times\exp\left(-\frac{W-E_1-M'u^2/2}{RT}\right)\right\}du=n_0\sqrt{\frac{RT}{2\pi M'}}\cdot\frac{1}{2}\left(\frac{W}{RT}\right)^2\exp\left(-\frac{W}{RT}\right).\qquad(2c)$$

where E_1 is one vibrational energy.

When vibrational energy is used for evaporation, a factor 1/2 is multiplied as iodine can evaporate from $I_2\cdot ROH$ only when iodine exists at the upside of ROH (or nearer to surface) in $I_2\cdot ROH$ molecule. Then, evaporation velocity $=\beta_2\left\{(2a)+\frac{(2b)}{2}+\frac{(2c)}{2}\right\}=\beta_2 n_0\sqrt{\frac{RT}{2\pi M'}}\,e^{-W/RT}$ $\times\left\{1+\frac{W}{RT}+\frac{1}{4}\left(\frac{W}{RT}\right)^2\right\}=\frac{\beta_2 C}{10^3}\sqrt{\frac{RT}{2\pi M'}}\,e^{-W/RT}\left(1+\frac{W}{2RT}\right)^2.$

$$\left.\begin{aligned}\therefore\quad K&=\frac{10^3}{RT}\frac{a}{\beta_2}\sqrt{\frac{M'}{M}}\,e^{W/RT}\Bigg/\left(1+\frac{W}{2RT}\right)^2\\ \gamma&=\frac{a}{\beta_2}\sqrt{\frac{M'}{M}}\,e^{W/RT}\Bigg/\left(1+\frac{W}{2RT}\right)^2\end{aligned}\right\}\qquad(2)$$

Plausible values of β_2 which has an analogous meaning as β_1 are obtained by (2) as shown in Table 3.

In the case of the aqueous solution of KI_3, any two iodine atoms can evaporate as an iodine molecule, hence the evaporation in which vibrational energy in I_3 takes part must be twice faster than the above-mentioned cases, i.e. $\beta_2\{(2a)+(2b)+(2c)\}$, accordingly solubility formula is a little different from (2) (see § 11).

Other Explanations of Abnormally High Values of β_1. (a) In the solubility formula, $\gamma=\exp(\Delta S/R)\exp(W/RT)$, the entropy increase on the evaporation of iodine is 11–14 E.U. for normal L, whereas 23.6, 24.4 and 23.4 E.U. for ethanol, methanol and water respectively, indicating remarkably limited numbers of configurations in these L probably due to strong interaction. If the method of absolute reaction rate is applied, the evaporation velocity $=n_0\frac{kT}{h}\exp(\Delta S^*/R)\exp(-W^*/RT)$, (quantities with * are those for transition state, taking the solution as standard), in which ΔS^* may be abnormally large analogous with ΔS for an alcoholic and aqueous solution of iodine, giving rise to large evaporation velocity corresponding to higher values of β_1 in (1).

(b) When we assume equilibrium, $L+I_2\rightleftarrows L.I_2$, in these solutions and assume that the heat of evaporation of free iodine is less than the average value (W), i.e. $(W-\Delta W)$, the increase of evaporation velocity or β_1 is expected. As the heat of combination of iodine and various organic compounds containing oxygen in carbon tetrachloride, 3–4 kcal./mol. are obtained from the temperature dependence of equilibrium constant(10), but the energy difference of combined iodine and free iodine in alcohols may be less than these values. The maximum value of β_1 obtained from various ratios of free iodine is 5 when $\Delta W=3$. Compared with values in Table 3., this mechanism seems to be unable to cover the whole phenomena, though it may be effective to some extent especially when S exists in two states of large energy difference.

(c) The probability that the reaction, $I_2+H_2O=H^{+}+I^{-}+HIO$, gives rise to the increase of α, accordingly that of calculated value of β_1 is denied by observations that an acid in water has no more effect on α of iodine than is expected from its ionic action.

(7) *Case* (iii) *Surface adsorption takes place and the heat of evaporation is not changed.* Surface concentration of surface active substances (especially in aqueous solution) is higher than that of bulk solution. If the excess amount, $\frac{C}{RT}\left(-\frac{d\sigma}{dC}\right)_T$ mol./sq.cm. is contained homogeneously in a layer δ cm. thick, the surface concentration is $C+\frac{C}{RT}\frac{10^3}{\delta}\left(-\frac{d\sigma}{dC}\right)_T$ mol./l. In a dilute solution, $d\sigma/dc$ is constant and considering adsorption layer monomolecular as were often ascertained surface-chemically, δ is calculated approximately as $\delta=\{M/(\mathit{density\ of\ S})N_A\}^{\frac{1}{3}}$. Though it is reported sometimes that the adsorption is several times larger than is given by the Gibbs's formula, δ is also thicker than the monolayer in these cases, and concentration is not very different from what is given above. Errors due to approximation is negligible compared with that of exponential term in (3). If an adsorbed molecule has equal heat of evaporation and evaporates in the same manner as that in the solution, the rate of evaporation =

$$\frac{\beta_3 C}{10^3}\left\{1+\frac{10^3}{RT\delta}\left(-\frac{d\sigma}{dC}\right)_T\right\}\sqrt{\frac{RT}{2\pi M'}}\,e^{-W/RT}=\frac{\alpha p}{\sqrt{2\pi MRT}}$$

$$\left.\begin{array}{l}
\therefore\ \ K=\dfrac{C}{p}=\dfrac{10^3\alpha}{RT\beta_3}\sqrt{\dfrac{M'}{M}}\,e^{W/RT}\Big/\left\{1+\dfrac{10^3}{RT\delta}\left(-\dfrac{d\sigma}{dC}\right)_T\right\},\\
\qquad\qquad\qquad\qquad\text{(Henry's law holds also in this case.)}\\
\gamma=\dfrac{C}{C_g}=\dfrac{\alpha}{\beta_3}\sqrt{\dfrac{M'}{M}}\,e^{W/RT}\Big/\left\{1+\dfrac{10^3}{RT\delta}\left(-\dfrac{d\sigma}{dC}\right)_T\right\}
\end{array}\right\}\quad(3)$$

---

(10) Gróh, *Z. anorg. Chem.*, **162** (1927), 287.

Table 4. $L = H_2O$. (at 25°)

S	Acetone	HCl; formally applied to $H_3O^+ + Cl$. As a matter of fact, HCl takes part.
δ cm.	4.95×10^{-8}	3.71×10^{-8}
$-\frac{d\sigma}{dC} \frac{\text{dyne/cm.}}{\text{mol. l.}}$	60.3	1.56
$\frac{\text{Conc. at surf.}}{\text{Conc. in soln.}}$	50.1	2.70
W kcal./mol.	10.09	17.3
K mol./l./mm. Hg	0.047	2.1×10^4
$\alpha \times 10^4$	4.2	1.9
β_1 (11)	16.6	2.2
β_3	0.34	0.8

(8) *Case* (iv). *Various factors act simultaneously.* (a) The case of solvate formation and comparatively weak adsorption. In the case of ammonia in water, the evaporation velocity is expressed analogously as in the cases of iodine in alcohols in § 6, though the number of bonds used for evaporation is assumed one in $NH_3 \cdot H_2O$. Adsorption is also taken into account, in which the sum of δ of ammonia and water (δ_H) is assumed as the value of δ.

$$\text{Evaporation velocity} = \beta_a n_0 \sqrt{\frac{RT}{2\pi M'}} e^{-W/RT}\left(1+\frac{W}{2RT}\right) \times \left\{1+\frac{10^3}{RT(\delta+\delta_H)}\left(-\frac{d\sigma}{dC}\right)_T\right\}$$

$$K = \frac{10^3 a}{RT\beta_a}\sqrt{\frac{M'}{M}}\, e^{W/RT} \Big/ \left(1+\frac{W}{2RT}\right)\left\{1+\frac{10^3}{RT(\delta+\delta_H)}\left(-\frac{d\sigma}{dC}\right)_T\right\} \quad (4a)$$

Table 5. $L = H_2O$. (at 25°)

S	NH_3	CH_3OH	
$(\delta + \delta_H)$ A	5.61	6.68	
$-d\sigma/dC$	3.0	9.27	
$\frac{\text{Surface. conc.}}{\text{Bulk conc.}}$	2.84	6.60	
W kcal./mol.	8.43	11.24	
K	0.0724	0.302	
$\alpha \times 10^4$	46	6.3 (15°)	
		Assuming di-	mono-hydrate
β_1	7.32	29.7	24.2
β_3*	2.58	4.54	3.59
β_a	0.32	0.43	0.34

* Only the effect of adsorption is considered.

---

(11) Calculated by (1) neglecting surface adsorption.

(b) The case where a solvate is formed and the heat of evaporation is diminished by strong adsorption.

Table 6. L = H_2O. (at 25°)

S	CH_3OH		C_2H_5OH		n-C_4H_9OH	Fermentation i-$C_5H_{11}OH$	n-$C_9H_{19}OH$
δA	4.06		4.59		5.34	5.64	6.61
$-d\sigma/dC$	9.27		28.7		250	800	2.39×10^4
$\frac{\text{Surf. conc.}}{\text{Bulk conc.}}$	10.2		26.2 (12)		190	573	1.46×10^4
W kcal./mol.	11.24		12.88		15.94	16.7	23.6
K	0.302		0.255		0.154	0.0936	
$\alpha\times10^4$	6.3 (15°)		5.9 (15.5°)		4.5 (30°)	4.7 (30°)	
Assumed number of hydrated water	2	1	3	1	1	1	1
β_1 in (1)	29.7	24.2	494	399	6.82×10^4	1.13×10^6	4.74×10^{10}
β_3 in (3)	2.91	2.37	18.8	15.2	359	1970	3.24×10^6
β_b in (4b)	0.145	0.119	0.828	0.670	12.9	67.5	7.94×10^4
θ in (4) which gives β_4 0.3			0.16	0.12	0.33	0.39	0.52

In Table 6, β_1 calculated by formula (1) increases very rapidly with increasing C number (m) in alcohol, and exact linear relation holds between log β_1 and m, by which β_1 of nonyl alcohol is obtained. Though adsorption is taken into consideration by formula (3), β_3 are still far larger than unity, especially for higher alcohols. The compound formation of lower alcohols with water is estimated from the volume or viscosity of a mixture and the heat of mixing etc. There may be two or three hydrogen bonds for one alcohol molecule and the position of surface-adsorbed alcohol molecule which contributes to the evaporation in a predominating degree may be as shown in Fig. 7, considering from surface potential(13) and σ.

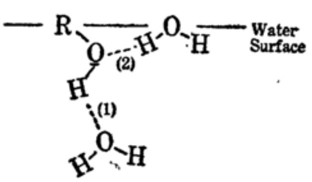


Fig. 7.

If upward vibration only is effective for evaporation of alcohol (§ 6) only one bond (1) can be used, but bond (2) and another analogous bond (3), if it exists, may have no effect on the evaporation velocity. As surface-adsorbed alcohol probably lies always at the upside in the solvate molecule (except lower ones) vibrational energy of bond (1) may be always used, accordingly $(1+W/RT)$ is taken instead of $(1+W/2RT)$ in the formula of evaporation velocity (4a).

---

(12) It is known from σ determination that at the mol. fraction of alcohol about 0.25, nearly close-packed mono-layer is formed at the surface of an aqueous solution. (Schofield and Rideal, *Proc. Roy. Soc.* (A), **109** (1925), 61.)

(13) Frumkin, *Z. physik. Chem.*, **109** (1924), 34.

$$\therefore \quad K=\frac{10^3\alpha}{RT\beta_b}\sqrt{\frac{M'}{M}}\,e^{W/RT}\Big/\left(1+\frac{W}{RT}\right)\left\{1+\frac{10^3}{RT\delta}\left(-\frac{d\sigma}{dC}\right)_T\right\}$$

$$\gamma=\frac{\alpha}{\beta_b}\sqrt{\frac{M'}{M}}\,e^{WR/T}\Big/\left(1+\frac{W}{RT}\right)\left\{1+\frac{10^3}{RT\delta}\left(-\frac{d\sigma}{dC}\right)_T\right\} \qquad (4b)$$

In the cases of lower alcohols, especially methanol, the molecule does not necessarily occupy the upper position in the solvate molecule, as the hydrophobic property of methyl radical is weak compared with higher alkyl. Methanol in water may probably be in an intermediate state of the two equilibriums expressed by (4a) and (4b).

For aqueous solutions of alcohols, β_b is more than normal value (under 1, or rather about 0.3) except for the lower alcohols, indicating that some factor besides adsorption and compound formation takes part in these phanomena. (If polymers or colloidal particles of higher alcohols exist in an aqueous solution β becomes still larger.)

Alkyl radical has little affinity to water, and consequently shows the tendency to be squeezed out from water (Langmuir's experiments). For slightly soluble aliphatic compound, the surface film is gaseous and the molecules move about separately and lie flat on the surface like rods, exposing the upper part in the air, the affinity of alkyl radical being satisfied by contact with water on one side only.(14) Langmuir(15) tried to calculate the heat of the solution by assuming that the interaction energy is determined mainly by short range force, and the arrangement of L molecules around one part of S molecule does not affect the other parts (this is more likely to be satisfied when L molecule is small compared with S molecule). Butler(16) applied this to the calculation of W of organic compounds in water with success, assuming pseudo-crystalline tetrahedral arrangement of water. According to his results for alcohols, $C_mH_{2m+1}OH$, W of alkyl radical is $(2m+1)\times 0.77$, and that of OH is 8.92 kcal./mol. When one side of alkyl of alcohol molecules adsorbed at the surface is exposed in the air, the heat of hydration (or evaporation) is somewhat diminished, i.e.

$W'=(1-\theta)\times 0.77\times(2m+1)+8.92$ kcal./mol., where θ shows the degree of exposure of alkyl radical. Accordingly, the equilibrium of the vapour and the solution is expressed as follows;

$$\beta_4\sqrt{\frac{RT}{2\pi M'}}\frac{C}{10^3}\left\{e^{-W/RT}\left(1+\frac{W}{RT}\right)+\frac{10^3}{RT\delta}\left(-\frac{d\sigma}{dC}\right)_T e^{-W'/RT}\left(1+\frac{W'}{RT}\right)\right\}$$

$$\equiv\beta_4\sqrt{\frac{RT}{2\pi M'}}\frac{C}{10^3}\cdot Z=\frac{\alpha p}{\sqrt{2\pi MRT}}$$

$$\therefore \quad K=\frac{10^3\alpha}{RT\beta_4}\sqrt{\frac{M'}{M}}\Big/Z \qquad \gamma=\frac{\alpha}{\beta_4}\sqrt{\frac{M'}{M}}\Big/Z \qquad (4)$$

---

(14) Adam, "The Physics and Chemistry of Surfaces," Oxford (1930), 65.

(15) Langmuir, *Colloid Symposium Monograph*, **3** (1925), 48.

(16) Butler, *Trans. Faraday Soc.*, **32** (1936), 233.

As the consequence of high concentration and diminution of the heat of evaporation, $W- W'=\theta\times 0.77\times(2m+1)$, the influence of adsorbed molecules on the equilibrium is overwhelming. θ which makes β_4 0.3 is given in Table 6. and this shows an increase as the hydrophobic alkyl radical becomes larger.

Some Thermodynamical Consideration on Surface Adsorption.

Chemical potential of S in solution$=\mu_0+RT\ \ln C$

that of S at the surface$=\mu_0'+RT\ \ln C'$.

Taking the heat content of vapour as standard, we obtain in equilibrium,

$$-W-TS_0+RT\ln C=-W'-TS_0'+RT\ln C'\ .$$

$$RT\ln C'/C=\mu_0-\mu_0'=\text{adsorption potential}=T(S_0'-S_0)-(W-W')$$

As alkyl radical itself has some affinity to water, the energy of an adsorbed molecule becomes higher than that when it is in solution as in the case (iv)b, $(W-W')>0$, (in the case (iii), $W-W'=0$). But the increase in entropy term due to the increase of freedom of alkyl radical accompanying the migration to the surface is more than this, and consequently surface adsorption takes place, $C'>C$. Strong adsorption, $C'\gg C$, means that $S_0'\gg S_0$, which is realized only when one part of a molecule is exposed out of the liquid, then necessarily $W>W'$.

Summary.

(1) The condensation coefficient (α) of iodine and other easily analysable vapours at the surface of various solvents were measured by newly deviced method. The orders of the magnitude of them are $10^{-3}\sim10^{-5}$ at room temperature.

(2) A solubility formula including α was derived kinetically, in which the effects of surface adsorption and compound formation were taken into considerations, and an explanation of the mechanism of evaporation and dissolution was tried by comparing with solubility data.

The author expresses his hearty thanks to Prof. M. Katayama, Prof. J. Horiuti, Prof. K. Otiai, and Prof. Y. Ohta for their kind advices and encouragements, and to Miss Sō-Si-Taimai for her assistances, and to Taihoku Higher School where the main part of this experiment was worked.

July 19, 1943.

Laboratory of Physical Chemistry, Imperial
University of Hokkaido.