CONTRIBUTION TO THE DETERMINATION OF HEATS
OF VAPORIZATION OF MIXTURES*

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The applicability of a calorimeter, originally designed for the determination of heats of vaporization of pure substances, to the measurement of integral isothermal heats of vaporization of mixtures was proved. Suitability of the method suggested was studied using the methanol–benzene system.

The determination of heats of vaporization of mixtures can be realized in isothermal or in isobaric arrangement. Hitherto, the integral isobaric heats of vaporization of mixtures were studied experimentally for practical reasons most often. Their determination is, however, conditioned by realization of the state of vapour–liquid equilibrium and often by its determination, too. This condition leads, in its consequences, to a considerable increase in requirements on time and consumption of substances and on the other hand, as a rule, to a decrease in accuracy of measurement. Knowledge of the determination of isothermal heats of vaporization of mixtures is so far very little. A facilitation of their measurements could be a methodical resemblance to heats of vaporization of pure substances. Therefore it is possible to suppose that their determination should be practicable by means of some methods originally designed for the measurement of heats of vaporization of pure substances. With a suitably chosen experimental arrangement it could give relatively easily such accuracy as it is expected in case of the determination of heats of vaporization of pure substances.

With regard to these facts we solved the problem in this work whether it is possible to employ the calorimeters for pure substances to determine the integral isothermal heats of vaporization of mixtures and what accuracy of the measured data might be expected. The study was performed using the methanol–benzene system. This system was chosen above all for the reason that, considering complete lack of representative data of integral isothermal heat of vaporization in the literature, it allowed to compare them after conversion with the corresponding values of integral isobaric heat of vaporization which are known from the literature. Since there was an endeavour to examine practically some relationships between different types of heats of vaporization presented in previous work[1], it was possible to assume that the strongly non-ideal properties of the methanol–benzene system (a large positive

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deviation from Raoult's law with an azeotropic point) would show clearly the relative magnitude of single terms in the conversion relations. Eventually, the choice of this system was supported by the fact that it had been already thoroughly studied in our department; therefore a number of experimental data were available and on the contrary the knowledge of heat of vaporization as a function of concentration and temperature could be valuable complementary data on its thermodynamic behaviour.

EXPERIMENTAL

Substances used. Methanol and benzene were purified in the same way and with the same values of physico-chemical constants obtained as it had been described in one of foregoing papers[2]. By using these pure substances, samples of mixtures of compositions $x_1 = 0.2050, 0.3515, 0.5034, 0.6128, 0.8219$ were prepared by weighing.

Apparatus. The isothermal adiabatic calorimeter which was used for the measurements had been described previously[2]. The extension of its use to binary mixtures brings about several problems which do not occur when evaporating pure substances and which may be a source of errors. Above all it is necessary to ensure the quantitative transfer of the liquid sample into the calorimeter, then to determine by means of a suitably chosen calculation the correction for the existing vapour space in calorimeter. Finally it is necessary to carry out the evaporation so that it takes place quantitatively. For precise weighing the sample, a new type of charging device was suggested the principle of which is apparent from Fig. 1. It consists of a filling weighing bottle and a needle which is passed through the stopper in the head of calorimeter before filling and reaches nearly to the bottom of evaporating vessel. The needle and the weighing bottle are mutually connected with a bolted joint with a Teflon packing.

Before filling, the outlet hole of filling weighing bottle is closed by the Teflon seat 6 controlled together with the whole piston by means of the screw 15. The liquid is then forced into the inside space of weighing bottle by a syringe and at the same time it is seen to it that the mixture gets through the through-flow channels of the piston 4 also below it. The filling neck 2 is then closed with the closure of filling hole 1. The weighing bottle is then weighed whereupon it is attached to the filling needle in the head of calorimeter. When filling the evaporating vessel, the closure of filling hole 1 of weighing bottle is loosened at first to connect the inside space with the atmosphere. By turning the screw 15, the piston with the Teflon seat 6 is lifted and the liquid is sucked through the filling needle 8 into the evacuated space of the evaporating vessel. After closing the outlet hole with the Teflon seat controlled by the screw 15 and the filling neck 2 of weighing bottle with the closure 1 (a part of liquid must always remain in weighing bottle lest air should enter the evaporation vessel) the filling needle is drawn out, all the time connected with weighing bottle by the bolted joint 9, of the rubber stopper of calorimeter. The amount of sample is then determined precisely as a difference in weights.

Procedure. The calorimeter was heated up to the working temperature and the filling needle was pulled through the rubber stopper in the head of calorimeter and tightened with the cap nut of closure so that the vacuum tightness was warranted. The head of calorimeter was heated about 1—2°C above the working temperature and the evaporating vessel with the condensing vessel were evacuated. Afterwards the connection between the evaporation and condensation vessel was closed and the calorimeter was disconnected from the vacuum station. The calorimeter was filled in the above-mentioned way and the filling needle together with the filling weighing bottle was pulled out. Usually after 45—75 minutes a regular running of calorimeter was estab-

lished. The evaporation itself was started by turning on the valve of condensing vessel. The input power of heating element of evaporating vessel was evaluated during evaporation by measuring the voltage across the heating resistance and the voltage across a unit standard resistance, the heating time by a counter BM 445 and the total evaporating time by a stop-watch. The end of evaporation was signalled on the oscilloscope tube for, as a result of the regulating lag in the adiabatic jacket circuit its gentle overheating occurred. At this moment the valve of condensing vessel was turned off and at the same time the counter and the stop-watch were stopped. The condensing vessel was weighed again to determine the amount of condensate. This information was, however, only checking one and served as establishment whether the evaporation was quantitative.

Correction for the vapour space. As it was found by the volume measurement with air, the total volume of evaporating vessel is 28·8 ml. Above the liquid, which occupies usually 3—4 ml, there is then a considerable vapour space a correction for which had to be determined. By this correction it is ment the amount of heat Q'' which is necessary to supply to form the equilibrium
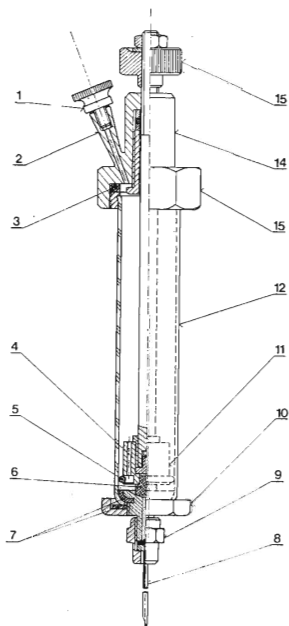

Fig. 1

Filling Weighing Bottle with Needle

1 Closure of filling hole, 2 filling neck, 3 packing of fluorinated rubber. 4 through-flow channel of piston, 5 Teflon packing ring of piston, 6 closing Teflon seat, 7 Teflon packings of screw caps, 8 filling needle, 9 bolted joint of filling needle with filling weighing bottle, 10 bolted joint of the jacket of weighing bottle with outlet seat, 11 revolving supporting face of Teflon closure, 12 glass jacket of weighing bottle, 13 screw cap of filling weighing bottle, 14 body of screw cap, 15 screw with rod for closure of weighing bottle.

vapour above the liquid after filling the calorimeter before measurement. By a multistage approximative calculation on using an isothermal phase diagram and on the assumption that the non-ideality of the vapour phase can be determined by the second virial coefficient, it was found that the amount of initial vapour n^g amounts to 2—3% of the total number of moles placed into the calorimeter. It was therefore possible to assume justifiably that the correction may be determined with a sufficient accuracy as the linear combination of heats of vaporization of pure components, i.e.

$$Q'' = (y_1 Q_1 + y_2 Q_2) \, n^g \, . \tag{1}$$

RESULTS

The isothermal heats of vaporization were measured at five concentrations for temperatures of 55 and 58°C which were chosen with respect to the subsequent treatment. One of compositions was the azeotropic point of the mixture at 55°C whose composition was calculated according to the method described in the literature[3]. The composition of the azeotropic mixture was chosen for the reason that this mixture may be evaporated in the same way like a pure substance, i.e. to evaporate only a part of liquid. On the basis of the comparison of values of heats of vaporization obtained on evaporating a part of liquid and on evaporating "to the end", it is possible to judge whether both methods give consistent results. The amount of heat Q' supplied during the measurement was determined from the relation

$$Q' = 0{\cdot}239UI\tau \, , \tag{2}$$

where $\tau = \tau_1 - \tau_2$, U and I is voltage and current, respectively, across the resistance heating of evaporating vessel, τ_1 time of heating during evaporation determined by the counter BM 445 and τ_2 time of the electric power supply into the heating of evaporating vessel during the experiment which is necessary for keeping constant temperature of the vessel without evaporating (this value is calculated from the total time of evaporating and the course of calorimeter determined before the experiment). The integral isothermal heat of vaporization is then given by

$$Q^{\mathrm{v}}_{\mathrm{T,x}} = (Q' + Q'')/n \, . \tag{3}$$

The results are presented in Table I. By the analysis of single errors in measuring heats of vaporization of pure substances, which was carried out previously[2], it was found that the error of measurement is about ±0·1%. For the reasons by which the difficulties were characterized when passing from the evaporation of pure substances to that of binary mixtures (the determination of sample weight, quantitative evaporation, correction for the vapour space) it is to be expected that the accurary of measurements will be somewhat worse. From these potential sources of inaccuracy, above all the estimation of error caused by the uncertainty in the correction for the vapour

space deserves an attention. Considering that the error in heats of vaporization of initial vapour determined as the linear combination of heats of vaporization of pure substances (Eq. (1)) is maximally 4% of the absolute value, the inaccuracy resulting from it does not exceed 0·12% of the total value of $Q_{T,x}^V$ with regard to a finding that n^g can amount to maximally 3% of the total amount of the original liquid mixture. The remaining two sources of errors can be reduced by a careful performance of experiment. Their effect is involved to a considerable extent in the scattering of measurements which amounted to maximally 0·25%. Under these conditions the maximum overall error in measurements of integral isothermal heat of vaporization can be estimated at 0·4% of its absolute value.

In previous work[1] which deals with the possibilities of conversion of some types of heats of vaporization of mixtures, the relation of the isothermal and the isobaric integral heats of vaporization was expressed by the equation

$$Q_{P,x}^V = \Delta h_{T,x}^V + \int_{T^b}^{T^d} (\partial h^g / \partial T)_{P^d, Y_1} \, dT + \int_{P^d}^{P^b} (\partial h^g / \partial P)_{T^d, Y_1} \, dP \,, \qquad (4)$$

where

$$\Delta h_{T,x}^V = Q_{T,x}^V + \Delta g_{T,x}^V \,. \qquad (5)$$

The second term on the right-hand side of Eq. (4) will be hereinafter denoted as the temperature correction (TC), the third one as the pressure correction (PC). The conversion of the experimentally determined isothermal heat to the isobaric heat at the pressure of 740 Torr was carriecd out according to this equation. The calculated values of isobaric heats were compared with the values measured by Tallmadge and

TABLE I

Measured Values of Integral Isothermal Heats of Vaporization in the Methanol(1)–Benzene(2) System

	$Q_{T,x}^V$, cal mol^{-1}	
x_1	55°C	58°C
0·2050	7 652	7 605
0·3515	7 802	7 761
0·5034	7 952	7 890
0·6128	8 057	7 995
0·8219	8·351	8 293

coworkers[4] in an isobaric evaporation calorimeter[5] at an atmospheric pressure (the pressure kept within $730-740$ Torr).

In case of the isothermal free enthalpy of vaporization $\Delta g_{T,x}^{V}$ we can write[1]

$$\Delta g_{T,x}^{V} = Y_1 \Delta g_1^{0} + Y_2 \Delta g_2^{0} + RT \ln P^{d} + BP^{d} - \\ - P^{b}(x_1 v_1^{01} + x_2 v_2^{01}) - g_{T,P^{b},x_i}^{1E}, \tag{6}$$

where

$$\Delta g_i^{0} = -RT \ln P_i^{0} - B_i P_i^{0} + v_i^{01} P_i^{0}. \tag{7}$$

For calculating the saturated vapour pressures of pure substances, the Antoine equation was used; its constants were taken over from the literature (methanol[6], benzene[7]). The values of v_i^{01} were calculated from the literary data on densities[8]. The virial coefficients of pure substances as well as the cross virial coefficient were estimated according to the method proposed by O'Connell and Prausnitz[9]. The values of P^{b} and P^{d} were read in the isothermal phase diagram. To construct the diagram the data measured by Scatchard and coworkers[10,11] were used for the temperature of 55°C, for the temperature of 58°C, the isothermal vapour–liquid equilibrium data were calculated on the basis of the six-constant expansion[12] whose constants were determined on the basis of simultaneous correlation of isobars measured at pressures 230·5, 340·0, 521·2 and 740·0 Torr and isotherms measured at 35, 45 and 55°C (ref.[13]). The calculated values of $\Delta g_{T,x}^{V}$ for single measurements are presented in Table II.

TABLE II
Calculated Values of Isothermal Free Enthalpy of Vaporization

x_1	t, °C	$\Delta g_{T,x}^{V}$, cal mol^{-1}
0·2050	55	$-130\cdot3$
	58	$-121\cdot5$
0·3515	55	$-131\cdot7$
	58	$-128\cdot5$
0·5034	55	$-45\cdot5$
	58	$-45\cdot6$
0·6128	55	$0\cdot0$
	58	$-3\cdot9$
0·8219	55	$-34\cdot8$
	58	$-32\cdot1$

The temperature correction can be expressed by the relation

$$(TC) = \int_{T^b}^{T^d} \sum_{i=1}^{2} Y_i C_{pi}^0 \, dT + P^d \left[(DER)_{T^d} - (DER)_{T^b} \right], \qquad (8)$$

where

$$(DER)_{T^d} = B_{T^d} - T^d (\partial B_{T^d} / \partial T)_y$$

and analogously for $(DER)_{T^b}$.

Constants for the polynomial expressing the temperature dependence of C_{pi}^0 were found in the literature[14]. To determine the values T^b, T^d, P^b, P^d the measured and calculated equilibrium data[10-13] were used.

The pressure correction can be expressed by the relation

$$(PC) = (DER)_{T^d} (P^b - P^d). \qquad (9)$$

For exact determination of the difference $(P^b - P^d)$ it is necessary to know the isotherm for the corresponding boiling temperature of the mixture investigated. Considering that the pressure correction is rather small, the values of $(P^b - P^d)$ were calculated by interpolating and in one case by extrapolating from the differences of pressure at boiling point of mixture and the pressure of beginning condensation of mixture read in the phase isothermal diagram for 55 and 58°C. The value of the expression $(DER)_{T^d}$ was calculated by means of the estimation method of O'Connell and Prausnitz[9].

For the conversion it is necessary to known the values $\Delta h_{T,x}^V$ at boiling temperature of corresponding mixture at the pressure of 740 Torr. In our case these temperatures lie, as it is evident from the isobar 740 Torr measured by Strubl and coworkers[15],

TABLE III
Calculated Values of Heats and Corrections (cal mol^{-1})

x_1	$\Delta h_{T,x}^V$	(TC)	(PC)	$Q_{P,x}^V$	$Q_{P,x}^{V'}$	$\% \, \Delta Q_{P,x}^V$
0·2050	7 473	295·2	−24·8	7 743	7 808	+0·84
0·3515	7 639	183·2	−23·0	7 799	7 846	+0·60
0·5034	7 863	56·4	−10·0	7 909	7 908	−0·01
0·6128	8 011	1·7	− 0·3	8 012	8 009	−0·04
0·8219	8 267	32·1	−11·9	8 287	8 319	+0·39

approximately in the interval 57·5 to 59°C. The $\Delta h_{T,x}^V$ for the corresponding temperatures are calculated by interpolating (and in one case by extrapolating) the values of isothermal enthalpies of vaporization at 55 and 58°C on the assumption of a linear dependence of $\Delta h_{T,x}^V$ on temperature which is justified owing to the small temperature interval.

In this way calculated values $\Delta h_{T,x}^V$, (TC), (PC), calculated integral isobaric heats of vaporization and values $Q_{T,x}^{V'}$ (data read from the diagram of dependence of isobaric heats of vaporization on composition plotted on the basis of experimental data[4]) are given in Table III (Tallmadge and coworkers[4] estimate the error of their measurements to be $\pm 0.3\%$).

The calculated values of isobaric heat are subjected to a greater error than the experimentally determined values of isothermal heat since each of three conversion terms $[\Delta g_{T,x}^V$, (TC) and (PC)] introduces a certain inaccuracy into the result. A decrease in accuracy occurs above all in that region where the conversion terms have a considerable absolute value (in our case for composition $x_1 = 0.3515$ and 0.2050). The highest absolute value (up to 4% of the value of isobaric heat) of all conversion terms has the temperature correction. However, it can be determined with the relatively highest accuracy. The term $\Delta g_{T,x}^V$ is subjected to a considerable error having its source above all in the very number of data needed for its evaluating. The inaccuracy in the second virial coefficient and the subjective error when reading in isothermal diagrams appear here; in case of the 58°C isotherm, the calculated equilibrium data are used whose accuracy is, of course, lower than that of experimental values. It is necessary to consider the error of this term to be $5-10\%$ absolute. The pressure correction (PC) is, as to its absolute value, the least of all conversion terms. Its accuracy is rather small for the value of the second virial coefficient is not known accurately. We estimate the error in this term at $10-15\%$ of its absolute value. Taking into account all these facts it can be assumed that the overall error in the calculated integral isobaric heat of vaporization does not exceed $\pm 0.7\%$ of the absolute value of calculated heat.

DISCUSSION

From the results reported in this work it follows that an apparatus originally designed to determine heats of vaporization of pure substances can be used in principle for the determination of integral isothermal heat of vaporization of mixtures as far as the calorimeter works on the principle of closed circuit. The obtainable accuracy is conditioned by two factors. Suitable constructional designs are above all those where the volume of the vapour space is minimum. Then the correction for the vapour space which forms a substantial source of inaccuracy may be neglected. The second factor is connected with the necessity of the accurate determination of weight of evaporated liquid. It was found that both for calculating the weight and also for estimat-

ing the corrections it is the most suitable to start with the amount of liquid put into the evaporating vessel. Consequently it is necessary to design a reliable charing device (*e.g.* filling weighing bottle) or to construct the evaporating vessel so as to be easily removable from the calorimeter. From the second part of the work it is evident that the conversion of integral isothermal heats of vaporization to integral isobaric heats of vaporization is satisfactory. The result is rather dependent on the accuracy of data which are required for calculating (vapour–liquid equilibrium data, molar heats, virial coefficients). However, on the other hand it is evident that for a number of systems these data are easily available. Considering that the calculation was checked with good results using the strongly non-ideal system (the difference of boiling points and dew points amounts to $12-15°C$, consistent data on vapour-liquid equilibrium can be obtained only by a difficult measurements) and, besides, precise values of all required data (*e.g.* the second virial coefficients) were not known, a satisfactory agreement on a wider scale it is to be assumed.

REFERENCES

1. Majer V., Svoboda V., Pick J., Holub R.: This Journal, in press.
2. Svoboda V., Hynek V., Veselý F., Pick J.: This Journal *37*, 3165 (1972).
3. Hála E., Pick J., Fried V., Vilím O.: *Vapour–Liquid Equilibrium*, 2nd Ed. Pergamon Press, London 1967.
4. Tallmadge J. A., Schroeder D. W., Edmister W. C., Canjar L. N.: Chem. Eng. Progr., Symposium Ser. *50*, 137 (1954).
5. Tallmadge J. A.: *Thesis*. Carnegie Inst. Technol., Pittsburgh 1953.
6. Holmes H. J., van Winkle M.: Ind. Eng. Chem. *62*, 21 (1970).
7. Dreisbach R. R.: *Physical Properties of Chemical Compounds*. Vol. 1, Am. Chem. Soc., Washington 1955.
8. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.
9. O'Connell J. P., Prausnitz J. M.: Ind. Eng. Chem., Proc. Des. Develop. *6*, 245 (1967).
10. Scatchard G., Wood S. E., Mochel J. M.: J. Am. Chem. Soc. *68*, 1960 (1946).
11. Scatchard G., Ticknor L. B.: J. Am. Chem. Soc. *74*, 3724 (1952).
12. Voňka P., Svoboda V., Strubl K., Holub R.: This Journal *36*, 18 (1971).
13. Strubl K., Voňka P., Svoboda V., Holub R.: This Journal *38*, 468 (1973).
14. Bareš J., Černý Č., Fried V., Pick J.: *Příklady a úlohy z fysikální chemie*, 3rd Ed. Published by SNTL, Prague 1971.
15. Strubl K., Svoboda V., Holub R.: This Journal *37*, 3523 (1972).

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