Analysis of the Multi-azeotropes in Terms of the Zeroth Approximation

By Ikuho YAMADA, Takatoshi YOSHIDA and Osamu KAWASE

(Received October 3, 1958)

Theoretical and experimental studies on the binary azeotropes, characterized by a maximum or a minimum in vapor pressure curves, have been made by many investigators. Among them, the theoretical studies of Prigogine[1], Mashiko[2] and Ikari[3], in terms of strictly regular solutions are viewed with interest.

However, most of these studies have dealt only with the case of binary systems. We shall report here the results obtained in the theoretical study of multi-azeotropes in the zeroth approximation by extending the method of Prigogine and Mashiko.

Theoretical Equation of the Vapor-liquid Equilibrium in Terms of the Zeroth Approximation.—The authors[4] have already published the theoretical equations of the vapor-liquid equilibrium in multi-component systems at the zeroth approximation.

Rewriting, now, the final result of activity coefficient γ_i of i-th component, the following equation is given

$$\boldsymbol{R}T\ln\gamma_i=\sum_{p=1}^{n}(1-x_i)x_p\omega_{ip}(i\neq p)-\sum_{p,q=1}^{n}x_p x_q\omega_{pq}\begin{pmatrix}p\neq q\\ p,q\neq i\end{pmatrix}\tag{1}$$

where x is mole fraction of component of subscription $1,2,\cdots\cdots,i,\cdots\cdots,n$ in liquid phase, ω the inter-molecular exchange energy in different molecules, $\boldsymbol{R}$ the gas constant and T the absolute temperature in the equilibrium state.

Taking as an example the case of a binary solution, Eq. 1 becomes as follows:

$$\begin{cases}\boldsymbol{R}T\ln\gamma_1=(1-x_1)x_2\omega_{12}\\ \boldsymbol{R}T\ln\gamma_2=(1-x_2)x_1\omega_{12}\end{cases}\tag{2}$$

which is the same as given by Guggenheim[5].

Condition of the Azeotropic Formation in Multi-component System.—The activity coefficient of the i-th component in liquid phase is given by

$$\gamma_i=\pi y_i/p_i^\circ x_i\tag{3}$$

where π is the total pressure, y the mole fraction in vapor phase and p° the vapor pressure of pure component at temperature T.

At an azeotropic point, $y_i=x_i$ and by the Clausius-Clapeyron's equation, $\ln\gamma_i$ is expressed as

$$\boldsymbol{R}\ln\gamma_i=\Delta H_i(1/T-1/T_i^\circ)\tag{4}$$

where ΔH is the heat of vaporization of

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1) I. Prigogine and R. Defay, "Chemical Thermodynamics", Translated by D. H. Everett, Longmans, London, (1954), p. 450.

2) Y. Mashiko, *Rep. Gov. Chem. Ind. Res. Inst. Tokyo*, **52**, 158 (1957).

3) A. Ikari, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 1375 (1957).

4) I. Yamada, will be published in *Chem. Eng. Japan*.

5) E. A. Guggenheim, "Mixtures", Oxford University Press (1952), p. 32.

TABLE I. EXAMPLES OF AZEOTROPIC RELATIONS IN TERNARY AZEOTROPES

Components of system	Boiling point (B. P.)	B. P. difference	$\omega_{ij}/\Delta S_i$	$\omega_{ij}/\Delta S_j$	Azeotropes
Ethanol (1)		$\Delta_{12}=2.2$	69.4	53.6	
—Cyclohexane (2)	62.1°C	$\Delta_{32}=19.2$	97.4	115.9	exist
—Water (3)		$\Delta_{13}=-21.4$	26.0	28.2	
iso-Propanol (1)		$\Delta_{12}=-1.2$	68.7	50.7	
—Cyclohexane (2)	63.8°C	$\Delta_{32}=19.2$	93.5	111.3	exist
—Water (3)		$\Delta_{13}=-17.5$	37.3	42.4	
Allylalcohol (1)		$\Delta_{12}=-16.3$	94.7	73.0	
—Cyclohexane (2)	65.2°C	$\Delta_{32}=19.2$	90.0	107.2	exist
—Water (3)		$\Delta_{13}=-2.9$	25.1	27.4	
Ethanol (1)		$\Delta_{12}=1.8$	55.4	71.5	
—Benzene (2)	64.8°C	$\Delta_{32}=19.8$	106.9	129.8	exist
—Water (3)		$\Delta_{13}=-21.6$	49.8	53.0	
iso-Propanol (1)		$\Delta_{12}=-1.7$	65.7	48.5	
—Benzene (2)	65.3°C	$\Delta_{32}=19.7$	89.7	104.6	exist
—Water (3)		$\Delta_{13}=-18.5$	31.6	27.8	
Allylalcohol (1)		$\Delta_{12}=-17.3$	109.1	79·6	
—Benzene (2)	67.8°C	$\Delta_{32}=19.8$	85.6	101.8	exist
—Water (3)		$\Delta_{13}=-2.5$	42.7	42.7	
Methanol (1)		$\Delta_{12}=8.2$	−6.1	−6.9	
—Acetone (2)	61.7°C	$\Delta_{32}=35.3$	31.2	31.1	none-exist
—Water (3)		$\Delta_{13}=-43.5$	64.8	57.6	

B. P. shows the azeotropic point under 1 atm.

pure component and T° is the boiling point under the pressure π.

From Eqs. 1 and 4, the following expressions for the i- and j-th components can be deduced by substituting ΔS for $\Delta H/T$

$$\Delta S_i(T_i^\circ - T) = \sum_{p=1}^{n}(1-x_i)x_p\omega_{ip}(i\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\binom{p\neq q}{p.q\neq i} \tag{5}$$

$$\Delta S_j(T_j^\circ - T) = \sum_{p=1}^{n}(1-x_j)x_p\omega_{jp}(j\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\binom{p\neq q}{p.q\neq j} \tag{6}$$

and

$$T_i^\circ - T_j^\circ = \left\{\sum_{p=1}^{n}(1-x_i)x_p\omega_{ip}(i\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\binom{p\neq q}{p.q\neq i}\right\}\Delta S_i^{-1} - \left\{\sum_{p=1}^{n}(1-x_j)x_p\omega_{jp}(j\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\binom{p\neq q}{p.q\neq j}\right\}\Delta S_j^{-1} \tag{7}$$

When $x_j=1$, Eq. 7 shows a maximum and when $x_i=1$, a minimum, so that the following relation should hold.

$$-\omega_{ij}/\Delta S_j \leqq T_i^\circ - T_j^\circ \leqq \omega_{ij}/\Delta S_i \tag{8}$$

Hence, in the case of multi-azeotropes, the same relation as Eq. 7 should hold for all such combinations made of n components.

In the case of binary azeotropes, Eq. 8 takes the form given by Mashiko[6]. Table I shows the azeotropic relations from the given data[7], and the values of ω_{ij} are calculated from Eq. 1 for ternary systems.

Constancy of ω_{ij}.—The theoretical equations of the vapor-liquid equilibrium in multicomponent systems on the zeroth approximation have been derived by assuming that the molecular configurations have pairs in the liquid phase and intermolecular exchange energy between molecules i and j are independent of each other. If these assumptions are correct ω_{ij} should have a constant value for any pair of components.

ω_{ij} can be obtained by solving Eq. 1 for a given set of values of T, x_i and γ_i, i being $1, 2, \cdots\cdots, n$.

In the case of ternary azeotropes, the following solution can be obtained

$$\omega_{12}\Delta = \boldsymbol{M}$$

where

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[6] M. Mashiko, *Rep. Gov. Chem. Ind. Res. Inst. Tokyo*, **52**, 160 (1957).

[7] L. H. Horsley, *Anal. Chem.*, **19**, 508 (1947); **21**, 831 (1949).

$$\varDelta=\begin{bmatrix}(1-x_1)x_2 & -x_2x_3 & (1-x_1)x_3\\ (1-x_2)x_1 & (1-x_2)x_3 & -x_1x_3\\ -x_1x_2 & (1-x_3)x_2 & (1-x_3)x_1\end{bmatrix}$$

and

$$\boldsymbol{M}=\begin{bmatrix}\varDelta H_1(1-T/T_1^\circ) & -x_2x_3 & (1-x_1)x_3\\ \varDelta H_2(1-T/T_2^\circ) & (1-x_2)x_3 & -x_1x_3\\ \varDelta H_3(1-T/T_3^\circ) & (1-x_3)x_2 & (1-x_3)x_1\end{bmatrix}$$

By plotting $\varDelta$ vs. $\boldsymbol{M}$, a linear relation is obtained for several ternary systems as shown in Figs. 1—3.

Temperature Effect upon Azeotropic Compositions.—Taking the difference between $\ln\gamma_i$ and $\ln\gamma_{i+1}$ for all i's in Eq. 1, all second order terms $x_px_q\omega_{pq}$ cancel each other and the following equation can be obtained.

$$\varDelta H_i(1-T/T_i^\circ)-\varDelta H_{i+1}(1-T/T_{i+1}^\circ)=(x_{i+1}-x_i)\omega_{i\ i+1}+\sum_{p=1}^{n}(\omega_{ip}-\omega_{j+p})x_p \quad (p\neq i,\ i+1) \qquad (12)$$

where $i=1,2,\cdots\cdots,n-1$

As $\sum x=1$, Eq. 12 becomes

$$\begin{bmatrix}1\\ \varDelta\phi_{1\ 2}\\ \vdots\\ \varDelta\phi_{i\ j+1}\\ \vdots\\ \varDelta\phi_{n-1,n}\end{bmatrix}=\begin{bmatrix}1 & 1 & \cdots\cdots & 1 & 1 & \cdots\cdots & 1\\ -\omega_{1\ 2} & \omega_{1\ 2} & \cdots\cdots & (\omega_{1\ i}-\omega_{2\ i}) & (\omega_{1\ i+1}-\omega_{2\ i+1}) & \cdots\cdots & \vdots\\ \vdots & \vdots & & \vdots & \vdots & & \vdots\\ (\omega_{1\ i}-\omega_{1\ i+1}) & (\omega_{2\ i}-\omega_{2\ i+1}) & \cdots\cdots & -\omega_{i\ i+1} & \omega_{i\ i+1} & \cdots\cdots & (\omega_{i\ n}-\omega_{i+1\ n})\\ \vdots & \vdots & & \vdots & \vdots & & \vdots\\ (\omega_{1\ n-1}-\omega_{1\ n}) & (\omega_{2\ n-1}-\omega_{2\ n}) & \cdots\cdots & (\omega_{i\ n-1}-\omega_{i\ n}) & (\omega_{i+1\ n-1}-\omega_{i+1\ n}) & \cdots\cdots & \omega_{n-1\ n}\end{bmatrix}\begin{bmatrix}x_1\\ x_2\\ \vdots\\ x_i\\ \vdots\\ x_n\end{bmatrix} \qquad (13)$$

where

$$\varDelta\phi_{i\ i+1}=\varDelta H_i(1-T/T_i^\circ)-\varDelta H_{i+1}(1-T/T_{i+1}^\circ)$$

Consequently, x's can be expressed by linear functions of T for given values ω_{ij}'s, $\varDelta H_i$'s and T_i°'s.

For binary azeotropes, the following results can be given.

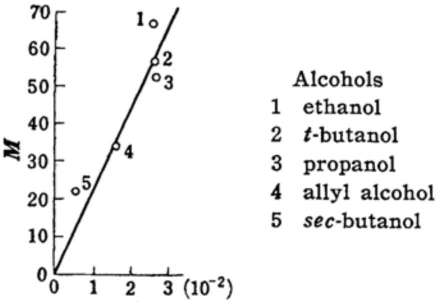

Fig. 1. Carbontetrachloride-water-alcohol system.

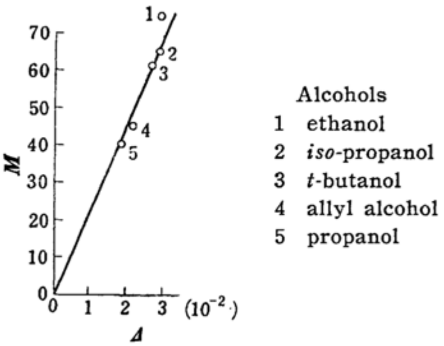

Fig. 2. Cyclohexane-water-alcohol system.

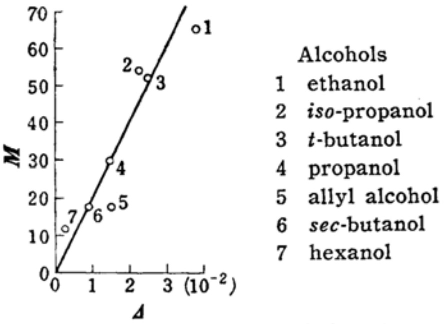

Fig. 3. Benzene-water-alcohol system.

$$\begin{bmatrix}1\\ \varDelta H_1(1-T/T_1^\circ)-\varDelta H_2(1-T/T_2^\circ)\end{bmatrix}=\begin{bmatrix}1 & 1\\ -\omega & \omega\end{bmatrix}\begin{bmatrix}x_1\\ x_2\end{bmatrix} \qquad (14)$$

Consequently

$$2x_1=1-\{\varDelta H_1(1-T/T_1^\circ)-\varDelta H_2(1-T/T_2^\circ)\}\omega^{-1} \qquad (15)$$

$$2x_2=1+\{\varDelta H_1(1-T/T_2^\circ)-\varDelta H_2(1-T/T_2^\circ)\}\omega^{-1} \qquad (16)$$

Eqs. 15 and 16 agree with those given by Prigogine[8).

Breaking Point of Azeotropes. — When x_i obtained by solving Eq. 13 is equal to zero or unity, the multi-azeotropes are broken; these points are predicted by solving the equation for $i=1,2,\cdots\cdots,n$.

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8) I. Prigogine and R. Defay, "Chemical Thermodynamics", Translated by D. H. Everett, Longmans, London, (1954), p. 462.

The closest value to initial T obtained for each may be considered as the break point.

Prediction of Azeotropic Temperature.— Substituting Eq. 4 and x_i given by Eq. 13 into Eq. 1, the azeotropic temperature can be predicted by solving the second-order equation in respect to T for given values of ω_{ii}, T_i°, ΔH and $\boldsymbol{R}$.

Summary

Assuming the zeroth approximation for the vapor-liquid equilibrium in multi-component systems the authors have analyzed multi-azeotropes, and the following results have been obtained.

1) For the condition of azeotropic formation in multi-component systems, Eq. 8 should hold for all combinations of n components.

2) The constancy of ω_{ij} is shown as Figs. 1 to 3.

3) Azeotropic composition effect upon temperature is given by solving Eq. 13, and the breaking temperatures are obtained by substituting $x_i=1$ or 0 into Eq. 13.

4) Azeotropic temperature can be deduced from Eqs. 2, 4 and 13.

Nagoya Institute of Technology
Gokiso-cho, Showa-ku, Nagoya