$$C = \tfrac{1}{2}c \ , \qquad (21)$$

we arrive to the final equation

$$\text{pH} = A - \log \frac{2r_{23} - r_{13})(1 - r_{23})}{(1 + r_{13})(r_{13} - r_{23})} + C \left( \frac{2r_{13} - r_{23}}{1 - r_{23}} \right)^{1/2} \left( \frac{9}{2} + \frac{2r_{13} - r_{23}}{1 - r_{23}} \right), \quad (22)$$

where $A$ and $C$ are constants which can be evaluated from experimental data.

The application of the method just described is illustrated on an example. In Table I direct experimental data of Johnstone[4] and Berdjanskaja and coworkers[5] are presented and compared with values calculated by means of Eq. (22) with constants $A = 6\cdot20$, $C = -0\cdot164$. The agreement can be considered as satisfactory.

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# CALCULATION OF THE INTEGRAL ISOTHERMAL HEAT OF VAPORIZATION OF MIXTURES

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An exact thermodynamic relation for calculating the integral isothermal heat of vaporization of mixtures is derived in this paper. Relations and formulations of the given problem published in the literature are often inaccurate. The dependence of the pure substance enthalpy on pressure at a given temperature $T < T_k$ is illustrated in Fig. 1. Experimentally accessible parts of the curve consist of the dependence of the vapour phase enthalpy on pressure for $P < P^\circ$, the dependence of the liquid phase enthalpy on pressure for $P > P^\circ$, and the difference between the enthalpies of the liquid and the vapour at $P = P^\circ$. These parts of the curve are represented by solid lines in the figure. The heat of vaporization $L_v$ at the temperature $T$ is given by the relation

$$L_v = [H^{(g)} - H^{(1)}]_{P^\circ} = T[S^{(g)} - S^{(1)}]_{P^\circ} , \qquad (1)$$

where the subscript $P^\circ$ denotes that we are dealing with the change of enthalpy or entropy at the constant pressure $P = P^\circ$.

For further procedure, it is expedient to define the enthalpy and entropy of vaporization of the substance for the pressure $P \neq P°$, too, as follows:

$$\Delta H_P = [H^{(g)} - H^{(1)}]_P , \tag{2}$$
$$\Delta S_P = [S^{(g)} - S^{(1)}]_P .$$

The $\Delta H_P$ and $\Delta S_P$ are nonequilibrium enthalpy and entropy changes accompanying the transfer of one mole of a substance from the liquid into the gaseous state at the pressure $P$. The values of these quantities are not experimentally accessible, because at $P \neq P°$ one of the phases is always in a metastable or unstable state. However, the values of $\Delta H_P$ and $\Delta S_P$ can be calculated for pressures not too far from $P°$.

On expanding the enthalpy of the substance into the Taylor series at the point $P = P°$, and substituting for the partial derivatives with respect to pressure, we obtain

$$H_P = H_{P°} + [V - T(\partial V/\partial T)_P]_{T,P°} (P - P°) + 1/2[(\partial V/\partial P)_T - T(\partial^2 V/\partial T \, \partial P)]_{T,P°} .$$
$$. (P - P°)^2 + \dots . \tag{3}$$

After substitution from the relation (3) into Eq. (2) and neglecting all terms with square and higher powers of $(P - P°)*$ we get

$$\Delta H_P = L_v + [V^{(g)} - T(\partial V/\partial T)^{(g)} - V^{(1)} + T(\partial V/\partial T)_P^{(1)}]_{T,P°} (P - P°) . \tag{4}$$

If the liquid entropy is expanded into the Taylor series, and if the higher-order terms are neglected, which is justified in a very wide temperature and pressure range, we have

$$S_P^{(1)} = S_{P°}^{(1)} - (\partial V/\partial T)_P^{(1)} (P - P°) . \tag{5}$$

For the vapour entropy, it is more suitable to expand into the Taylor series only the part corresponding to the correction for nonideal behaviour:

$$S_P^{(g)} = S_{P°}^{(g)} - R \ln (P/P°) + [(R/P) - (\partial V/\partial T)_P^{(g)}]_{T,P°} (P - P°) . \tag{6}$$

By combining the last two equations, the relation for $\Delta S_P$ is obtained

$$\Delta S_P = (L_v/T) - R \ln (P/P°) + [(R/P) - (\partial V/\partial T)_P^{(g)} + (\partial V/\partial T)_P^{(1)}] (P - P°) . \tag{7}$$

Above introduced concepts of the enthalpy of vaporization and the entropy of vaporization are to be used to advantage for calculating the heats of vaporization for mixtures. For pure substances alone, these quantities are of no practical use. In this connection it is necessary to call reader's attention to a sometimes occurring assertion that $H_{P=0}^{(g)} - H_{P=P°}^{(1)}$ equals to the heat of vaporization into vacuum. While this difference is always single-valued, it is not like this in the case of the heat which is not a state variable and the value of which depends on the path followed. Choosing the reversible path, then in this case the amount of the heat will be even infinite.

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* At reduced temperatures $T_r < 0.93$, neglecting the higher-order terms does not cause an error which exceeds 20 percent of the linear term. Besides, data on volumetric behaviour of gases are available only exceptionally for further terms in Eq. (3) to be used.

Further we will deal with calculating the integral isothermal heat of vaporization only. The integral isothermal heat of vaporization of a mixture is defined as the amount of heat required for the reversible transfer of one mol of the saturated liquid (at pressure $P^{(1)}$) to the state of the saturated vapour (at pressure $P^{(g)}$) at constant temperature. This amount of heat is given by the relation

$$Q_T = T(S^{(g)} - S^{(1)}),\qquad(8)$$

where $S^{(g)}$ and $S^{(1)}$ are the entropies of the mixture in the given states.

It is interesting to compare the quantity $Q_T$ with the heat of vaporization of a pure component, given by Eq. (1). The dependence of the enthalpy of a constant-composition mixture on pressure is illustrated in Fig. 2 by analogy with Fig. 1. Unlike the pure substance, for the mixture the pressures $P^{(1)}$ and $P^{(g)}$ are identical only at the azeotropic point and therefore, the integral isothermal heat of vaporization is not generally equal to the difference of enthalpies in the initial and final state, as it is assumed in some papers[1-4]. An exact procedure must get out of Eq. (8).

Eq. (8) is arranged into a form more suitable for the further calculations. The entropy of the given mixture at the pressure $P$, we can write as follows

$$S = \sum x_i(S_i)_P + R \sum x_i \ln x_i + S_P^E,\qquad(9)$$

where $(S_i)_P$ is the entropy of the $i$-th pure component at temperature $T$ and pressure $P$ and $S_P^E$ is the excess mixing entropy under the same conditions. On combining Eqs (8) and (9) and substituting for $(S_i)_P$ from Eqs (5) and (6) we obtain

$$Q_T = \sum x_i L_{vi} + T \sum x_i [(R/P) - (\partial V/\partial T)_P]_{P_i^0}^{(g)} (P^{(g)} - P_i^0) +$$
$$+ T \sum x_i [(\partial V/\partial T)_P (P^{(1)} - P_i^0)]_{P_i^0}^{(1)} - RT \sum x_i \ln (P^{(g)}/P_i^0) +$$
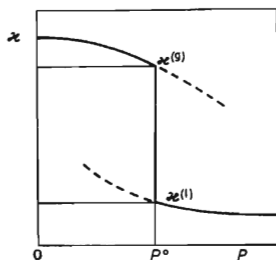$$+ T[(S_{P(g)}^E)^{(g)} - (S_{P(1)}^E)^{(1)}].\qquad(10)$$



FIG. 1

Dependence of the Enthalpy of Pure Component on Pressure at $T < T_k$
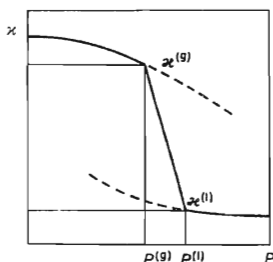


FIG. 2

Dependence of the Enthalpy of Mixture (with no azeotropic point) on Pressure below the Critical Temperature

For calculating the integral isothermal heat of vaporization from Eq. (10) it is sufficient to know the properties of pure substances and excess entropies in liquid and vapour phases. The excess entropy in the liquid phase is to be determined on the basis of calorimetric measurements of heats of mixing ($H^E$), and vapour–liquid equilibrium measurements ($G^E$):

$$(S_{P(l)}^E)^{(1)} = (1/T) \, [H^E - G^E]_{P(l)}^{(1)} = [(H^E)^{(1)}/T] - R \sum x_i \ln \gamma_i \,, \qquad (11)$$

where $\gamma_i$ is the activity coefficient of the i-th component with the standard state chosen as that of the pure constituent at the temperature and pressure of the system.

The excess entropy in the saturated vapour can be determined on the basis of the knowledge of the $P-V-T$ behaviour of the given mixture. For the reduced temperatures $T_r < 0\cdot75$ just the knowledge of the second virial coefficients is sufficient:

$$(S_P^E)^{(g)} = -x_1 x_2 P(\mathrm{d}\delta_{12}/\mathrm{d}T) \,, \qquad (12)$$

where $\delta_{12} = 2B_{12} - B_{11} - B_{22}$.

The data required for calculating the pressure corrections (the second and third term on the right side of Eq. (10)) can be determined from the $P-V-T$ behaviour of pure substances in the liquid and gas state. For the gas phase we recommend to arrange the terms in Eq. (10) into the form

$$[(R/P) - (\partial V/\partial T)^P]_{P_0}^{(g)} = (R/P^\circ)(1 - z_T)_{P_0}^{(g)} \qquad (13)$$

and for the liquid phase

$$[(\partial S/\partial P)_T]_{P^0}^{(1)} = - \, V_k(\alpha/d_r)_{P^0}^{(1)} \,, \qquad (13a)$$

where $z_T = z + T_r(\partial z/\partial T_r)_{P_r}$ and $\alpha$ is the coefficient of volume thermal expansion. The values of the quantities $z$, $z_T$, $\alpha$, $d_r$ are to be found in the literature[5–10].

LIST OF SYMBOLS

$B$    second virial coefficient
$d$    density
E    excess quantity (superscript)
$G$    molar Gibbs energy
g    vapour phase (superscript)
$H$    molar enthalpy of component
i    $i$-th component (subscript)
k    critical quantity (subscript)
l    liquid phase (superscript)
$L_v$    molar heat of vaporization of component
$P$    pressure
$P^\circ$    vapour pressure of pure component at the system temperature
$Q_T$    integral isothermal heat of vaporization of one mol of mixture
$R$    gas constant
r    reduced quantity (subscript)
$S$    molar entropy
$T$    absolute temperature
$V$    molar volume
$x$    mol fraction of component
$z$    compressibility factor

$z_T$ function tabulated by Reid and Valbert[9]
$\alpha$ coefficient of volume thermal expansion

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# HETEROGENE KATALYSE DER LUMINOLLUMINESZENZ

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Die Oxydation des Luminols (3-Aminophthalsäurehydrazid) wird von zahlreichen anorganischen und organischen Substanzen aktiviert. Eine hervorstechende Wirkung weisen hier die Verbindungen mit komplex gebundenem $Fe^{III}$ oder $Cu^{II}$ auf. Die überwiegende Mehrheit dieser Aktivatoren wirkt in homogenen Lösungen. Vorläufig wurden zwei Fälle der sog. heterogenen Katalyse bei der Luminoloxydation verzeichnet. Von Thielert und Pfeiffer[1] und von Cook[2] wurde gefunden, daß verschiedene Phthalocyanine, insbesondere die Verbindung des Phthalocyanins mit zweiwertigem Eisen, welche nach Kristallisieren aus Anilin sechs seiner Moleküle bindet, eine Erhöhung der Reaktionsgeschwindigkeit und der Lumineszenzintensität bewirken. Sie machten auch darauf aufmerksam, daß auch das Salicylaldehydäthylendiimin-eisen(III)-chlorid eine ähnliche Wirkung ausübt.

Der Verlauf dieser Reaktionen wurde von Weber und Schultz[3] untersucht. Sie fanden keine wesentlichen Abweichungen des Reaktionsverlaufs bei Verwendung von Aktivatoren und den dispergierten Verbindungen des Phthalocyanins mit Eisen. Bei der Kupfer(II)-verbindung des