Studies on the Equilibrium between Dilute Solution and Solute Vapour. III. *Calculation of the Evaporation and Dissolution* Velocity.

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Part IV. Application of Absolute Rate Method to Evaporation and Dissolution of Solute.

(15) *Nature of A.* Condensation coefficient (α) of iodine on various solvents (L) is expressed as follows:⁽¹⁾

$$\alpha = \text{constant} \times e^{\frac{A}{RT}} \equiv D\, e^{\frac{A}{RT}} \qquad (14)$$

It is most noticeable that the heat of activation(-A) of dissolution of gaseous molecule is negative. In Eyring and Polanyi's method for calculating reaction velocity, the state of maximum energy is assumed as the transition state. This has already met difficulties in some reactions of nitric oxide and in the catalytic hydrogenation of crotonic and maleic acid (on platinum)⁽²⁾ and ethylene (on nickel)⁽³⁾ which give maximum velocities at certain temperatures showing the existence of the negative heat of activation at higher temperature. Accordingly the energy of the transition state is lower than that of the initial state and this is attributed to the high heat of adsorption of reactants. Remarkably negative values of the heat of activation obtained in our case for the dissolution of vapour in L, together with the facts above, show the assumption that energy is maximum at the transition state has no general validity. Since, in general, the state of maximum free energy (G) must be taken instead of maximum energy as the transition state, these failures are not necessarily strange. Thermodynamical data of various states, e.g., for iodine-toluene system are given in Table 1, which ascertain the conclusion stated above.

Table 1. (at 25°)

	H	TS	G = H − TS (kcal./mol.)
Gas	0	0	0
The Transition State	− 4.5	−21.3*	+16.8
Solution	− 9.3	− 3.1**	− 6.2

* Calculated by introducing observed value of D in the formula, $e^{\Delta S^* R} = \frac{Dh}{\sqrt{2\pi mkT}}$ (obtained from (16 ab)).

** Calculated from solubility data.

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(1) I. Uhara, this Bulletin, **18**(1943), 412, 429.

(2) Maxted and Moon, *J. Chem. Soc.* **(1935)** 1190.

(3) Rideal, *ibid.*, (1922) 309; Zur Strassen, *Z. physik. Chem.*, **169**(1934) 81.

From this point of view, the Horiuti's method⁽⁴⁾ is superior to those of Eyring etc. in principle, in which a surface is constructed in the configuration space so that the number of representative points passing through it may be minimized and this is taken as the critical (transition) surface. As the dissolution velocity is expressed by $c_g \frac{kT}{h} e^{\Delta S^*/R} e^{-H^*/RT}$, we obtain by comparing with (14) and (16a) approximately $-H^*=A$. (c_g=concentration of gas, ΔS^* and H^*=entropy and heat content of the transition state taking those of gas as the standard). α is smaller than the accommodation coefficient (which is>0.01, usually>0.1, though they have been given for light molecules) owing to the circumstance that S molecule must lose the adsorption energy and further more creep into L to dissolve. The following transition state may be supposed on the basis of values of A obtained experimentally.

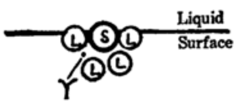

Fig. 1. The Transition State (See § 16.)

(i) If the transition state is as shown in Fig. 1, A may be 1/2–2/3 of W, and A/W=0.50–0.67. (W is the heat of solution of S vapour).

(iia) If S exists at Y, a point on the cage surrounding S, in Fig. 1 in the transition state, $W=(W-5/6\ W)-E_{\text{dif}}$, in which factor 5/6 was taken arbitrarily. Eyring, considering diffusion as evaporation in one degree of freedom, put $E_{\text{dif}}\equiv$the heat of activation of diffusion =1/3 (inner heat of evaporation of L, or $W_L - RT$). $\therefore\ A=(W-5/6W)-1/3(W_L - RT)$. This, however, gives too high values of A as shown in Table 2.

(iib) It may be rational to take the quantity ($W - RT$) which depends both on S and L instead of $W_L - RT$; we have then $A=(2/3-1/2)W-RT/3$ and A/W=0.65–0.5.

Table 2. S = I_2. (at 25°)

L	A/W		D	β_1
	Observed	Calculated by (ii a)		
H_2O	0.68	0.66—0.49	4.9×10^{-9}	42
C_2H_5OH	0.54	0.76—0.59	2.5×10^{-9}	65
CH_3OH	0.62	0.78—0.61	5.3×10^{-10}	94
$C_5H_{11}OH$			7.4×10^{-9}	
$C_6H_5CH_3$	0.48	0.77—0.61	3.7×10^{-7}	0.15
			(calc. 0.85×10^{-7}	0.06)
C_6H_6	Assumed 0.6—0.5		$2.5\times10^{-8}-1.4\times10^{-7}$	0.69
			(calc. 0.96×10^{-7}	0.64—0.12)
CS_2			$2.3\times10^{-8}-1.1\times10^{-7}$	0.12—0.26
			(calc. 1.3×10^{-7}	0.33—0.066)

(16) *Calculation of D (or α)*. The following assumed conditions of the transition state are approximately the same for both cases, (i) and

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(4) J. Horiuti, this Bulletin, **13**(1938) 210.

(5) Eyring, "The Theory of Rate Processes", (1941) 525.

(iib). In the case of dissolution of iodine molecule in normal L, it has no translational freedom except that of the direction of dissolution, and does not rotate. The change of inner molecular vibration (if exists) does not greatly affect the partition function. The dissolution velocity of vapour at the fresh L surface=

$$= c_g c_n \frac{kT}{h}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{R_{\mathrm{S}}^*}{R_{\mathrm{Sg}}}\cdot\frac{Q_{\mathrm{L}}^*}{Q_{\mathrm{L}}}e^{A/RT}\frac{\text{molecules}}{\text{sq.cm.sec.}} = c_g\frac{kT}{h}e^{\Delta S^*/R}e^{A/RT}, \tag{16 a}$$

and this is also expressible by

$$\frac{pN}{\sqrt{2\pi MRT}}\alpha = \frac{c_g kT}{\sqrt{2\pi mkT}}(D\,e^{A/RT})\,, \tag{16 b}$$

where R_{S}^*, R_{Sg} = Partition functions for rotation of S in the transition state and in gas. $R_{\mathrm{S}}^*=1$, $R_{\mathrm{Sg}}=8\pi^2IkT/\sigma'h^2=2.74\times10^3$, in which I = moment of inertia, and σ' = symmetry number.

Q_{L}^*, Q_{L} = Partition function of L at the transition state and in pure L.

Partition functions are assumed to be separable into the term depending only on S and that for L.

$$D = \frac{c_n}{\dfrac{2\pi mkT}{h^2}\,\dfrac{8\pi^2IkT}{\sigma'h^2}}\,\frac{Q_{\mathrm{L}}^*}{Q_{\mathrm{L}}}\,. \tag{16}$$

The number of position for dissolution of S per sq. cm. of the L surface, $c_n=1.3\times10^{16}/V_L^{2/3}$, if it is assumed that L molecules are closest-packed and one molecule is surrounded by six molecules at the L surface and each of six gaps is common to three molecules (V_L is molecular volume of L.). If the difference between S–L and L–L interaction is little (which can be estimated by comparing W and W_L, the heat of evaporation of L) and we can put $Q_L^*\simeq Q_L$, D of iodine in toluene becomes 0.85×10^{-7}. Since the error in α and consequently those in A and D are large in the case of non-polar L with high volatility, we assume $A=(0.6\text{–}0.5)W$, then D is obtained from A and observed value of α by (14) and is compared with the result of calculation by (16) in Table 2. Low values of D (far less than 10^{-7}) for aqueous and alcoholic solutions of iodine are attributed to the restriction of motion of $\mathrm{L}(Q_L^*/Q_L<1)$ due to strong interaction between S and L.

(17) *Calculation of* β_1. β_1 is the calculated probability of evaporation of S molecules in the solution when they come to the L surface with sufficient energy for evaporation, assuming that S molecules have the same velocity as the gas molecule in their free paths in the solution.⁽¹⁾ The formula of evaporation velocity of S from dilute solution can be derived from both absolute rate method and kinetic theory (§ 5), from which we obtain by equating,

$$c_n n_0\frac{kT}{h}K^*e^{\ B/RT} = \beta_1 n_0\sqrt{RT/2\pi M'}\,e^{-W/RT},$$

where K^*=ratio of the partition functions per unit area or volume of the transition state and initial state, without the exponential factor of zero-point energy difference, n_0=the number of S molecules in the solution/c.c. From the solubility formula, $\gamma = \frac{a}{\beta_1}\sqrt{\frac{M'}{M}}e^{W/RT}$ (1) and (14), it comes out that $\beta_1 \propto e^{A/RT}$, $A=W-B$ and $B=W-A$, indicating that the transition state is the same as in the case of dissolution.

$$\therefore \quad \beta_1 = \sqrt{2\pi M'/RT}\, c_n \frac{kT}{h} K^* e^{A/RT} \tag{17 a}$$

The molecular state in the solution is assumed as follows: Iodine molecules in the solution have three translational degrees of freedom and free volume v_f per c.c. solution. The partition function for vibration is put equal both in solution and transition state, then

$$\beta_1 = c_n \sqrt{2\pi M'/RT}\, \frac{kT}{h} \frac{e^{A/RT}}{\left(\frac{2\pi mkT}{h^2}\right)^{3/2} v_f} \frac{R_{\mathrm{S}}^*}{R_{\mathrm{S}l}} \frac{Q_{\mathrm{L}}^*}{Q_{\mathrm{L}l}} \tag{17}$$

where R_{Sl}=rotational partition function of S in the solution,
Q_{Ll}=the partition function of L molecules surrounding S molecule in the solution. $R_{\mathrm{S}}^* = 1$.

It is assumed that $R_{Sl} \simeq R_{Sg}$, and $Q_L^* \simeq Q_{Ll}$, if L is normal. Though v_f for S differs from that for L, the latter is used for the following approximate calculation, as the molecular volume of iodine (51.3 c.c.), hence the molecular diameter does not differ largely from those of ordinary L and $W \simeq W_{\mathrm{L}}$.

Table 3. v_f, free volume per c.c. L. at 25°.(6)

C_6H_6	n-C_7H_{16}	ether	CCl_4	CS_2	acetone	CH_3OH	Hg
3.5×10^{-3}	1.2×10^{-3}	6.8×10^{-3}	4.0×10^{-3}	8.3×10^{-3}	5.5×10^{-3}	6.9×10^{-4}	1.28×10^{-5}

Calculated values of D and β_1 (Table 2) coincide with observations within errors in data used, indicating that the postulated transition state is approximately correct one.

Large values of β_1 (large evaporation velocity for their high values of W) of iodine from aqueous and alcoholic solutions may be attributed to the following causes though the quantitative discussion is impossible: (a) v_f of these L is smaller than that for normal L (Table 3), and volume contraction on mixing is often observed when S–L interaction is strong, especially in the case of chemical combination; (b) $e^{A/RT}$ is larger if A/W is constant; (c) free rotation of iodine molecules in the solution is restricted (decrease of R_{Sl}) by the strong S–L interaction. On dissolving electrolytes which increase the internal pressure of L, β_1 may be increased by the same reason.

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(6) Eyring, *J. Chem. Phys.* **6** (1938) 620, obtained from sound velocity or vapour pressure.

Table 4. $S = I_2$. (at 25°)

L	$\alpha \times 10^4$	$W \frac{\text{kcal.}}{\text{mol.}}$	Solubility (mol./l.)	β_1
H_2O …………………	3.11	9.57	1.32×10^{-3}	42
$MgSO_4$ aqueous solution (1 mol./l.) ….	1.8	10.4*	6.2×10^{-4}	190

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* Calculated from solubility data obtained by the author.

By far too high value of β_1 is obtained if the pure vibrational partition function is taken in (17) in the place of translational one.

(18) *Nature of entropy term or entropy change* (ΔS) *on dissolution.* Ostwald's absorption coefficient γ can be expressed by either of following formulae,

$$\gamma = e^{\Delta S/R} e^{W/RT}, \quad \gamma = \frac{a}{\beta_1}\sqrt{\frac{M'}{M}}\, e^{W/RT} \tag{1}$$

hence $e^{\Delta S/R} = \frac{a}{\beta_1}\sqrt{\frac{M'}{M}}$ or a/β_1 if no solvate is formed. We have then by (14), (16a) and (17),

$$e^{\Delta S/R} = \frac{R_{Sl}}{R_{Sg}} \frac{Q_{Ll}}{Q_L} v_f \tag{18}$$

though the assumptions concerning the transition state are unnecessary to derive (18).

Table 5. The observed entropy (ΔS) and the heat of solution at 25°.

S	L	$e^{\Delta S/R}$	$-\Delta S$	W
Hydroquinone	H_2O	9.0×10^{-7}	27.8	20.35
I_2	C_2H_5OH	7.0×10^{-6}	23.6	13.18
I_2	H_2O	7.8×10^{-6}	23.4	9.57
$HgCl_2$	H_2O	2.3×10^{-5}	21.4	16.62
Naphthalene	C_2H_5OH	1.9×10^{-4}	17.2	12.40
H_2O	Benzene	4.0×10^{-4}	15.7	5.73
I_2	Non-polar L	$(1\text{—}5) \times 10^{-3}$	14—10	9—10
Ordinary L	Ordinary L	$2 \times 10^{-3}\text{—}5 \times 10^{-4}$	12—15	6—11
S_8	Benzene	2.6×10^{-3}	12.0	15.2
CO_2	CH_3OH	6.3×10^{-3}	10.2	3.7
CO_2	Benzene	3.7×10^{-2}	6.5	2.5
N_2	Benzene	0.43	1.7	−0.78
H_2	CH_3OH	0.43	1.7	−1.01
He	Benzene	0.97	0.06	−2.26
H_2	Benzene	1.40	−0.67	−1.71

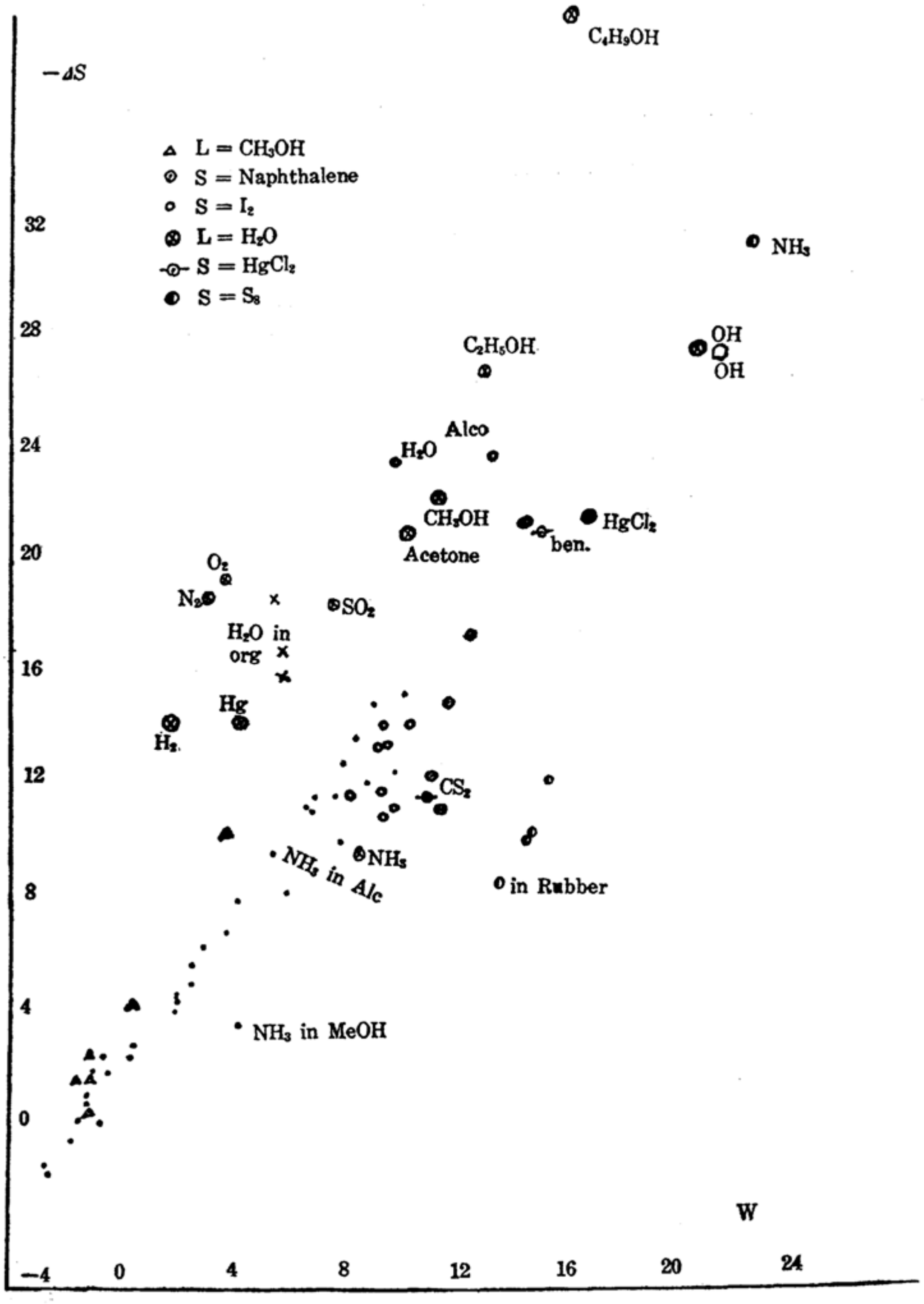

Fig. 2. Entropy and the Heat of Solution.

The relation between entropy term and W may be stated as follows:

(a) When W and consequently S–L interaction (compared with L–L interaction) are large, rotation of S molecule in the solution is hindered

($R_{Sl} < R_{Sg}$) especially in the case of chemical interaction and $Q_{Ll} < Q_L$ and v_f is small, hence $\Delta S \leqslant 0$.

(b) In the normal case in which S–L and L–L interactions are of the same order of magnitude, $Q_{Ll} \simeq Q_L$, and v_f does not differ largely from that of pure L (Table 3). R_{Sl} approaches R_{Sg} with diminishing S–L interaction, accordingly $e^{\Delta S/R} \simeq v_f \simeq 10^{-2}$–$10^{-3}$.

(c) If the S–L interaction is weaker than L–L, W is small, sometimes negative in the case of light molecule with small Van der Waals constants, because $W-RT$ is the difference between the energy of cohesion of S–L and the energy of cavity formation in L for S molecule. v_f is relatively large partly because of small dimension of S molecule, $R_{Sl} \simeq R_{Sg}$, and L molecules increase freedom of motion owing to the decrease of L–L interaction by the intervention of S, hence $Q_{Ll} > Q_L$, and $e^{\Delta S/R}$ becomes larger than those in (a) and (b).

Generally speaking, vapour or gas with large heat of solution (W) has less solubility than is expected from W only. The linear relations between W and ΔS were observed by Evans and Polanyi⁽⁷⁾ for one large molecule in various L, and by Bell⁽⁸⁾ for various light gases in one L (from solubility data by Horiuti⁽⁹⁾ and Lannung),⁽¹⁰⁾ and by Butler⁽¹¹⁾ for S of smaller or nearly same magnitude as that of L in normal L. The linear relation, however, holds only in a limited extent, as is apparent from Table 5 and Fig. 2, and for the general case in which various factors must be taken into account (dipole-interaction, hydrogen bonds, association, ratio of molecular dimension, molecular shape and surface adsorption etc.) nothing more than an approximate parallelism is observable.

(19) *The case of very weak S–L Interaction.* As an extreme case endothermic dissolution of gas ($W<0$) is discussed. We obtain in an analogous manner as in § 5,

$$\gamma = \frac{\alpha'}{\beta}\sqrt{\frac{M'}{M}}\,e^{W/RT}, \qquad e^{\Delta S/R} = \frac{\alpha'}{\beta}\sqrt{\frac{M'}{M}} \qquad (19),$$

where, usually $M' = M$, $\alpha =$ condensation coefficient, $\alpha' =$ that of molecule with more energy than W in the direction normal to the L surface, hence $\alpha = \alpha' e^{W/RT}$.

In hydrogen-benzene system at 25°, $W = -1.71$ kcal./mol. and solubility increases with rising temperature. If the model (i) in § 15 is adopted, A/W is 1/2–2/3 and A is -0.86–-1.14 kcal. In (18), $R_{Sl} = R_{Sg}$, v_f is put 2×10^{-2}, and from solubility data $e^{\Delta S/R} = 1.40$, then $Q_{Ll} = Q_L \times 1.40 \div (2\times10^{-2})$. If it is assumed that hydrogen molecule is half immersed in L in the transition state and $Q_L^* = (70)^{1/2}\,Q_L$, the data in Table 6 are obtained from (16), (19) and (17).

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(7) Evans and Polanyi, *Trans. Faraday Soc.*, **32** (1936) 1333; **33** (1937) 166.

(8) Bell, *ibid.*, **33** (1937) 498.

(9) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **17** (1931) 125.

(10) Lannung, *J. Am. Chem. Soc.*, **52** (1932) 68.

(11) Butler, *Trans. Faraday Soc.*, **33** (1937) 171, 229.

Table 6. L = Benzene. (at 25°)

S	Assumed v_f	D	α	α'	β_1
H_2	2×10^{-2}	0.16	$(4—2)10^{-2}$	0.7—0.4	4—2
H_2	5×10^{-2}	0.10	$(2—1)10^{-2}$	0.4—0.2	2—1
He	5×10^{-2}	0.085	1×10^{-2}	0.5	0.2

We see that the elementary kinetic discussion that all molecules with sufficient energy can evaporate or dissolve is valid approximately only in the case of such a weak S–L interaction.

The author expresses his hearty thanks to Prof. J. Horiuti for his kind advices and useful suggestions.

Summary.

(1) The absolute rate method was applied to the dissolution and evaporation processes of the solute vapour in the solution.

(2) The energy of the transition state was estimated from the temperature coefficient of condensation coefficient (α) of iodine experimentally determined. The energy is not maximum at the transition state as is usually assumed in the transition state method.

(3) α, evaporation probability (β_1) and entropy of dissolution (ΔS) were calculated for simple cases by means of simple models of the transition state and solution. For complex cases only qualitative explanation is possible.

(4) α of very light gases may be of the order of 10^{-2}.

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