# On the Vapor Pressure of Liquid Mixture⑴

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## Introduction

The theories of "*regular solutions*" were developed by Hildebrand⑵ and others⑶ with good success in qualitative description of various properties concerning the vapor pressure of liquid mixture. But these theories seem not to be enough for quantitative discussion, especially for the systems exhibiting appreciable departure from "*regular solution*".

In this paper, we shall develop a theory based on the kinetic theory and derive an equation which relates the vapor pressure of a mixture to its composition and the vapor pressures of its constituents. Of course, it is desirable to develop the statistical theory of "*real solutions*", not of "*regular solutions*", because the statistical method gives the most rigorous approach to the problem in question. However, the equation of vapor pressure which results from this approach will come to have a complex form⑷, and this is undesirable for the present purpose of deriving a practical equation.

## Vapor Pressure of Regular Solution

At first, we will treat of regular solution and confirm that the kinetic method coincides with the statistical method. The treatment of this section corresponds to Penner's method for the vapor pressure of pure liquid⑸.

Let us consider the regular solution composed of liquids $A$ and $B$ and denote the molar fractions of each component by $x_A$ and $x_B$. According to the kinetic theory of gases, the velocities of condensation of each kind of molecule per unit area of surface of the solution, $C_A$ and $C_B$, may be given by

$$\left.\begin{aligned} &C_A=p_A/(2\pi m_A kT)^{1/2} \\ \text{and}\qquad &C_B=p_B/(2\pi m_B kT)^{1/2}, \end{aligned}\right\} \qquad (1)$$

where $k$ is the Boltzmann constant and $T$ the absolute temperature. And $p_A$ and $p_B$ represent the partial vapor pressures of the indicated components, $m$'s are the masses of molecule of the indicated species. Here the condensation coefficient is assumed to be unity for simplicity's sake. On the other hand, if we use the theory of absolute rate⑹, the velocities of vaporization per unit area, $D_A$ and $D_B$, are given by

$$\left.\begin{aligned} &D_A=(x_A n)[(kT/h)(F_A{}^{\neq}/F_A)\exp(-\bar{u}_A/kT)] \\ &\text{and} \\ &D_B=(x_B n)[(kT/h)(F_B{}^{\neq}/F_B)\exp(-\bar{u}_B/kT)]' \end{aligned}\right\} \qquad (2)$$

Here $n$ is the total number of molecules per unit area, $h$ is the Planck constant and $\bar{u}_A$ and $\bar{u}_B$ are the activation energies of vaporization of molecule-$A$ and -$B$ respectively. And $F_A$ (or $F_B$) represents the partition function of molecule $A$ (or $B$) at the equilibrium state, $F_A{}^{\neq}$ (or $F_B{}^{\neq}$) represents the partition function of the activated molecule, which does not include the contribution due to translational motion in the one degree of freedom along the coordinate of vaporization, and they are connected with the free volumes $\omega_A$ (or $\omega_B$) and $\omega_A{}^{\neq}$ (or $\omega_B{}^{\neq}$) by the familiar relations⑺,

$$\left.\begin{aligned} &F_A=(2\pi m_A kT/h^2)^{3/2}\cdot\omega_A \\ \text{and}\qquad &F_A{}^{\neq}=(2\pi m_A kT/h^2)\cdot\omega_A{}^{\neq 2,3}\ \text{etc.,} \end{aligned}\right\} \qquad (3)$$

respectively. Further, as is shown in Fig. 1 schematically, $\omega_A{}^{\neq}$ and $\omega_B{}^{\neq}$ can be approximated by the cell volume, $v$, of the quasi-crystalline lattice or by the volume occupied by one liquid molecule; i. e.

$$\omega_A{}^{\neq}=\omega_B{}^{\neq}=v=(1/n)^{3/2}. \qquad (4)$$

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(1) Read at the 2nd Annual Meeting of the Society in April, 1949.

(2) J. H. Hildebrand, "Solubility of Non-electrolytes", New York, 1939.

(3) For example, R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge, 1939, Chap. VIII.

(4) T. S. Chang, (*Proc. Camb. Phil. Soc.*, **35**, 265 (1939)) had treated of liquid mixture of single size molecule and double size molecule.

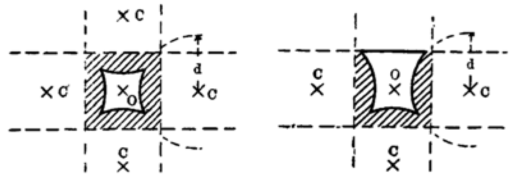
(5) S. S. Penner, *J. Phys. Colloid Chem.*, **52**, 949, 1262 (1948); See also, M. Mizushima, *Kagaku*, **16**, 67 (1946), in Japanese.

(6) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", New York, 1941.

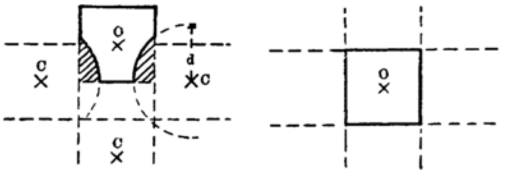
(7) See ref. (6) or ref. (2).

Then Eq. (2) with Eqs. (3) and (4) becomes

$$\left.\begin{array}{l} D_A = x_A(kT/2\pi m_A)^{1/2}(1/\omega_A)\exp(-\bar{u}_A/kT) \\ \text{and} \\ D_B = x_B(kT/2\pi m_B)^{1/2}(1/\omega_B)\exp(-\bar{u}_B/kT). \end{array}\right\} \quad (5)$$



(i) free vol. of liquid molecule, $\omega$. (ii) free vol. of surface molecule.



(iii) free vol. of activated molecule, $\omega^{\neq}$. (iv) free vol. of gas molecule, $v$.

o: center of the molecule whose free volume is in question.
c: center of the adjacent molecules of o-molecule.
d: diameter of molecule.
Shaded area: Region excluded by c-molecules.

Fig. 1.—Schema of free volume.

As the velocities of condensation should be equal to those of vaporization in equilibrium, we put $C_A = D_A$ and $C_B = D_B$ and then obtain

$$\left.\begin{array}{l} p_A = x_A(kT/\omega_A)\exp(-\bar{u}_A/kT), \\ p_B = x_B(kT/\omega_B)\exp(-\bar{u}_B/kT). \end{array}\right\} \quad (6)$$

Now if we denote the potential energies of $A$ and $B$ molecules surrounded only by $A$ (or $B$) molecules by $-u_A$ (or $-u_{AB}$) and $-u_{AB}$ (or $-u_B$), respectively, and use the Bragg-Williams approximation, the total energy $U$ of a solution composed of $N(=N_A+N_B)$ molecules is given by

$$U = N_A u_A + N_B u_B + 2x_A x_B \cdot N\Delta u \quad (7a)$$

$$\text{with} \quad \Delta u \equiv u_{AB} - \{(u_A+u_B)/2\}, \quad (7b)$$

and then $\bar{u}_A$ and $\bar{u}_B$ are given by

$$\left.\begin{array}{ll} & \bar{u}_A = (\partial U/\partial N_A)_{N_B} = u_A + 2x_B^2\Delta u \\ \text{and} & \bar{u}_B = (\partial U/\partial N_B)_{N_A} = u_B + 2x_A^2\Delta u. \end{array}\right\} \quad (8)$$

Inserting Eq. (8) into Eq. (6) and putting

$$\left.\begin{array}{ll} & P_A = (kT/\omega_A)\exp(-u_A/kT) \\ \text{and} & P_B = (kT/\omega_B)\exp(-u_B/kT), \end{array}\right\} \quad (9)$$

we can get the well-known formulae

$$\left.\begin{array}{ll} & p_A = x_A P_A \exp(-2x_A^2\Delta u/kT) \\ \text{and} & p_B = x_B P_B \exp(-2x_B^2\Delta u/kT), \end{array}\right\} \quad (10)$$

which coincide with the ones obtained by the statistical method(3). Of course, $P_A$ and $P_B$ are the vapor pressures of pure liquids $A$ and $B$ respectively. And $u_A$ and $u_B$ are connected with the heats of vaporization, $\lambda_A$ and $\lambda_B$, by

$$\lambda_A = u_A - (kT/2) \text{ and } \lambda_B = u_B - (kT/2). \quad (11)$$

## Derivation of Practical Equation for the Total Vapor Pressure, *P*

In order to take into consideration the difference of sizes between $A$ and $B$ molecules which has been ignored in the preceding section, we should use rather the expression of energy of van Laar's type(8),

$$U - (N_A u_A + N_B u_B) = \varphi_A\varphi_B B \equiv \Delta U, \quad (12)$$

than Eq. (7). Here $\varphi$'s are the volume fractions and $B$ is the parameter corresponding to $2N\Delta u$ in Eq. (7). As is well-known, Eq. (12) is derived from the consideration that each molecule is surrounded by $A$ and $B$ molecules in proportion of $\varphi_A$ and $\varphi_B$.

In this paper, we will use the following assumption, instead of Eq. (12), for the purpose of deriving a practical equation.

**Assumption.**—$\varphi_A N_A$ molecules of $A$ are surrounded by $A$ molecules only and they have the potential energy of $-u_A$. The remaining $\varphi_B N_A$ molecules of $A$ are surrounded by $B$ molecules only and they have the potential energy of $-u_{AB}$. Similarly, $\varphi_A N_B$ molecules of $B$ and the remaining $\varphi_B N_B$ have the potential energies of $-u_{AB}$ and $-u_B$ respectively.

Using this assumption and denoting the free volume of a molecule surrounded by the molecules of different species only by $\omega_{AB}$, we get

$$\left.\begin{array}{l} D_A = x_A(kT/2\pi m_A)^{1/2}[(\varphi_A/\omega_A)\cdot \\ \exp(-u_A/kT) + (\varphi_B/\omega_{AB})\exp(-u_{AB}/kT)], \\ D_B = x_B(kT/2\pi m_B)^{1/2}[(\varphi_A/\omega_{AB}) \\ \exp(-u_{AB}/kT) + (\varphi_B/\omega_B)\exp(-u_B/kT)]. \end{array}\right\} \quad (13)$$

These equations correspond to Eq. (5) for regular solution.

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(8) J. J. van Laar, Z. phys. Chem., A 137, 421 (1928).

Now let us define the "mutual vapor pressure" $P_{AB}$ by the similar relation as Eq. (9),

$$P_{AB}=(kT/\omega_{AB})\exp(-u_{AB}/kT). \qquad (14)$$

Then, equating Eqs. (1) and (13) and using Eqs. (9) and (14), we can easily obtain

$$\left.\begin{aligned} p_A&=x_A\varphi_A P_A+x_A\varphi_B P_{AB} \\ \text{and} \qquad p_B&=x_B\varphi_A P_{AB}+x_B\varphi_B P_B. \end{aligned}\right\} \qquad (15)$$

For practical purposes, we may put

$$x_A\varphi_B+x_B\varphi_A=2(x_Ax_B\varphi_A\varphi_B)^{1/2}, \qquad (16)$$

obtaining our final result,

$$\begin{aligned} P=p_A+p_B&=x_A\varphi_A P_A+x_B\varphi_B P_B \\ &+2(x_Ax_B\varphi_A\varphi_B)^{1/2}P_{AB}. \end{aligned} \qquad (17)$$

## Comparison of Eq. (17) with the Experimental Data

To make comparison of Eq. (17) with the experimental values, we must evaluate $P_{AB}$, which is the sole unknown parameter in the equation. In this section, we will use for $P_{AB}$ the value evaluated from the observed value of $P$, $P_{obs}$, at a composition $x_A \doteqdot x_B$.

Table 1

List of the Systems Compared and the Results Obtained.—I.

| System (Ref.*) | °C. | $P_{AB}$ | $\bar{\Delta}$, % |
|---|---|---|---|
| $CCl_4+C_6H_6$ (i) | 0 | 33.3 | 0.3 |
| | 10 | 58.0 | 0.3 |
| | 20 | 90.5 | 0.2 |
| | 30 | 138.0 | 0.1 |
| | 40 | 206.5 | 0.1 |
| $CS_2+C_6H_6$ (ii) | 0 | 120.0 | 2.2 |
| | 10 | 177.0 | 2.2 |
| | 20 | 263 | 2.0 |
| | 30 | 380 | 1.3 |
| | 40 | 530 | 1.3 |
| $CCl_4+C_2H_5OH$ (i) | 34.8 | 328 | 3.4 |
| | 50 | 626 | 3.5 |
| | 60 | 928 | 3.7 |
| | 66 | 1162 | 3.9 |
| $CCl_4+C_6H_5CH_3$ (ii) | 10 | 40.8 | 0.8 |
| | 20 | 60.5 | 1.1 |
| | 30 | 94.7 | 1.3 |
| | 40 | 138.0 | 0.8 |
| | 50 | 210.5 | 0.5 |
| | 60 | 304 | 0.5 |
| | 70 | 420 | 0.4 |
| $CS_2+CHCl_3$ (ii) | 0 | 141.0 | 1.4 |
| | 10 | 217 | 1.4 |
| | 20 | 322 | 1.7 |
| | 30 | 467 | 1.0 |
| | 40 | 660 | 0.9 |
| $CS_2+CH_3COCH_3$ (ii) | 0 | 235 | 5.9 |
| | 10 | 371 | 5.3 |
| | 20 | 557 | 4.5 |
| | 30 | 817 | 3.8 |
| | 35 | 960 | 3.6 |
| $CS_2+C_6H_5CH_3$ (ii) | 10 | 147 | 4.3 |
| | 20 | 222 | 4.0 |
| | 30 | 324 | 3.5 |
| | 40 | 460 | 1.8 |
| $C_6H_6+CHCl_3$ (ii) | 0 | 45.4 | 0.6 |
| | 20 | 122.5 | 1.1 |
| | 40 | 266 | 0.3 |
| | 60 | 574 | 0.2 |
| $C_6H_6+CH_3OH$ (ii) | 0 | 81.9 | 5.6 |
| | 10 | 144.0 | 5.4 |
| | 20 | 236 | 4.9 |
| | 30 | 379 | 5.5 |
| | 40 | 590 | 6.7 |
| | 60 | 1300 | 7.8 |
| $C_6H_6+CH_3COOH$ (ii) | 20 | 95.0 | 2.2 |
| | 30 | 157.0 | 2.8 |
| | 40 | 239 | 4.0 |
| | 50 | 357 | 3.2 |
| | 60 | 520 | 3.0 |
| | 70 | 737 | 2.0 |
| $C_6H_6+C_2H_5OH$ (i) | 34.8 | 288 | 5.0 |
| | 50 | 557 | 5.3 |
| | 60 | 830 | 5.5 |
| | 66 | 1057 | 5.8 |
| $C_6H_6+n\text{-}C_3H_7OH$ (ii) | 10 | 63.0 | 8.4 |
| | 20 | 106.0 | 6.3 |
| | 30 | 172.0 | 5.7 |
| | 40 | 270 | 5.5 |
| | 50 | 410 | 6.4 |
| $C_6H_6+C_2H_5OC_2H_5$ (ii) | 0 | 98.0 | 0.4 |
| | 10 | 157.0 | 0.4 |
| | 20 | 242 | 0.2 |
| | 30 | 347 | 0.3 |
| $C_6H_6+CH_3CO_2C_2H_5$ (ii) | 10 | 84.5 | 3.3 |
| | 20 | 138.3 | 0.9 |
| | 30 | 214 | 1.3 |
| | 40 | 330 | 1.4 |
| | 50 | 466 | 1.4 |
| | 60 | 657 | 1.1 |
| $C_6H_6+C_6H_5CH_3$ (ii) | 10 | 34.7 | 1.6 |
| | 20 | 59.4 | 1.1 |
| | 30 | 98.5 | 0.9 |
| | 40 | 149.0 | 1.1 |
| | 50 | 214 | 0.9 |
| | 60 | 303 | 0.4 |
| | 80 | 574 | 0.5 |

* References:

(i) *International Critical Tables*, Vol. III, pp. 285, 358 (1928).

(ii) Schmidt, *Z. Phys. Chem.*, **121**, 221 (1926).

The comparison of $P_{calc}$ with $P_{obs}$ has been performed in regard to about 20 systems which are chosen from various types of mixtures as shown in Tables 1 and 2. In these tables are arranged the systems in three classes: mixtures of (A) non-polar and non-polar liquids, (B) non-polar and polar liquids and (C) polar and polar liquids, for convenience's sake. In these tables are also tabulated $P_{AB}$ in terms of mm. Hg and $\bar{\varDelta}$ which is the arithmetical mean of $|P_{calc}-P_{obs}|\times 100/P_{obs}$ at various compositions. $\bar{\varDelta}$ is regarded as a kind of measure of the coincidence of $P_{calc}$ with $P_{obs}$. Some of the results of calculations are plotted in Figs. 2 and 3, where the circles and the full lines represent the observed and the calculated values respectively. The agreement of $P_{calc}$ with $P_{obs}$ seems to be fairly good for all of the systems listed in Tables 1 and 2.

Table 2

List of the Systems Compared and the Results Obtained.—II.

| System (Ref.*) | °C. | $P_{AB}$ | $\bar{\varDelta}$, % |
|---|---|---|---|
| $H_2O+CH_3OH$ (i) | 39.9 | 165 | 3.3 |
| | 59.4 | 416 | 2.8 |
| $H_2O+C_2H_5OH$ (i) | 40 | 159 | 4.4 |
| | 55 | 338 | 4.4 |
| | 75 | 823 | 4.2 |
| $H_2O+n\text{-}C_3H_7OH$ (i) | 30.3 | 83.0 | 3.7 |
| | 49.9 | 240 | 4.9 |
| | 65.9 | 510 | 4.2 |
| | 79.8 | 930 | 3.7 |
| $CHCl_3+CH_3COCH_3$ (ii) | 0 | 43.8 | 0.9 |
| | 10 | 65.2 | 2.1 |
| | 20 | 112.3 | 1.9 |
| | 30 | 178 | 2.0 |
| | 40 | 270 | 1.7 |
| | 50 | 395 | 1.5 |
| $CHCl_3+C_2H_5OC_2H_5$ (ii) | 0 | 86.4 | 2.2 |
| | 10 | 135.0 | 1.0 |
| | 20 | 213 | 0.6 |
| | 30 | 309 | 0.3 |
| $CH_3OH+C_2H_5OH$ (ii) | 10 | 41.6 | 1.4 |
| | 20 | 74.2 | 0.4 |
| | 30 | 134.0 | 0.7 |
| | 40 | 215 | 0.2 |
| | 50 | 345 | 0.3 |
| | 60 | 528 | 0.4 |
| $CH_3OH+n\text{-}C_3H_7OH$ (ii) | 10 | 40.6 | 0.6 |
| | 20 | 72.5 | 1.3 |
| | 30 | 134.0 | 0.3 |
| | 40 | 217 | 0.8 |
| | 50 | 346 | 0.6 |
| | 60 | 495 | 0.5 |
| $C_2H_4Br_2+C_3H_6Br_2$ (i) | 85.1 | 152.0 | 0.4 |
| $C_2H_5OH+C_2H_5CO_2H_5$ (i) | 0 | 173 | 5.6 |
| | 10 | 269 | 5.0 |
| | 20 | 405 | 4.6 |
| | 30 | 594 | 3.9 |
| | 35 | 713 | 4.0 |
| $CH_3COCH_3$ | 20 | 432 | 0.7 |
| $+C_2H_5OC_2H_5$ (i) | 30 | 642 | 1.4 |
| $CH_3CO_2C_2H_5$ | 0 | 109.0 | 0.3 |
| $+C_2H_5OC_2H_5$ (ii) | 10 | 167.0 | 0.2 |
| | 20 | 258 | 0.2 |
| | 30 | 388 | 0.8 |

* References are given in Table 1.

Further, if we plot log $P_{AB}$ against $1/T$, a straight line will be obtained according to the definition of $P_{AB}$, Eq. (14). That is, defining the "mutual heat of vaporization", $\lambda_{AB}$, by

$$\lambda_{AB}=u_{AB}-(kT/2), \tag{18}$$

and putting

$$b=\lambda_{AB}/2.303\,k, \tag{19}$$

we can write Eq. (14) in the form,

Table 3

Values of $a$ and $\lambda_{AB}$.

| System A | System B | $a$ | $b$ | $\lambda_{AB}$ (kcal./mole) | $(\lambda_A+\lambda_B)/2$ (kcal./mole) | $\lambda_A(\lambda_B)$* (kcal./mole) |
|---|---|---|---|---|---|---|
| $CCl_4$ | $C_6H_6$ | 7.720 | 1691 | 7.74 | 7.77 | 7.67 |
| $CS_2$ | $C_6H_6$ | 7.265 | 1420 | 6.50 | 7.25 | 6.65 |
| $CCl_4$ | EtOH | 8.490 | 1840 | 8.42 | 8.83 | |
| $CCl_4$ | $PhCH_3$ | 7.600 | 1705 | 7.80 | 7.96 | (8.24) |
| $CS_2$ | $CHCl_3$ | 7.388 | 1431 | 6.55 | 7.03 | |
| $CS_2$ | $Me_2CO$ | 7.672 | 1445 | 6.61 | 7.17 | |
| $CS_2$ | $PhCH_3$ | 7.335 | 1463 | 6.69 | 7.44 | |
| $C_6H_6$ | $CHCl_3$ | 7.850 | 1694 | 7.75 | 7.64 | 7.86 |
| $C_6H_6$ | MeOH | 8.590 | 1823 | 8.34 | 8.43 | |
| $C_6H_6$ | AcOH | 8.096 | 1792 | 8.20 | 8.73 | (9.60) |
| $C_6H_6$ | EtOH | 8.671 | 1915 | 8.76 | 8.93 | |
| $C_6H_6$ | PrOH | 8.396 | 1868 | 8.55 | 9.48 | (11.10) |
| $C_6H_6$ | $Et_2O$ | 7.766 | 1578 | 7.22 | 7.31 | |
| $C_6H_6$ | AcOEt | 7.875 | 1682 | 7.70 | 8.15 | |
| $C_6H_6$ | $PhCH_3$ | 7.714 | 1742 | 7.97 | 8.05 | |
| $H_2O$ | MeOH | 9.063 | 2143 | 9.81 | 9.65 | 10.30 |
| $H_2O$ | EtOH | 9.316 | 2228 | 10.19 | 10.15 | |
| $H_2O$ | PrOH | 9.411 | 2273 | 10.40 | 10.70 | |
| $CHCl_3$ | $Me_2CO$ | 7.850 | 1698 | 7.77 | 7.56 | 7.42 |
| $CHCl_3$ | $Et_2O$ | 7.538 | 1530 | 7.00 | 7.08 | (6.75) |
| MeOH | EtOH | 8.962 | 2077 | 9.50 | 9.50 | 9.00 |
| MeOH | PrOH | 9.114 | 2125 | 9.72 | 10.05 | |
| EtOH | $Et_2O$ | 7.648 | 1478 | 6.76 | 8.37 | 10.00 |
| $Me_2CO$ | $Et_2O$ | 7.847 | 1528 | 6.99 | 7.23 | 7.70 |
| AcOEt | $Et_2O$ | 7.632 | 1530 | 7.00 | 7.60 | 8.45 |

* Values in parentheses are the heat of vaporization of B-component given in the same row.

$$\log_{10} P_{AB} = a - (b/T), \tag{20}$$

to a good approximation. The demand for this linearity is, indeed, satisfied by the values of $P_{AB}$ tabulated in Tables 1 and 2. In Table 3 are given the values of $a$ and $b$ in Eq. (20). Using these values, we can obtain $P_{AB}$ at any temperature. In this Table, are also tabulated $\lambda_{AB}$ in terms of kcal./mole and, for comparison's sake, $(\lambda_A+\lambda_B)/2$ and $\lambda_A$ (or $\lambda_B$). It should be noticed that the signs of $\varDelta\lambda$ defined by

$$\varDelta\lambda = \lambda_{AB} - \{(\lambda_A+\lambda_B)/2\} = \varDelta u \tag{21}$$

are consistent with the sign of the heat of mixing for all of the systems cited here. Especially,

$$\varDelta\lambda = (6.99-7.23) = -0.24 \text{ kcal./mole}$$

for the mixture of acetone and ethyl ether, which is regarded as "regular solution", coincides with the value of $\varDelta u$ evaluated by Porter⁽⁹⁾ from Eq. (10), $2\varDelta u/kT = -0.741$ at 30°C., quantitatively. These results are to be compared with the fact that the sign of $\varDelta u$ evaluated by Eq. (10) conflicts some times with the one expected from the heat of mixing for the system exhibiting appreciable departure from regular solution (for example, $H_2O+CH_3OH$). And $\lambda_{AB}$ obtained from the present method is consistent with the value of "activation energy of flow" estimated from the data of the viscosity coefficient as was illustrated in our previous paper⁽¹⁰⁾.

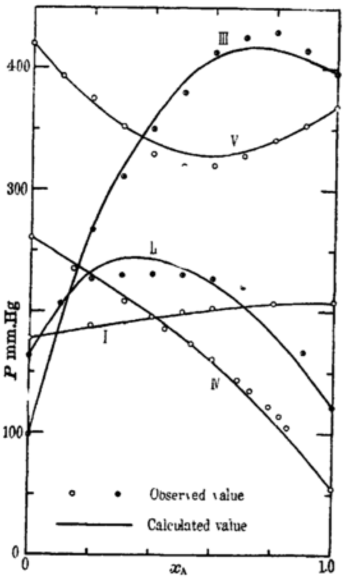

Fig. 2.—Observed and calculated values of $P$–1: Curve I, $A=CCl_4$, $B=C_6H_6$ (40°C.); Curve II, $A=C_6H_6$, $B=CH_3OH$ (30°C.); Curve III, $A=C_6H_6$, $B=CH_3COOH$ (60°C.); Curve IV, $A=H_2O$, $B=CH_3OH$ (39.9°C.); Curve V, $A=CHCl_3$, $B=CH_3COCH_3$ (40°C).

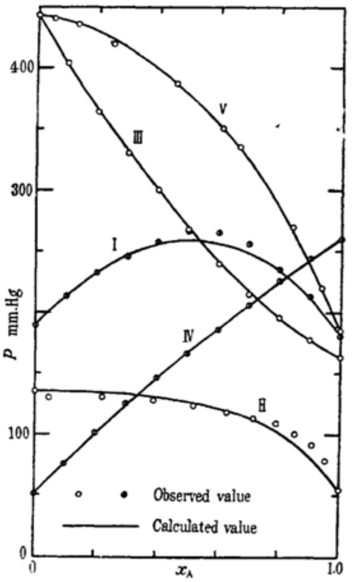

Fig. 3.—Observed and calculated values of $P$–2: Curve I, $A=C_6H_6$, $B=CH_3CO_2C_2H_5$ (40°C.); Curve II, $A=H_2O$, $B=C_2H_5OH$ (40°C.); Curve III, $A=CHCl_3$, $B=C_2H_5OC_2H_5$ (20°C.); Curve IV, $A=CH_3OH$, $B=n\text{-}C_3H_7OH$ (40°C.); Curve V, $A=CH_3COCH_3$, $B=C_2H_5OC_2H_5$ (20°C.).

However, our formula for the partial vapor pressure shows, unfortunately, only poor agreement with the experimental data. So, we cannot calculate the so-called "$x$ to $y$ diagram" (diagram of the composition of solution to that of vapor) from the present theory.

## Estimation of $\varDelta\lambda$ from Heat of Mixing

In this section, we will compare $\lambda_{AB}$ or $\varDelta\lambda$ given in Table 3 with those estimated from the heat of mixing, $\varDelta H$.

As the difference between $H$ (enthalpy) and $U$ (energy) can be neglected in liquid phase, we get from Eqs. (12) and (21)

$$\varDelta H \equiv \varDelta U = 2\varphi_A\varphi_B(N\varDelta\lambda), \tag{22}$$

where plus sign of $\varDelta H$ represents the heat evolved by the solution. Using this relation, we can again estimate $\varDelta\lambda$ from the observed values of $\varDelta H$. In Table 4 are given the results of calculation for some examples.

Though the constancy of $\varDelta\lambda$ to $x_A$ is not enough in examples 2 or 3, the values of $\varDelta\lambda$ thus estimated will give, at least, their correct

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(9) A. W. Porter, *Trans. Farad. Soc.*, **16**, 336 (1920).

(10) M. Tamura and M. Kurata, This Bulletin, **25**, 32 (1952), Eq. (17) and Table 3.

order. As the values of $\Delta\lambda$ obtained from Table 3 are in agreement with the ones estimated here within small error, 50～60 cal./mol., we can conclude that $\lambda_{AB}$ tabulated in Table 3 gives the correct measure of energy of molecular contact of A—B type within small error, probably less than 0.1 kcal./mole (or less than 2%).

Table 4

Estimation of $\Delta\lambda$ from Heat of Mixing.

Example 1. $A=CCl_4$, $B=C_6H_6$ at 25°C.

| $x_A$ | $\Delta H \frac{\text{kjoule}}{\text{mole}}$ | $\Delta\lambda$ kcal./mole Eq. (22) | Table 3 |
|---|---|---|---|
| 0.300 | −0.091 | −0.050 | |
| 0.351 | −0.106 | −0.054 | |
| 0.501 | −0.107 | −0.051 | −0.03 |
| 0.618 | −0.104 | −0.053 | |
| 0.731 | −0.089 | −0.056 | |

Example 2. $A=C_6H_6$, $B=C_2H_5OH$ at 15°C.

| $x_A$ | $\Delta H \frac{\text{joule}}{\text{g. soln.}}$ | $\Delta\lambda$ kcal./mole Eq. (22) | Table 3 |
|---|---|---|---|
| 0.202 | −6.067 | −0.194 | |
| 0.282 | −6.867 | −0.197 | |
| 0.469 | −7.556 | −0.230 | −0.17 |
| 0.579 | −7.338 | −0.264 | |
| 0.702 | −6.706 | −0.331 | |

Example 3. $A=C_6H_6$, $B=CHCl_3$ at 18°C.

| $x_A$ | $\Delta H \frac{\text{joule}}{\text{g. soln.}}$ | $\Delta\lambda$ kcal./mole Eq. (22) | Table 3 |
|---|---|---|---|
| 0.219 | 2.64 | 0.170 | |
| 0.396 | 3.31 | 0.160 | |
| 0.496 | 3.31 | 0.157 | 0.11 |
| 0.604 | 3.18 | 0.160 | |
| 0.723 | 2.89 | 0.178 | |

Data of $\Delta H$ are adopted from "*International Critical Tables*" Vol. V, p. 154.

Table 5

Total Vapor Pressure of the Mixture of $CCl_4$ (A), $C_2H_5OH$ (B) and $C_6H_6$ (C).

| | | 34.8°C. | | | 60°C. | | |
|---|---|---|---|---|---|---|---|
| $x_A$ | $x_B$ | $P_{obs}$ | $P_{calc}$ | $\Delta$, % | $P_{obs}$ | $P_{calc}$ | $\Delta$, % |
| 0.131 | 0 | 153 | 153 | 0 | 407 | 404 | − 0.7 |
| 0.126 | 0.040 | 191 | 161 | −15.7 | 515 | 431 | −16.3 |
| 0.112 | 0.144 | 201 | 181 | − 9.9 | 559 | 492 | −12.0 |
| 0.094 | 0.288 | 204 | 200 | − 2.0 | 580 | 556 | − 4.1 |
| 0.078 | 0.408 | 204 | 209 | + 2.5 | 585 | 591 | + 1.0 |
| 0.058 | 0.561 | 199 | 208 | + 4.5 | 577 | 603 | + 4.5 |
| 0.045 | 0.661 | 193 | 199 | + 3.1 | 564 | 588 | + 4.3 |
| 0.035 | 0.736 | 186 | 188 | + 1.1 | 546 | 562 | + 2.9 |
| 0.022 | 0.833 | 167 | 165 | − 1.2 | 508 | 509 | + 0.2 |
| 0.013 | 0.900 | 143 | 144 | + 0.7 | 462 | 457 | − 1.1 |
| 0.007 | 0.945 | 130 | 127 | − 2.3 | 421 | 415 | − 1.4 |
| 0.386 | 0 | 163 | 162 | − 0.6 | 426 | 426 | 0 |
| 0.363 | 0.061 | 203 | 175 | −13.8 | 551 | 466 | −15.4 |
| 0.342 | 0.116 | 208 | 185 | −11.1 | 575 | 499 | −13.2 |
| 0.289 | 0.253 | 212 | 205 | − 3.3 | 599 | 564 | − 5.8 |
| 0.232 | 0.400 | 212 | 217 | + 2.3 | 603 | 611 | + 1.3 |
| 0.178 | 0.540 | 208 | 216 | + 3.8 | 598 | 619 | + 3.5 |
| 0.100 | 0.742 | 190 | 192 | + 1.1 | 560 | 572 | + 2.1 |
| 0.058 | 0.850 | 167 | 163 | − 2.4 | 508 | 506 | − 0.4 |
| 0.035 | 0.909 | 147 | 143 | − 2.7 | 465 | 455 | − 2.2 |
| 0.019 | 0.951 | 128 | 126 | − 1.6 | 417 | 415 | − 0.5 |
| 0.587 | 0 | 166 | 167 | − 0.6 | 435 | 436 | + 0.2 |
| 0.550 | 0.063 | 207 | 181 | −12.6 | 561 | 480 | −14.4 |
| 0.501 | 0.147 | 215 | 196 | − 8.8 | 600 | 532 | −11.3 |
| 0.432 | 0.266 | 218 | 212 | − 2.8 | 612 | 583 | − 4.7 |
| 0.329 | 0.440 | 216 | 224 | + 3.7 | 615 | 632 | + 2.8 |
| 0.269 | 0.542 | 213 | 221 | + 3.8 | 608 | 634 | + 4.3 |
| 0.190 | 0.675 | 203 | 207 | + 2.0 | 588 | 608 | + 3.4 |
| 0.134 | 0.773 | 187 | 188 | + 0.5 | 559 | 566 | + 1.3 |
| 0.094 | 0.839 | 173 | 170 | − 1.7 | 522 | 519 | − 0.6 |
| 0.045 | 0.921 | 144 | 141 | − 2.1 | 459 | 448 | − 2.4 |
| 0.013 | 0.978 | 115 | 114 | − 0.9 | 387 | 382 | − 1.3 |
| 0.745 | 0 | 170 | 170 | 0 | 441 | 442 | + 0.2 |
| 0.538 | 0.277 | 221 | 218 | − 1.4 | 625 | 596 | − 4.6 |
| 0.420 | 0.436 | 219 | 227 | + 3.7 | 624 | 637 | + 2.1 |
| 0.323 | 0.566 | 215 | 223 | + 3.7 | 615 | 640 | + 4.1 |
| 0.204 | 0.726 | 199 | 202 | + 1.5 | 583 | 595 | + 2.1 |
| 0.141 | 0.811 | 184 | 180 | − 2.2 | 543 | 548 | + 0.9 |
| 0.093 | 0.875 | 163 | 160 | − 1.8 | 497 | 496 | − 0.2 |
| 0.045 | 0.940 | 137 | 133 | − 2.9 | 437 | 429 | − 1.8 |
| 0.497 | 0.503 | 223 | 232 | + 4.0 | 637 | 655 | + 2.8 |
| 0.416 | 0.421 | 220 | 226 | + 2.7 | 628 | 633 | + 0.8 |
| 0.357 | 0.361 | 217 | 220 | + 1.4 | 617 | 612 | − 0.8 |
| 0.284 | 0.288 | 213 | 209 | − 1.9 | 602 | 579 | − 3.8 |
| 0.215 | 0.218 | 209 | 197 | − 5.7 | 589 | 542 | − 8.0 |
| 0.139 | 0.141 | 201 | 180 | −10.4 | 566 | 489 | −13.6 |
| 0.083 | 0.085 | 194 | 169 | −12.9 | 535 | 455 | −14.9 |
| 0.041 | 0.042 | 182 | 158 | −13.2 | 490 | 411 | −16.1 |
| 0.018 | 0.019 | 170 | 152 | −10.6 | 446 | 404 | − 9.4 |
| 0.190 | 0.810 | 187 | 185 | − 1.1 | 554 | 558 | + 0.7 |
| 0.178 | 0.760 | 194 | 194 | 0 | 571 | 576 | + 0.9 |
| 0.168 | 0.717 | 199 | 201 | + 1.0 | 581 | 593 | + 2.1 |
| 0.157 | 0.669 | 202 | 206 | + 2.0 | 586 | 603 | + 2.9 |
| 0.139 | 0.590 | 205 | 212 | + 3.4 | 589 | 615 | + 4.4 |
| 0.114 | 0.486 | 205 | 214 | + 4.4 | 589 | 611 | + 3.7 |
| 0.079 | 0.334 | 203 | 205 | + 1.0 | 583 | 573 | − 1.7 |
| 0.052 | 0.221 | 200 | 191 | − 4.5 | 570 | 526 | − 7.7 |
| 0.033 | 0.140 | 194 | 176 | − 9.3 | 548 | 481 | −12.2 |
| 0.013 | 0.057 | 185 | 160 | −13.5 | 509 | 429 | −15.7 |
| 0.006 | 0.027 | 172 | 154 | −10.5 | 457 | 408 | −10.7 |

| | $P_A$ | $P_B$ | $P_C$ | $P_{AB}$ | $P_{BC}$ | $P_{AC}$ |
|---|---|---|---|---|---|---|
| 34.8°C. | 173 | 103 | 147 | 328 | 288 | 170 |
| 60°C. | 446 | 354 | 389 | 928 | 830 | 443 |

Data of $P_{obs}$ are adopted from Ref. (i) in Table 1.

## Total Vapor Pressure of Ternary Liquid Mixture

Extending the treatment mentioned above to ternary mixture of liquids composed of $A$, $B$ and $C$ components, we can easily obtain the relation having the similar type to Eq. (17);

$$\begin{aligned}P=&x_A\varphi_A P_A+x_B\varphi_B P_B+x_C\varphi_C P_C\\&+2(x_Ax_B\varphi_A\varphi_B)^{1/2}P_{AB}+2(x_Bx_C\varphi_B\varphi_C)^{1/2}P_{BC}\\&+2(x_Cx_A\varphi_C\varphi_A)^{1/2}P_{AC}.\end{aligned}\tag{23}$$

Then, if we know $P_{obs}$ at least at three compositions, for example, (i) $x_A=x_B=1/2$, (ii) $x_B=x_C=1/2$ and (iii) $x_A=x_C=1/2$, it will be possible to calculate $P$ at any composition. In Table 5 are given the results of calculation for the system, carbon tetrachloride+benzene +ethyl alcohol. The degree of agreement of $P_{calc}$ with $P_{obs}$ is the same order as the one obtained for the binary mixture. The values of $P_A$, $P_B$, $P_C$, $P_{AB}$, $P_{BC}$ and $P_{AC}$ used in this calculation are tabulated in the last part of this table. Among these values, $P_{AB}$ and $P_{BC}$ were already given in Table 1 and $P_{AC}$ was calculated by Eq. (20) with $a$ and $b$ given in Table 3.

It seems to be a strong point of the present method that the extension to the multicomponent system can be performed very easily as shown here.

## Summary

(1) The kinetic method was applied to the vapor pressure of regular solution; the result being in agreement with that of the statistical method.

(2) New semi-empirical equations having simple form were derived for the vapor pressures of binary and ternary mixtures of liquids and satisfactory agreements of these equations with the experimental data were illustrated in regard to about 20 examples.

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