RELATIONSHIP BETWEEN HEATS OF VAPORIZATION OF BINARY MIXTURES*

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Relations were derived between basic types of heats of vaporization of binary mixtures which make their calculation and mutual conversion possible on the basis of experimentally available data.

Heat of vaporization of a mixture is defined exactly on the basis of the dependence of entropy of vaporization on temperature, pressure, and composition[1]. In this way derived relation is, however, very broad and therefore it provides the possibility of a practical employment only after introducing restricting conditions chosen with regard to the purpose pursued: As a rule, either to reach a satisfactory experimental arrangement or to facilitate theoretical considerations. In this manner it is possible to reduce the number of different kinds of heats of vaporization of mixtures to a bearable extent.

Single types, which are delimited in this way, are not independent to one another and therefore it is possible to convert them mutually. The mutual conversion is conditioned by the derivation of exact relations by which the connection of single heats of vaporization with the state thermo-dynamic quantities would be expressed.

Considering that a considerable lack of uniformity in definitions of single types of heats of vaporization has appeared in the literature so far it was considered expedient to clear up the relations for four most often used heats of vaporization of binary mixtures.

Definitions of Heats of Vaporization

The differential heat of vaporization and of condensation and the integral isothermal and isobaric heats of vaporization of binary systems belong to the most often used types of heats of vaporization of binary systems.

Differential heat of vaporization ($Q_{T,P}^V$) is intended to mean the heat absorbed during reversible evaporating one mole of equilibrium vapour from such amount of liquid its composition not to be changed in this process. Analogously, differential heat of condensation ($Q_{T,P}^C$) is the heat liberated during the reversible condensation

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of one mole of equilibrium liquid from such amount of vapour its composition not to be changed by it.

The relation of differential heat of vaporization and condensation to the state thermodynamic quantities is given by the equations

$$Q_{T,P}^{V} = T\Delta s_{T,P}^{V} = \Delta h_{T,P}^{V} = T\sum y_i(\bar{s}_i^g - \bar{s}_i^l) = \sum y_i(\bar{h}_i^g - \bar{h}_i^l), \qquad (1)$$

$$Q_{T,P}^{C} = T\Delta s_{T,P}^{C} = \Delta h_{T,P}^{C} = T\sum x_i(\bar{s}_i^l - \bar{s}_i^g) = \sum x_i(\bar{h}_i^l - \bar{h}_i^g), \qquad (2)$$

where the summation in both equations as well in all following ones are ment for $i = 1, 2$.

$Q_{T,P}^{V}$ and $Q_{T,P}^{C}$ can be also expressed, as it is evident from the enthalpy diagram H, x at constant pressure (see Fig. 1), by the relations

$$Q_{T,P}^{V} = h^g - \left[h^l + (y_1 - x_1)(\partial h^l / \partial x_1)_{T,P} \right] \qquad (3)$$

and

$$Q_{T,P}^{C} = h^l - \left[h^g + (x_1 - y_1)(\partial h^g / \partial y_1)_{T,P} \right], \qquad (4)$$

where h^g and h^l denote molar enthalpy of the equilibrium vapour and the equilibrium liquid, respectively,

$$h^g = \sum y_i \bar{h}_i^g \quad \text{and} \quad h^l = \sum x_i \bar{h}_i^l. \qquad (5)$$

As it follows from the definition, these differential heats are not accessible from experimental measurements.

FIG. 1

H, x-Diagram at Constant Pressure

Integral isobaric heat of vaporization (also only isobaric heat $Q_{P,x}^V$) is defined as the heat amount absorbed during the complete equilibrium evaporation of one mole of mixture at constant pressure. Considering that an isobaric change is concerned, it is possible to put

$$Q_{P,x}^V = \Delta h_{P,x}^V = h_{T^d,P,Y_1}^g - h_{T^b,P,x_1}^l. \tag{6}$$

The value $Q_{P,x}^V$ is apparent well in the enthalpy diagram H, x at constant pressure.

Integral isothermal heat of vaporization (also isothermal heat $Q_{T,x}^V$) is defined as the heat amount absorbed during the complete equilibrium evaporation of one mole of a mixture at constant temperature. In the literature this isothermal heat is very often identified with isothermal enthalpy of vaporization $\Delta h_{T,x}^V$ [2-5] (probably on the basis of the analogy with isobaric heat). Considering that in this case an isothermal change is concerned, this statement is not correct[6]. The connection between the experimentally measurable isothermal heat and the isothermal enthalpy of vaporization follows from the relation

$$Q_{T,x}^V = T\Delta s_{T,x}^V = T\left(s_{T,P^d,Y_1}^g - s_{T,P^b,x_1}^l\right) = \Delta h_{T,x}^V - \Delta g_{T,x}^V =$$
$$= h_{T,P^d,Y_1}^g - h_{T,P^b,x_1}^l + g_{T,P^d,Y_1}^g - g_{T,P^b,x_1}^l. \tag{7}$$

The meaning of single indexes is evident from Figs 1 and 2. For P^d it is expedient to introduce the denotation the pressure of beginning condensation lest the confusion with the pressure at T^d should come about (see Fig. 3), $\Delta h_{T,x}^V$ and its relation to $Q_{P,x}^V$ is apparent well from the H, T-diagram of a hypothetical mixture in Fig. 3.
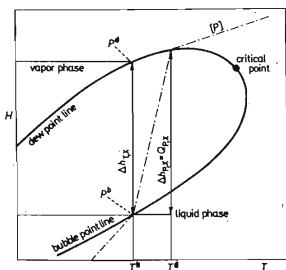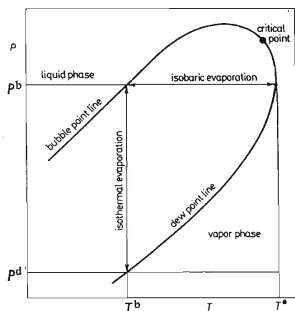

Fig. 2

H,T-Diagram of Binary Mixture

Fig. 3

P,T-Diagram of Binary Mixture

Relationship between Heats of Vaporization

The conversion of in this way defined heats of vaporization to each other can be made in terms of their relations to state thermodynamic quantities, above all entropy and enthalpy.

Integral isobaric and integral isothermal heats of vaporization. To convert the integral latent heats it is suitable to employ above all enthalpy. The isothermal heat of vaporization is not the direct difference of enthalpies but the corresponding change of enthalpy $\Delta h_{T,x}^V$ may be calculated by adding the value $\Delta g_{T,x}^V$ to isothermal heat (see Eq. (7)). $\Delta g_{T,x}^V$ can be expressed from the known pressure-volume-temperature behaviour of mixture and from the vapour–liquid equilibrium data. Even in case that the data are not very accurate the error in $\Delta h_{T,x}^V$ caused by it is small for $\Delta g_{T,x}^V$ is, as to its absolute value, considerably smaller than isothermal heat.

Let us observe, in the P, T-diagram of a hypothetical mixture, a path from the point given by the coordinates T^b, P^b to the point T^d, P^b. This change can be realized *e.g.* by these two ways:

1) The mixture will be evaporated at constant pressure P; temperature will be changed by it from T^b to T^d. The change in enthalpy in this transition will be directly equal to the isobaric heat of mixture.

2) The mixture will be evaporated isothermally at T first; pressure will decrease from P^b to P^d during it. Then the vapour will be heated from T^b to T^d at P^d and afterwards compressed to P^b at T^d.

Considering that the initial and final states are the same in both processes, the changes in enthalpy must be equal for both transitions, too. With regard to Eqs (6) and (7) it will consequently hold

$$Q_{P,x}^V = Q_{T,x}^V + \Delta g_{T,x}^V + \int_{T^b}^{T^d} (\partial h^g / \partial T)_{P^d, Y_i} \, dT + \int_{P^d}^{P^b} (\partial h^g / \partial P)_{T^d, Y_i} \, dP . \qquad (8)$$

By rearranging Eq. (8) on using the second virial coefficient to express volume we get

$$Q_{P,x}^V = Q_{T,x}^V + \Delta g_{T,x}^V + \int_{T^b}^{T^d} \sum Y_i (C_i^0)_P \, dT + P^d .$$

$$. \left[B_{T^d} - B_{T^b} - T^d (\partial B_{T^b} / \partial T)_y + T^b (\partial B_{T^b} / \partial T)_y \right] +$$

$$+ (P^b - P^d) \left[B_{T^d} - T^d (\partial B_{T^d} / \partial T)_y \right] . \qquad (9)$$

Integral isobaric heat of vaporization and differential heats. Owing to the validity of Eqs (1), (2) and (6) it is also suitable to employ enthalpy for the mutual conversion. Evaporating can be again represented well in the enthalpy diagram H, x at constant

pressure, as it follows from Fig. 1, by a transition between the points x_1, T^b and $Y_1 = x_1$, T^d, or between the points $X_1 = y_1$, T^{by} and y_1, $T^{dy} = T^b$. This transition can be realized, besides the evident isobaric evaporation in which temperature changes from T^b to T^d (or from T^{by} to T^{dy}), as well by the following process of thought: The mixture passes to the gas phase at a pressure P and temperature T^b, whereupon this supersaturated vapour is heated from T^b to T^d. In the second case the liquid mixture is heated from T^{by} to T^{dy} at constant pressure and then evaporated at a temperature T^{dy} and pressure P. With regard to the coincidence of the initial and final states it is possible to write

$$\Delta h_{P,x}^V = h_{T^b,P,Y_1}^g - h_{T^b,P,x_1}^l + \int_{T^b}^{T^d} (\partial h^g / \partial T)_{P,Y_1} \, dT, \qquad (10)$$

or

$$\Delta h_{P,y}^V = h_{T^{dy},P,y_1}^g - h_{T^{dy},P,X_1}^l + \int_{T^{by}}^{T^{dy}} (\partial h^l / \partial T)_{P,X_1} \, dT, \qquad (11)$$

where the index y at the symbol $\Delta h_{P,y}^V$ denotes that the quantity is concerned referring to the composition of the equilibrium vapour.

By adding and subtracting the expression $\sum Y_i (\bar{h}_i^g)_{T^b,P,y_1}$ to the right-hand side of Eq. (10), or the expression $\sum X_i (\bar{h}_i^l)_{T^b,P,x_1}$ to the right-hand side of Eq. (11), we obtain

$$Q_{P,x}^V = - Q_{T,P}^C + \sum Y_i [(\bar{h}_i^g)_{T^b,P,Y_1} - (\bar{h}_i^g)_{T^b,P,y_1}] + \int_{T^b}^{T^d} (\partial h^g / \partial T)_{P,Y_1} \, dT \qquad (12)$$

and

$$Q_{P,y}^V = Q_{T,P}^V + \sum X_i [(\bar{h}_i^l)_{T^b,P,x_1} - (\bar{h}_i^l)_{T^b,P,X_1}] + \int_{T^{by}}^{T^{dy}} (\partial h^l / \partial T)_{P,X_1} \, dT. \qquad (13)$$

If volume is again expressed by means of the second virial coefficient the relations are obtained

$$Q_{P,x}^V = - Q_{T,P}^C + P(\delta_{T^b} - T^b(d\delta_{T^b}/dT))(Y_1 y_2 - Y_1 y_2^2 - Y_2 y_1^2) +$$
$$+ \int_{T^b}^{T^d} \sum y_i (C_i^0)_P \, dT + P[B_{T^d} - B_{T^b} - T^d (\partial B_{T^d} / \partial T)_y + T^b (\partial B_{T^b} / \partial T)_y], \qquad (14)$$

and

$$Q_{P,y}^V = Q_{T,P}^V + \sum X_i (h_i^{lE})_{T^b,P,x_1} - h_{T^b,P,X_1}^{lE} + \int_{T^{by}}^{T^{dy}} C_P^l \, dT. \qquad (15)$$

An equivalent expression of Eq. (15) is the relation

$$Q_{P,y}^V = Q_{T,P}^V + R'(T^b)^2 \sum X_i \big[(\partial \ln \gamma_i / \partial T)_{P,X_1} - (\partial \ln \gamma_i / \partial T)_{P,x_1} \big] + \int_{T^{by}}^{T^{dy}} C_P^l \, dT .$$
$$(16)$$

Integral isothermal heat of vaporization and differential heats. To express the relationship between isothermal heat and differential heats it is suitable, owing to the validity of Eqs (1), (2) and (7), to employ entropy. The derivation is quite analogous to the previous case. The isothermal evaporation of a mixture of x_1 or $X_1 = y_1$ at a temperature T may be realized ideally in two following steps:

1) The mixture will pass to the gas phase at the temperature T and pressure P^b,
2) the vapour will expand from the pressure P^b to P^d at constant temperature, or
1) the pressure above the liquid will decrease from P^{by} to P^{dy} at the temperature T,
2) the mixture will be evaporated at the pressure P^{dy} and the temperature T.

Then for the change of entropy it holds

$$\Delta s_{T,x}^V = s_{T,P^b,Y_1}^g - s_{T,P^b,x_1}^l + \int_{P^b}^{P^d} (\partial s^g / \partial P)_{T,Y_1} \, dP ,$$
$$(17)$$

or

$$\Delta s_{T,y}^V = s_{T,P^{dy},y_1}^g - s_{T,P^{dy},X_1}^l + \int_{P^{by}}^{P^{dy}} (\partial s^l / \partial P)_{T,X_1} \, dP .$$
$$(18)$$

By an analogous rearrangement as in the conversion between the isobaric heat and differential heats, the equations are reached

$$Q_{T,x}^V = -Q_{T,P}^C + T \sum Y_i \big[(\bar{s}_i^g)_{T,P^b,Y_1} - (\bar{s}_i^g)_{T,P^b,y_1} \big] + T \int_{P^b}^{P^d} (\partial s^g / \partial P)_{T,Y_1} \, dP \quad (19)$$

and

$$Q_{T,y}^V = Q_{T,P}^V + T \sum X_i \big[(\bar{s}_i^l)_{T,P^b,x_1} - (\bar{s}_i^l)_{T,P^b,X_1} \big] + T \int_{P^{by}}^{P^{dy}} (\partial \bar{s}^l / \partial P)_{T,X_1} \, dP \quad (20)$$

and further the relations

$$Q_{T,x}^V = -Q_{T,P}^C + RT \sum Y_i \ln (y_i / Y_i) + RT \ln (P^b / P^d) -$$
$$- PT(\partial \delta / \partial T)(Y_1 Y_2 - Y_1 y_2^2 - Y_2 y_1^2) + (P^b - P^d)(\partial B / \partial T)_y ,$$
$$(21)$$

$$Q_{T,y}^V = Q_{T,P}^V + T \sum X_i (\bar{s}_i^{IM})_{T,P^b,x_1} - T s_{T,P^b,X_1}^{IM} - T \int_{P^{by}}^{P^{dy}} v \alpha^l \, dP .$$
$$(22)$$

An equivalent expression of Eq. (22) is the relation

$$Q^V_{T,y} = Q^V_{T,P} + RT \sum X_i \{\ln (X_i \gamma_i / x_i \gamma_i) + T[(\partial \ln \gamma_i / \partial T)_{P^b, X_i} -$$

$$- (\partial \ln \gamma_i / \partial T)_{P^b, x_i}]\} - T \int_{P^by}^{P^dy} v \alpha^l \, dP . \qquad (23)$$

In Eqs (12) and (13) or (19) and (20) there are the values of partial molar enthalpies and entropies of liquid and vapour in a hypothetical state and their dependence on temperature and pressure. It is not possible to determine exactly these values and dependences. Mostly it is assumed that in a hypothetical region close to real state, analogous dependences hold as in actual regions.

Calculation of isothermal free enthalpy of vaporization. In the relation for conversion of integral heats (see Eq. (8)) here is the quantity $\Delta g^V_{T,x}$ whose meaning is elucidated by Eq. (7). The value of this quantity can be calculated in two ways:

1) If the standard state in the gas phase is considered a pure component in the ideal-gas state at a pressure $P = 1$ atm and at the temperature of system, $(g^{og}_i)_{T,P=1,*}$, and the standard state in the liquid phase a hypothetical pure liquid component at a pressure $P = 0$ and at the temperature of system, $(g^{ol}_i)_{T,P=0}$, then it holds

$$\Delta g^V_{T,x} = g^g_{T,P^d,Y_i} - g^l_{T,P^b,x_i} = \sum x_i (g^{og}_i)_{T,P=1,*} + RT \ln P^d +$$

$$+ \int_0^{P^d} (v - RT/P) \, dP - \sum x_i (g^{ol}_i)_{T,P=0} + v^{ol}_i P^b) - g^{1E}_{T,P^b,x_i} , \qquad (24)$$

where g^{1E}_{T,P^b,x_i} denotes the molar excess free enthalpy of liquid mixture. On the assumption that the molar volumes of pure liquid components v^{ol}_i do not change with pressure and on expressing the volume of the gas phase by an equation of state with the second virial coefficient, we get

$$\Delta g^V_{T,x} = \sum x_i [(g^{og}_i)_{T,P=1,*} - (g^{ol}_i)_{T,P=0}] + RT \ln P^d + BP^d -$$

$$- P^b \sum x_i v^{ol}_i - RT \sum x_i \ln \gamma_i . \qquad (25)$$

Considering that it is not possible to determine directly the difference of molar standard free enthalpies, it is necessary to calculate them on the basis of the knowledge of the saturated vapour pressure data of pure component from the relation for equilibrium in one-component system where it holds

$$(g^{ol}_i)_{T,P=0} + v^{ol}_i P^o_i = (g^{og}_i)_{T,P=1,*} + RT \ln P^o_i + B_i P^o_i . \qquad (26)$$

2) By combining Eqs *(12)* and *(17)* it is possible to obtain, with regard to the validity of relation *(8)*, the expression for $\Delta g_{T,x}^{V}$ in the form

$$\Delta g_{T,x}^{V} = \sum Y_i \left[(\bar{g}_i^g)_{T,P^b,Y_1} - (\bar{g}_i^g)_{T,P^b,y_1} \right] + \int_{P^b}^{P^d} (\partial g^g / \partial P)_{T,Y_1} \, \mathrm{d}P \qquad (27)$$

and by rearranging

$$\Delta g_{T,x}^{V} = RT \sum Y_i \ln \left(Y_i / y_i \right) - RT \ln \left(P^b / P^d \right) +$$
$$+ P^b \delta (Y_1 Y_2 - Y_1 y_2^2 - Y_2 y_1^2) - B(P^b - P^d) \,. \qquad (28)$$

Practical application of some derived conversion relations together with the necessary experimental data which were measured will be presented in next paper.

LIST OF SYMBOLS

B	second virial coefficient
C_P	molar heat capacity of mixture at constant pressure
$(C_i^0)_P$	molar heat capacity of pure component at constant pressure in the ideal-gas state
g	molar free enthalpy
h	molar enthalpy
P	pressure
P_i^0	saturated vapour pressure of pure component i
P^b	pressure at boiling point of mixture of composition x_i
P^*	pressure of beginning condensation of mixture of composition Y_i
P^{by}	pressure at boiling point of mixture of composition X_i
P^{*y}	pressure of beginning condensation of mixture of composition y_i
Q	latent heat of the liquid–vapour phase transition
R	gas constant
s	molar entropy
T	temperature (K)
T^b	temperature of boiling point of mixture of composition x_i
T^*	temperature of dew point of mixture of composition Y_i
T^{by}	temperature of boiling point of mixture of composition X_i
T^{*y}	temperature of dew point of mixture of composition y_i
v	molar volume of mixture
v_i^0	molar volume of pure component i
x	mole fraction in equilibrium liquid
y	mole fraction in equilibrium vapour
X	mole fraction in liquid of $X_i = y_i$
Y	mole fraction in vapour of $Y_i = x_i$
α	coefficient of thermal expansion
γ	activity coefficient
δ	$= (2B_{12} - B_{11} - B_{22})$

Indexes

C	condensation property
E	excess property
g	gas phase property
i	property of component i
l	property of liquid phase
M	mixing property
V	evaporation property
x_i	property of liquid of composition x_i
y_i	property of vapour of composition y_i

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