

HEAT CAPACITY OF AQUEOUS SOLUTIONS OF SULFURIC ACID AT LOW TEMPERATURES

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Results of an experimental determination of the specific heat of $H_2O-H_2SO_4$ solutions at low temperatures are presented and the heat capacity of a heterogeneous two-component system is analyzed.

Results of an experimental study of the heat capacity of aqueous solutions of nitric acid at low temperatures [1] revealed the existence of a negative value for the heat capacity at 78% HNO_3 and 22% H_2O . Data was presented [2] for the existence of two forms of ice and of a transition state between them in certain solutions. The phenomena observed are characterized by the authors as anomalous.

In an experimental determination of the specific heat of $H_2O-H_2SO_4$ solutions, a dependence of the heat capacity on temperature and on the relative content of components at constant pressure was established as well as the existence of negative values at 40 and 80% H_2SO_4 , 60 and 20% H_2O . The dependence of specific heat on temperature obtained with a continuous-heat adiabatic calorimeter [3] is shown in Figs. 1 and 2.

We define the heat capacity of an equilibrium, two-component heterogeneous thermodynamic system at constant pressure ($p = \text{const}$) by the expression

$$C_p = T \frac{dS}{dT} \quad (1)$$

Here and in the following, we understand the heat capacity C_p of a thermodynamic system to be, as is conventional in the literature, the heat capacity of a thermodynamic system at constant pressure p and for constant masses M_1 and M_2 of the components.

A thermodynamic system which is considered in accordance with the conditions on the definition of the heat capacity C_p will be defined by a set of external parameters S , p , M_1 , and M_2 where all parameters except the first – the entropy – are fixed and the entropy can vary freely. We consider a system of equations which describes a two-component heterogeneous system where the defining external parameters will be S , p , M_1 , and M_2 and the temperature T will be included in the unknown internal parameters.

In accordance with the analytical theory for multicomponent heterogeneous system [4], we write a complete equation system which uniquely expresses the dependence of all internal parameters of this thermodynamic system on its external conditions:

$$\mu_{i1}(T, \bar{v}_1, x_{11}, x_{21}) = \dots = \mu_{ir}(T, \bar{v}_r, x_{1r}, x_{2r}) \quad (i = 1, 2), \quad (2)$$

$$p_1(T, \bar{v}, x_{11}, x_{21}) = \dots = p_r(T, \bar{v}_r, x_{1r}, x_{2r}) = p, \quad (3)$$

$$\sum_{j=1}^r m_j \bar{s}_j(T, \bar{v}_j, x_{1r}, x_{2r}) = S, \quad (4)$$

$$\sum_{j=1}^r m_j x_{ij} = M_i \quad (i = 1, 2), \quad (5)$$

$$\sum_{i=1}^2 x_{ij} = 1 \quad (j = 1, 2, \dots, r). \quad (6)$$

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It is easy to verify that in the equation system (2)-(6), equality of the number of equations and the number of unknowns — the internal parameters T , \bar{v}_j , x_{1j} , x_{2j} , and m_j (their number is $4r + 1$) — is satisfied. The heat capacity of this thermodynamic heterogeneous system can be written in the following form:

$$C_p = T \frac{d \sum_{j=1}^r m_j \bar{s}_j(T, \bar{v}_j, x_{ij})}{dT} \quad (i = 1, 2; j = 1, 2, \dots, r), \quad (7)$$

where the heat capacity C_p is a function of the internal intensive parameters T , \bar{v}_j , x_{1j} , x_{2j} and of the extensive internal parameters m_j ($j = 1, 2, \dots, r$).

We represent the heat capacity C_p in a different form by expressing the differential of the expression in parentheses in Eq. (7) through the partial derivatives of the internal parameters \bar{v}_j , x_{ij} , and m_j ($i = 1, 2; j = 1, 2, \dots, r$) with respect to T . Equation (7) takes the form

$$C_p = T \sum_{j=1}^r \left(m_j \frac{\partial \bar{s}_j}{\partial T} + m_j \frac{\partial \bar{s}_j}{\partial \bar{v}_j} \frac{d\bar{v}_j}{dT} + \sum_{i=1}^2 m_j \frac{\partial \bar{s}_j}{\partial x_{ij}} \frac{dx_{ij}}{dT} + \bar{s}_j \frac{dm_j}{dT} \right) \quad (j = 1, 2, \dots, r). \quad (8)$$

In Eq. (8), each partial derivative of the function $\bar{s}_j(T, \bar{v}_j, x_{1j}, x_{2j})$ ($j = 1, 2, \dots, r$) is calculated as usual for fixed values of all the variables on which \bar{s}_j depends except for the one with respect to which the derivative is being taken.

We first note that a thermodynamic system with a given set of external parameters S , p , M_1 , M_2 , \dots , M_n (n is the number of components) of which all are fixed except the entropy S (S can vary freely) has all internal intensive parameters uniquely determined (fixed) [4], i.e., does not have intensive degrees of freedom, in the cases where the number of phases $r = n + 1$ and $r = n + 2$.

Thus the two-component thermodynamic system being considered has all internal intensive parameters uniquely fixed with free variation of the external extensive parameter S for the two cases of maximum phase number ($r = 3, 4$).

From what has been said above follows an important conclusion — the heat capacity of this two-component heterogeneous system is infinity for the phase numbers $r = 3, 4$ since the parameter T is fixed during free variation of the external parameter S . A change in state of this thermodynamic system for $r = 3, 4$ occurs under isothermal conditions.

We investigate the meaning of the derivatives $d\bar{v}_j/dT$, dx_{ij}/dT , and dm_j/dT ($i = 1, 2; j = 1, 2$) in Eq. (8). We write the system of thermodynamic equations (2)-(6) in differential form for the case of two components and two phases:

$$\frac{\partial \mu_{11}}{\partial T} dT + \frac{\partial \mu_{11}}{\partial \bar{v}_1} d\bar{v}_1 + \frac{\partial \mu_{11}}{\partial x_{11}} dx_{11} + \frac{\partial \mu_{11}}{\partial x_{21}} dx_{21} - \frac{\partial \mu_{12}}{\partial T} dT - \frac{\partial \mu_{12}}{\partial \bar{v}_2} d\bar{v}_2 - \frac{\partial \mu_{12}}{\partial x_{12}} dx_{12} - \frac{\partial \mu_{12}}{\partial x_{22}} dx_{22} = 0, \quad (9)$$

$$\frac{\partial \mu_{21}}{\partial T} dT + \frac{\partial \mu_{21}}{\partial \bar{v}_1} d\bar{v}_1 + \frac{\partial \mu_{21}}{\partial x_{11}} dx_{11} + \frac{\partial \mu_{21}}{\partial x_{21}} dx_{21} - \frac{\partial \mu_{22}}{\partial T} dT - \frac{\partial \mu_{22}}{\partial \bar{v}_2} d\bar{v}_2 - \frac{\partial \mu_{22}}{\partial x_{12}} dx_{12} - \frac{\partial \mu_{22}}{\partial x_{22}} dx_{22} = 0, \quad (10)$$

$$\frac{\partial p_1}{\partial T} dT + \frac{\partial p_1}{\partial \bar{v}_1} d\bar{v}_1 + \frac{\partial p_1}{\partial x_{11}} dx_{11} + \frac{\partial p_1}{\partial x_{21}} dx_{21} = 0, \quad (11)$$

$$\frac{\partial p_2}{\partial T} dT + \frac{\partial p_2}{\partial \bar{v}_2} d\bar{v}_2 + \frac{\partial p_2}{\partial x_{12}} dx_{12} + \frac{\partial p_2}{\partial x_{22}} dx_{22} = 0, \quad (12)$$

$$m_1 \frac{\partial \bar{s}_1}{\partial T} dT + m_1 \frac{\partial \bar{s}_1}{\partial \bar{v}_1} d\bar{v}_1 + m_1 \frac{\partial \bar{s}_1}{\partial x_{11}} dx_{11} + m_1 \frac{\partial \bar{s}_1}{\partial x_{21}} dx_{21} + m_2 \frac{\partial \bar{s}_2}{\partial T} dT + m_2 \frac{\partial \bar{s}_2}{\partial \bar{v}_2} d\bar{v}_2 + \quad (13)$$

$$+ m_2 \frac{\partial \bar{s}_2}{\partial x_{12}} dx_{12} + m_2 \frac{\partial \bar{s}_2}{\partial x_{22}} dx_{22} + \bar{s}_1 dm_1 + \bar{s}_2 dm_2 = dS,$$

$$m_1 dx_{11} + m_2 dx_{12} + x_{11} dm_1 + x_{12} dm_2 = 0, \quad (14)$$

$$m_1 dx_{21} + m_2 dx_{22} + x_{21} dm_1 + x_{22} dm_2 = 0, \quad (15)$$

$$dx_{11} + dx_{21} = 0, \quad (16)$$

$$dx_{12} + dx_{22} = 0. \quad (17)$$

This system (9)-(17) of thermodynamic equations, which is given in differential form, interrelates the total differentials dT , $d\bar{v}_1$, $d\bar{v}_2$, dx_{11} , dx_{12} , dx_{21} , dx_{22} , dm_1 , and dm_2 .

Solving the system of linear equations (9)-(17) with respect to each of the total derivatives $d\bar{v}_j/dT$, dx_{ij}/dT , and dm_j/dT ($i = 1, 2; j = 1, 2$), we obtain the following relations:

$$\frac{d\bar{v}_j}{dT} = \frac{\Delta_{\bar{v}_j}}{\Delta_T} \quad (j = 1, 2), \quad (18)$$

$$\frac{dx_{ij}}{dT} = \frac{\Delta_{x_{ij}}}{\Delta_T} \quad (i = 1, 2; j = 1, 2), \quad (19)$$

$$\frac{dm_j}{dT} = \frac{\Delta_{m_j}}{\Delta_T} \quad (j = 1, 2), \quad (20)$$

where Δ_T , $\Delta_{\bar{v}_j}$, $\Delta_{x_{ij}}$, and Δ_{m_j} ($i = 1, 2; j = 1, 2$) are determinants which are obtained from the determinant of the system (9)-(17) by replacement of the column made up of the coefficients corresponding to the subscripts in Δ_T , $\Delta_{\bar{v}_j}$, $\Delta_{x_{ij}}$, and Δ_{m_j} by a column made up of the free terms.

The heat capacity C_p of a two-component, single-phase thermodynamic system is obtained from Eq. (8) by omitting the last two terms, which are zero:

$$C_p = Tm \left(\frac{\partial \bar{s}}{\partial T} \right)_{\bar{v}} + Tm \left(\frac{\partial \bar{s}}{\partial v} \right)_T \frac{d\bar{v}}{dT}. \quad (21)$$

It is clear that the first term in Eq. (21) is the heat capacity of this single-phase thermodynamic system at constant volume and constant masses of the components - C_V - and the difference between C_p and C_V is given by the second term in Eq. (21) and physically reflects the work done by the thermodynamic system during its expansion. In the latter case, the total derivative $d\bar{v}/dT$ is easily found from Eq. (11) by omitting the last two terms, which are zero,

$$\left(\frac{\partial p}{\partial T} \right)_{\bar{v}} dT + \left(\frac{\partial p}{\partial T} \right)_{\bar{v}} d\bar{v} = 0. \quad (22)$$

Knowing that $(\partial p / \partial T)_{\bar{v}} / (\partial p / \partial \bar{v})_T = -(\partial \bar{v} / \partial T)_p$, we find that

$$\frac{d\bar{v}}{dT} = \left(\frac{\partial \bar{v}}{\partial T} \right)_p. \quad (23)$$

The physical significance of the first two terms in Eq. (8) for the heat capacity C_p of a two-phase, two-component system is similar to the terms in Eq. (21) for the heat capacity C_p of a single-phase, two-component system. The third term in Eq. (8) denotes the change in heat capacity of a thermodynamic system resulting from a change in the composition of the phase components. The last term in Eq. (8) represents the portion of the heat capacity associated with change in mass of a phase.

We analyze the experimentally obtained relations for the specific heat of $H_2O-H_2SO_4$ solutions and set up laws governing the occurrence of heterogeneous processes. Unfortunately, a quantitative description of a heterogeneous system is impossible because the explicit form of the majority of thermodynamic relations is unknown. There is no definite form for the phase diagram.

An $H_2O-H_2SO_4$ solution has three azeotropic points for the solid-liquid phase transition corresponding to each of the hydrates [5]: the first hydrate $H_2SO_4 \cdot H_2O$ (81.6% solution of H_2SO_4) has the mp $+8.5^\circ C$, the second hydrate $H_2SO_4 \cdot 2H_2O$ (69.0% solution of H_2SO_4) has the mp $-39^\circ C$, and the third hydrate $H_2SO_4 \cdot 4H_2O$ (57.7% solution of H_2SO_4) has the mp $-28^\circ C$; the mp of H_2SO_4 is $+10.4^\circ C$.

We investigate the behavior of the heat capacity of an $H_2O-H_2SO_4$ solution in the portion of the phase diagram from pure water to the hydrate $H_2SO_4 \cdot 4H_2O$. The curves for the specific heat of 10, 20, 30, 40, 50, and 60% aqueous solutions of H_2SO_4 point to the existence of an isotherm for the eutectic transition ($\sim -60^\circ C$) with the exact eutectic at 32-37% H_2SO_4 solution from which the liquidus line in the phase diagram runs to the melting point of ice and of the hydrate $H_2SO_4 \cdot 4H_2O$ (azeotropic point).

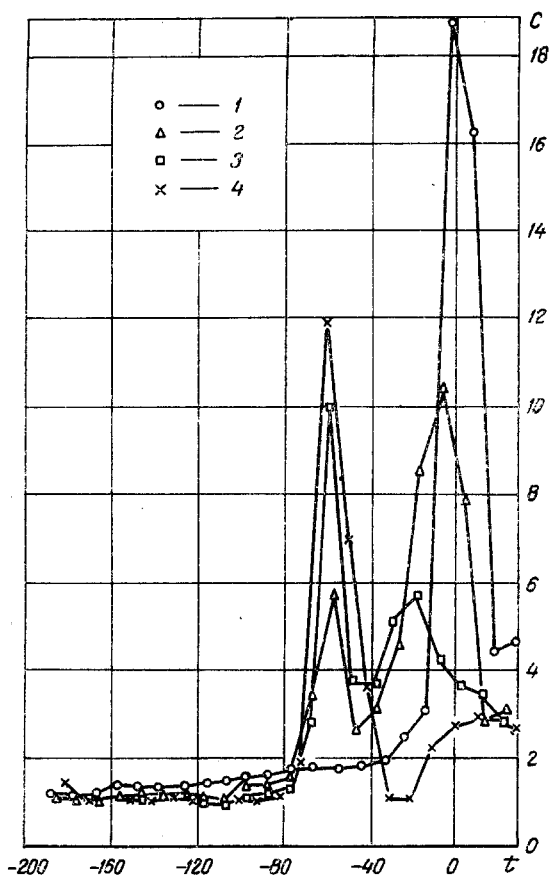


Fig. 1

Fig. 1. Specific heat of water (1) and 10 (2), 20 (3), and 30% (4) aqueous solutions of sulfuric acid in the range -196 to $+20^{\circ}\text{C}$; C , $\text{kJ}/\text{kg}\cdot\text{deg}$; t , $^{\circ}\text{C}$.

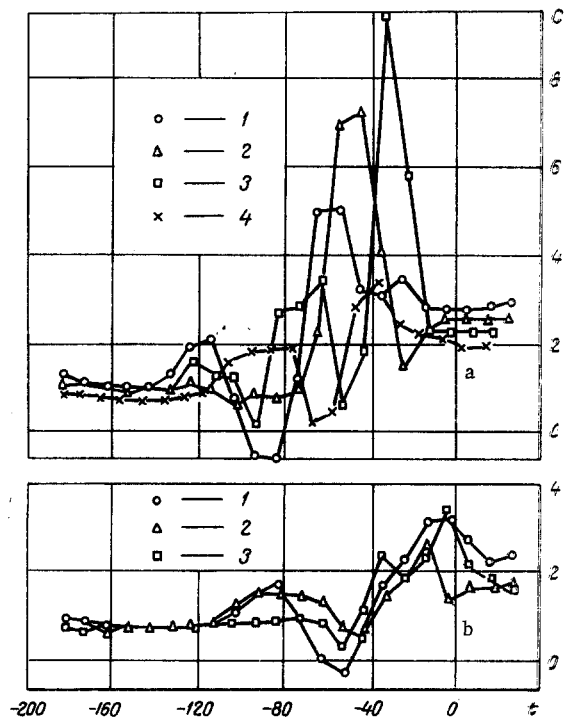


Fig. 2

Fig. 2. Specific heat: a) 40 (1), 50 (2), 60 (3), and 70% aqueous solutions; b) 80 (1), 90 (2), and 95% (3) aqueous solutions of H_2SO_4 in the range -196 to $+20^{\circ}\text{C}$.

Such behavior of a thermodynamic system in the portion of the phase diagram from water to the hydrate $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ is caused by peaks in heat capacity (Figs. 1, 2a). The first peaks in the heat capacity at -60°C correspond to a phase transition on the isotherm for the eutectic transition, and the displaced second peaks at higher temperatures for compositions other than the eutectic correspond to phase transitions on the liquidus line. The height of the transition peaks on the isotherm for eutectic transition increase as one approaches the eutectic point, and the height of the shifted peaks increases toward the azeotropic points at which phase transition occurs for constant phase composition. Azeotropic compositions in the solid state form a new phase – the hydrates.

From what has been said, one can draw an analogy between the portions of the phase diagrams for $\text{H}_2\text{O}-\text{HNO}_3$ solutions [6] and $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ solutions from water to the first azeotropic composition. One can suppose that the $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ phase diagram in all portions between the lines of azeotropic composition is a eutectic system for the liquid – solid transition and is similar to the $\text{H}_2\text{O}-\text{HNO}_3$ diagram. From the experimentally obtained values for heat capacity, it is impossible to make a complete analysis of the behavior of an $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ solution between azeotropic compositions in the remaining three portions of the diagram.

For the phase transition on the isotherm for eutectic transition, three phases coexist: two solid phases (two hydrates or a hydrate and component) and a liquid phase. In this case a two-component heterogeneous system does not have intensive degrees of freedom ($T = \text{const}$). When this system is heated, which corresponds to an experiment for the determination of heat capacity, one of the solid phases on the eutectic isotherm completely transforms into a liquid up to eutectic composition, and with further increase in temperature phase transition occurs on the solidus where the system has two coexisting phases and an intensive degree of freedom. The heat capacity of this thermodynamic system is described by Eq. (8).

Equation (8), which was obtained on the basis of thermodynamic laws, describes the behavior of the heat capacity C_p of $H_2O-H_2SO_4$ solutions (Figs. 1, 2) when two phases are present. The heat capacity C_p on the isotherm for eutectic transition ($T = \text{const}$), where a shift of three-phase equilibrium occurs, is infinite. Equation (21) for the heat capacity C_p of a single-phase solution is trivially obtained from Eq. (8) without the last two terms. The experimentally observed negative values of the heat capacity are also described by Eq. (8). It is clear that the value of the first term is always positive and the values of the last three terms may differ. For example, if the value of the fourth term has a negative sign and its absolute value is greater than the sum of the other terms, the total heat capacity of the system then takes on a negative value. The fourth term in Eq. (8) has a negative value in the case where a supercooled phase is transformed by heating into a phase with a lower temperature state and heat is released in the phase transition.

NOTATION

C	is the heat capacity;
p	is the pressure;
T	is the absolute temperature;
S	is the entropy;
μ_{ij}	is the chemical potential of the i -th component of the j -th phase;
M_i	is the mass of the i -th component of thermodynamic system;
\bar{v}_j	is the specific volume of the j -th phase;
x_{ij}	is the concentration of the i -th component in the j -th phase;
m_j	is the mass of the j -th phase;
\bar{s}_j	is the specific entropy of the j -th phase;
r, n	are the number of phases and components of thermodynamic system.

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