
TO THE PROBLEMS OF DETERMINATION OF HEATS OF VAPORIZATION OF SOLVENTS FROM SOLUTIONS OF ELECTROLYTES*

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A survey is presented of thermodynamic relations for describing the heat of vaporization of solvent from solutions of electrolytes and an outline is given of the feasible calorimetric methods for its determination.

When discussing the vaporization calorimetry we nearly always mean the determination of heats of vaporization of pure substances or mixtures of non-electrolytes. These determinations have been also fully characterized¹ and described^{2,3} in the literature.

There is, however, quite contrary situation as to the determination of heats of vaporization of solvents from solutions of non-volatile substances, usually electrolytes. We are lacking here not only in a survey of the fundamental relations but also we do not find considerations or just prognoses about the feasible experimental methods. The heats of vaporization of solvents from electrolyte solutions were measured only occasionally⁴; in practical applications these values are substituted by the values of heats of vaporization of pure solvents.

Therefore it seems to be useful to carry out the survey of the thermodynamic relations describing this area and thus to point out simultaneously the possibilities of exploiting these data to describe the systems studied and further to use it as a starting point for an *a priori* proposal of experimental methods.

Summary of Thermodynamic Relations

The theoretical basis is the region of two-phase multicomponent systems which is described by the system of differential equations as given *e.g.* by Storonkin⁵:

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$$\left. \begin{aligned}
 & [V^{(2)} - V^{(1)} - \sum_{i=1}^{n-1} (x_i^{(2)} - x_i^{(1)}) (\partial V / \partial x_i)^{(1)}] dP = \\
 & = [S^{(2)} - S^{(1)} - \sum_{i=1}^{n-1} (x_i^{(2)} - x_i^{(1)}) (\partial S / \partial x_i)^{(1)}] dT + \\
 & + \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} (x_i^{(2)} - x_i^{(1)}) (\partial^2 G / \partial x_i \partial x_k)^{(1)} dx_k^{(1)}, \\
 & [V^{(2)} - V^{(1)} - \sum_{i=1}^{n-1} (x_i^{(2)} - x_i^{(1)}) (\partial V / \partial x_i)^{(2)}] dP = \\
 & = [S^{(2)} - S^{(1)} - \sum_{i=1}^{n-1} (x_i^{(2)} - x_i^{(1)}) (\partial S / \partial x_i)^{(2)}] dT + \\
 & + \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} (x_i^{(2)} - x_i^{(1)}) (\partial^2 G / \partial x_i \partial x_k)^{(2)} dx_k^{(2)}, \\
 & [(L_i - L_n)/T] dT + (\Delta V_n - \Delta V_i) dP - D(\partial G / \partial x_i)^{(2)} + D(\partial G / \partial x_i)^{(1)} = 0,
 \end{aligned} \right\} (I)$$

where V , S and G denote the molar volume, the entropy and the Gibbs energy of phases, respectively, T and P is the system temperature and pressure, x_i the mole fraction of a component and the superscripts (1) and (2) are symbols of the first and second phases.

L_i and L_n are the partial molar heats of phase transition of the i -th and the n -th component from the phase (1) to the phase (2). The symbols ΔV_i and ΔV_n then represent the difference of partial molar volumes of the i -th and n -th components between the phase (2) and the phase (1). The symbol D with the derivative term represents then an abridged record of the relation

$$D(\partial G / \partial x_i) \equiv \sum_{k=1}^{n-1} (\partial^2 G / \partial x_i \partial x_k) dx_k.$$

The first two equations of the system (I) are ordinary differential equations, the third one is a supplementary condition of equilibrium.

To reach the aims of this work it will be sufficient to consider only the simple two-phase two-component systems. The perspective extension of the validity of the relations for multicomponent systems will not cause any difficulties. For the chosen limitation the following relations follow from the first two equations of the system (I):

$$\left. \begin{aligned}
 [V^{(2)} - V^{(1)} - (x_1^{(2)} - x_1^{(1)}) (\partial V / \partial x_1)^{(1)}] dP &= \\
 &= [S^{(2)} - S^{(1)} - (x_1^{(2)} - x_1^{(1)}) (\partial S / \partial x_1)^{(1)}] dT + \\
 &+ (x_1^{(2)} - x_1^{(1)}) (\partial^2 G / \partial x_1^2)^{(1)} dx_1^{(1)}, \\
 [V^{(2)} - V^{(1)} - (x_1^{(2)} - x_1^{(1)}) (\partial V / \partial x_1)^{(2)}] dP &= \\
 &= [S^{(2)} - S^{(1)} - (x_1^{(2)} - x_1^{(1)}) (\partial S / \partial x_1)^{(2)}] dT + \\
 &+ (x_1^{(2)} - x_1^{(1)}) (\partial^2 G / \partial x_1^2)^{(2)} dx_1^{(2)}.
 \end{aligned} \right\} \quad (2)$$

Further let us present the differential equation for a two-component two-phase system whose one phase is formed only by one component, *i.e.* by a solvent. The theoretical basis is as well the system of equations (1). Storonkin⁵ gives it in the form

$$(V^{(2)} - \bar{V}_1^{(1)}) dP = (S^{(2)} - \bar{S}_1^{(1)}) dT + RT(\partial \ln \gamma_1 x_1 / \partial T), \quad (3)$$

where \bar{V}_1 and \bar{S}_1 are the partial molar volume and entropy, γ_1 , x_1 the activity coefficient and mole fraction, respectively, all for the solvent in the liquid phase.

The systems of equations (2) and (3) form the theoretical basis of the relations sought. The possible variants we can meet with in determining the heat of vaporization of solvent from the solutions of electrolytes will be given further. Hereinafter the following symbolism will be introduced for the systems of equations (2) and (3): the superscripts (1) and (2) denote the liquid (l) and vapour (g) phases, (s) is the symbol for the solid phase; the subscript 1 denotes the solvent property and 2 the solute property.

Let us consider a solution which is in contact with two one-component phases, *e.g.* a three-phase system which forms a solution being in equilibrium with the one-component vapour phase and with the one-component solid phase. The condition of equilibrium for the solvent following from the first equation of the system (2) for the solution–vapour equilibrium is then given by the relation

$$\begin{aligned}
 [V^g - V^l - (y_1 - x_1) (\partial V / \partial x_1)^l] dP &= [S^g - S^l - (y_1 - x_1) (\partial S / \partial x_1)^l] dT + \\
 &+ (y_1 - x_1) (\partial^2 G / \partial x_1^2) dx_1^l.
 \end{aligned} \quad (4)$$

Since the vapour phase is formed solely by the pure component 1 it holds $y_1 = 1 = \text{const.}$ Consequently both sides of Eq. (4) can be arranged in the following way

$$V^g - [V^l + (1 - x_1) (\partial V / \partial x_1)^l] = V_{01}^g - \bar{V}_1^l$$

and

$$S^g - [S^l + (1 - x_1) (\partial S / \partial x_1)^l] = S_{01}^g - \bar{S}_1^l.$$

For the chosen type of system which is characterized by a constant composition of the liquid phase, Eq. (4) can be rearranged into the form

$$(V_{01}^g - \bar{V}_1^l) dP = (S_{01}^g - \bar{S}_1^l) dT. \quad (5)$$

The subscript 01 denotes a property of pure component (solvent) in the vapour phase.

For the component 2, which is in equilibrium in the system solution–solid phase, it is possible to derive, by an analogous procedure, a similar relation in the form

$$(V_{02}^s - \bar{V}_2^l) dP = (S_{02}^s - \bar{S}_2^l) dT, \quad (6)$$

where the subscript 02 denotes a property of pure component in the solid phase. By multiplying Eq. (5) by the mole fraction of solvent x_1 and Eq. (6) by the mole fraction of solute x_2 in the solution and by adding them we get

$$[(V_{01}^g - \bar{V}_1^l) + r(V_{02}^s - \bar{V}_2^l)] dP = [(S_{01}^g - \bar{S}_1^l) + r(S_{02}^s - \bar{S}_2^l)] dT. \quad (7)$$

Hence we have

$$dP/dT = [(S_{01}^g - \bar{S}_1^l) + r(S_{02}^s - \bar{S}_2^l)] / [(V_{01}^g - \bar{V}_1^l) + r(V_{02}^s - \bar{V}_2^l)] \quad (8)$$

and

$$dP/dT = \Delta H_{vk} / T \Delta V. \quad (9)$$

In Eqs (7)–(9), r denotes the ratio of mole fractions, x_2/x_1 .

Eq. (9) describes the change of pressure with temperature along the equilibrium curve of the three-phase system when evaporating 1 mol of solvent and separating out r mol of the solid phase. The solution composition does not change under these conditions. The heat absorbed in this process is

$$[(H_{01}^g - \bar{H}_1^l) + r(H_{02}^s - \bar{H}_2^l)] \equiv \Delta H_{vk}$$

and comprises both the heat of vaporization of the solvent from the given solution and the heat of separation (heat of crystallization) of r mol of the solute.

A special case of the preceding example is the system for which the volumes of phases do not change and the composition of the solution is constant. As an example let us present the evaporation of one mol of solvent from an infinitely big volume of saturated solution of a solute.

To derive the relation sought we start as well from Eq. (4) and by the way described we reach Eq. (5) which is the defining relation for the sought type of heat of vaporization.

Thus it holds

$$\begin{aligned} dP/dT &= (S_{01}^g - \bar{S}_1^l)/(V_{01}^g - \bar{V}_1^l) = (H_{01}^g - \bar{H}_1^l)/T(V_{01}^g - \bar{V}_1^l) = \\ &= \Delta H_{vn}/T(V_{01}^g - \bar{V}_1^l). \end{aligned} \quad (10)$$

The relation (10) is a special form of the Clausius–Clapeyron equation expressing the dependence of saturated vapour pressures of solvent in an electrolyte solution on temperature. ΔH_{vn} is the symbol for its heat of vaporization, V_{01}^g is then the molar volume of pure solvent in the vapour and \bar{V}_1^l its partial molar volume in the solution.

Meanwhile such systems have been characterized for which the solution composition does not change during evaporating the solvent. It has been the systems of saturated solutions.

To describe unsaturated solutions it is possible to begin with Eq. (3). For the isobaric condition it turns into the form

$$(d \ln \gamma_1 x_1/dT)_P = -(S_{01}^g - \bar{S}_1^l)/RT \quad (11)$$

and for

$$S_{01}^g - \bar{S}_1^l = \Delta H_{v1}/T$$

it holds

$$(d \ln \gamma_1 x_1/dT)_P = -\Delta H_{v1}/RT^2. \quad (12)$$

ΔH_{v1} is the symbol for the heat of vaporization of solvent from unsaturated solutions of electrolytes.

Aspects of Experimental Determination

From Eqs (9), (10) and (12), three possible regions of the experimental interest follow in the determination of heats of vaporization of solvents from solutions of electrolytes. It is: (1) the region of complete evaporation of solvent, (2) the region of saturated solutions and (3) the region of unsaturated solutions.

1) In the first case the simultaneous isothermal determination of heat of vaporization from a solution of non-volatile component and its heat of crystallization seems to be experimentally easiest. The measurement can be carried out in an isothermal-adiabatic calorimeter and, moreover, in apparatus designed initially for the determination of heats of vaporization of pure substances. Certain difficulties are to be expected when realizing the conditions of the complete solvent evaporation which most likely will manifest itself in an uncertainty and unsharpness of the end of the experiment. The only solution offers assuming as large as possible evaporating surface. It can be realized by built-in parts of the vaporization vessel which would consist of the as high as possible number of evaporating plates.

For these reasons success is to be expected only with sparingly soluble substances.

The overall values of the heat supplied represents a sum of heat of vaporization of solvent from the solution and heat of crystallization. To separate both the heat effects will be apparently difficult because single data, especially the data on heat of crystallization, will not be generally available. This fact diminishes importance of the experiment for theoretical applications.

However, the chemical-engineering consequences would be considerable and for industrial applications invaluable.

2) Carrying-out such an experiment which would enable to determine the values of heat of vaporization from saturated solutions would contribute to a more reliable separation of the heats of vaporization and crystallization.

The model imagination of evaporating one mol of solvent from an infinitely big volume of saturated solution could be realized in a practical execution so that the experimental equipment would ensure the continuity of the vapour and liquid flows. It means that the just evaporated and drawn off differential amount of solvent would be replaced by the same amount of mass of the pure solvent in the liquid phase.

This performace of the experiment is realizable in two arrangements. Either it is possible to condensate the evaporated differential amount of the solvent vapours in a calibrated receiver at a given electrical energy input and to weight it. In this way the calibration of the evaporation rate under the chosen stable experimental conditions is carried out and the same calibrated amount of the liquid pure solvent is then pumped into the vaporization vessel. In a real experiment we must then assume that these conditions do not change. Or, perhaps more suitably, by means of level sensors, to maintain the constant level of solution in the vaporization vessel by pumping up the pure solvent into the vaporization vessel and to ensure an intimate mixing of the vessel volume.

3) The experimental determination of heat of vaporization of solvent from unsaturated solutions of electrolytes appears to be the most difficult.

The evaporation can take place either at constant pressure or at constant temperature.

In the first case the experimental arrangement requires a strictly adiabatic calorimeter whose command variable is pressure. As far as it is known from the literature, no description of this type of the calorimeter control was published. Besides, the overall heat effect represents a sum of the heat of vaporization of solvent from a solution ($x_1 \rightarrow x_2$) and the corresponding heat of dilution. Consequently, similar difficulties appear with the separation of heat effects as in case of the heats of vaporization and crystallization.

In the second case it is possible to perform the evaporation at constant temperature with changing pressure and solution composition. This experiment is easily realizable

in an isothermal-adiabatic calorimeter but the difficult separation of values of the entropy of vaporization and the corresponding heat of dilution remains.

Thus, it seems that for theoretical applications, the hitherto known vaporization calorimetric methods are not suitable. However, for chemical-engineering applications these data are indispensable.

Therefore it is to be assumed that the outline of fundamental problems and the difficulties encountered in the experimental determination of heat of vaporization of solvent together with the unfamiliarity and difficulties connected with the determination of the relation quantities and dependences in Eqs (9), (10) and (12) are the reasons why this region has remained up to now outside the framework of investigations.

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