

HEATS OF VAPORIZATION OF ALKYL BROMIDES*

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Temperature dependences of heats of vaporization and saturated vapour pressures of alkyl bromides were measured. The measured data were used for estimating the values of the second virial coefficient.

As a part of our long-term study of heats of vaporization of pure liquids, the temperature dependence of heats of vaporization of six alkyl bromides was measured (ethyl, propyl, butyl, isopropyl, isobutyl, and allyl bromides). For the purpose of the experimental performance, of calculation of corrections for the change of the vapour space of the calorimetric vessel, and of estimation of values of the second virial coefficient, the saturated vapour pressures of these substances was also measured.

EXPERIMENTAL

Purity of Substances

Ethyl bromide, butyl bromide, isopropyl bromide and isobutyl bromide, pure, were shaken with concentrated H_2SO_4 till the last portion of the acid remained colourless. The substances were washed with water, neutralized by an aqueous solution of Na_2CO_3 or $NaHCO_3$, and dried by $CaCl_2$ or possibly by $MgSO_4$ or CaH_2 . Propyl bromide, pure, was dried directly by $CaCl_2$; allyl bromide, pure, was at first washed with an aqueous solution of $NaHCO_3$, and dried by solid $CaCl_2$. The substances were rectified from their solutions containing drying agents on a packed column and middle fractions were used for the measurements. All prepared substances were protected from effects of light. Measured values of the n.b.p., refractive index, and density of ethyl, propyl, and butyl bromides agree well with literature data¹ (ethyl bromide: n.b.p. 38·38°C, n_D^{20} 1·4241, d_4^{25} 1·45148 (ref.: 38·386—38·4, 1·4241, 1·4515); propyl bromide: n.b.p. 70·85°C, n_D^{20} 1·4313, d_4^{30} 1·3348 (ref.: 71·0—70·97, 1·43123, 1·33475); butyl bromide: n.b.p. 101·28°C, n_D^{20} 1·4399, d_4^{25} 1·26781 (ref.: 101·5—102·0, 1·4399, 1·2678)). Due to the lack of values of the physicochemical constants of isopropyl, isobutyl, and allyl bromides in the literature, their purity was verified chromatographically and the concentration of impurities was found to be lower than 0·1%. Densities of isopropyl and allyl bromides were measured to supplement literature data; for temperature of 10°, 25°, 40°, and 55°C they are 1·27932, 1·25824, 1·23528, and 1·21367 g·cm⁻³ for isopropyl bromide and 1·44383, 1·42190, 3·39431, and 1·38820 g·cm⁻³ for allyl bromide.

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We have also measured the refractive index of all the three bromides and the agreement with literature data¹ is good (isopropyl bromide n_D^{20} 1.4252 (1.4251), isobutyl bromide n_D^{20} 1.4343 (1.4341) and allyl bromide n_D^{20} 1.4689 (1.4692)).

Apparatus

The heats of vaporization were measured in an isothermal adiabatic calorimeter, which was being developed in our laboratory during several last years and which has been described in detail in our earlier works^{2,3}. For the present measurements the calorimeter head was adjusted so that two experiments might be performed immediately one after the other without filling the evaporating vessel with the measured substance and without stabilizing the calorimeter run. This adjustment consisted of replacing the vacuum path outlet 1, 2 above the saddle of closing valve 6 and of a parallel bifurcation of vapour path 3. This enables to connect simultaneously two condensation vessels to joints 4.

The working procedure during the filling, stabilization, and evaporation of the investigated liquid is the same as with the preceding type of the calorimeter. The second experiment begins by opening the valve of the second condensation vessel immediately after closing the valve of the first condensation vessel and after recording time and other quantities necessary for determining the heat input during the first experiment. The adjustment of the calorimeter head is illustrated schematically on Fig. 1.

The temperature dependence of the saturated vapour pressure was measured on a standard apparatus⁴ whose measuring part consisted of a Swietoslowski dynamic ebulliometer. The achieved accuracy of this measurement was $\pm 0.01^\circ\text{C}$ and ± 10 Pa.

RESULTS

Experimental values of the saturated vapour pressure of individual substances are given in Table I. In addition to experimental values of temperatures and corresponding saturated vapour pressures, this table also contains percentual deviations between experimental and calculated values for each experimental point and the standard

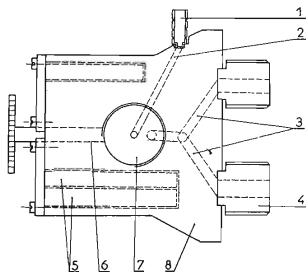


FIG. 1

A Schematic View of the Adjusted Calorimeter Head

1, 2 vacuum path, 3 vapour path, 4 connection of the condensation vessel, 5 heating and thermometers of the automatic control, 6 closing valve, 7 filling, 8 body of the calorimeter head.

deviation of the whole set for each investigated substance. Constants in the Antoine equation

$$\log P = A - \frac{B}{C + t}, \quad (1)$$

calculated from our experimental data are collected for individual bromides in Table II. Table III contains experimental values of the heat of vaporization of bromides at different temperatures together with their critical temperatures and constants in the Watson relation, which was used in the form

$$\Delta H_v = K(1 - T_r)^a; \quad (2)$$

corresponding deviations are also given in this table. The values of $\Delta H_{v,exp}$ are experimental values which, after the correction for the change of the vapour space

TABLE I
Results of the Measurements of Saturated Vapour Pressures of the Alkyl Bromides

Pressure kPa	Temperature, °C/deviation in pressure, %				
	propyl	butyl	isopropyl	isobutyl	allyl
11.876				32.69/ -0.27	
13.159				34.92/ 0.21	
15.372				38.62/ -0.13	
18.252				42.68/ 0.06	24.55/ 0.42
21.892	28.91/ 0.07			47.14/ 0.14	28.69/ 0.44
25.265	32.36/ -0.09			50.76/ 0.17	32.20/ -0.16
30.864	37.25/ 0.03	65.03/ 0.01	26.54/ 0.03	55.99/ 0.12	37.07/ -0.21
37.544	42.27/ -0.04	70.45/ -0.03	31.43/ -0.05	61.29/ 0.06	42.01/ -0.23
45.356	47.26/ 0.04	75.84/ 0.05	36.30/ 0.04	66.57/ 0.05	46.92/ -0.11
56.449	53.32/ -0.04	82.38/ -0.02	42.21/ -0.03	73.02/ -0.34	52.83/ 0.03
69.487	59.29/ 0.02	88.85/ -0.05	48.06/ 0.01	79.38/ -0.66	58.70/ 0.11
86.046	65.72/ 0.04	95.74/ 0.08	54.35/ 0.04	85.78/ 0.28	65.07/ -0.01
97.525			58.20/ -0.03		
97.538				89.82/ 0.31	
98.058		100.17/ -0.04			
99.578	70.31/ -0.04				
100.432					69.81/ 0.03
Standard deviation, %	0.04	0.04	0.03	0.21	0.18

of the evaporating vessel of the calorimeter, give final values of the heat of vaporization, ΔH_v . Critical temperatures T_c were either found in the literature⁵ (ethyl bromide) or estimated by the Lydersen method⁶.

Estimation of the Second Virial Coefficient

Considering the significance of the state behaviour for a detailed thermodynamic description of a system, we utilized the possibility to estimate deviations from the ideal state behaviour by using known values of the heat of vaporization and the temperature dependence of the saturated vapour pressure. Because the state behaviour of gases and vapours is still more often expressed through virial expansions, which at not too high pressures can be usually limited to their first two terms, we concentrated our attention on the estimation of the second virial coefficient.

Neglecting the volume of the liquid phase, the molar volume of the vapour phase may be expressed through the Clapeyron equation as

$$v^g = \frac{\Delta H_v}{T(dP/dT)} \quad (3)$$

On employing the density virial expansion and taking into account only the second virial coefficient, we get

$$B = v^g[(Pv^g/RT) - 1] \quad (4)$$

Calculated values of B of individual alkyl bromides and corresponding temperatures are given in the last column of Table III.

It is desirable to estimate the reliability of data obtained in this manner as well as the extent to which they can replace values obtained from direct experimental measurements of the state behaviour.

TABLE II
Constants in the Antoine Equation

Bromide	A	B	C
Propyl	6.03960	1 194.33	225.223
Butyl	6.13420	1 346.27	224.814
Isopropyl	5.92741	1 106.82	222.851
Isobutyl	6.50036	1 533.44	249.998
Allyl	6.10533	1 212.57	225.677

The estimated upper bound of the relative error of a calculation using Eq. (4) follows from the difference equation

TABLE III
The Temperature Dependence of the Heat of Vaporization ΔH_v (kJ mol⁻¹) and the Second Virial Coefficient B (cm³ mol⁻¹)

Bromide	<i>t</i> , °C	$\Delta H_{v,exp}$	ΔH_v	Dev. %	<i>B</i>
Ethyl	31.40	27.55	27.47	0.02	— 815
	38.70	27.03	26.94	-0.02	— 705
	49.50	26.21	26.10	0.09	— 558
	$K = 45.38$		$\alpha = 0.541$	$T_k = 503.9$ K	
Propyl	49.1	31.06	31.00	0.03	— 955
	58.6	30.52	30.45	-0.02	— 709
	66.0	30.10	30.01	-0.03	— 642
	79.2	29.29	29.16	0.03	— 573
$K = 45.22$		$\alpha = 0.421$	$T_k = 544.5$ K		
Butyl	49.1	35.58	35.57	-0.18	-1 841
	58.6	34.95	34.92	0.08	-1 730
	66.0	34.50	34.45	0.16	-1 695
	79.2	33.73	33.65	0.12	-1 173
	93.2	32.97	32.86	-0.17	— 912
$K = 49.91$		$\alpha = 0.417$	$T_k = 577.5$ K		
Isopropyl	31.4	29.83	29.79	0.07	-1 295
	44.8	29.15	29.08	-0.04	-1 180
	56.6	28.54	28.45	-0.19	-1 037
	64.5	28.00	27.87	0.17	
$K = 42.49$		$\alpha = 0.417$	$T_k = 532.0$ K		
Isobutyl	56.6	33.09	33.04	-0.02	-2 310
	67.5	32.56	32.50	0.02	-2 227
	79.8	31.96	31.87	0.03	-2 031
	92.3	31.35	31.23	-0.02	-1 809
$K = 44.60$		$\alpha = 0.345$	$T_k = 567.2$ K		
Allyl	44.8	31.66	31.61	-0.01	-1 063
	56.6	31.00	30.93	0.03	-1 042
	67.5	30.39	30.30	0.02	-1 011
$K = 44.60$		$\alpha = 0.378$	$T_k = 531.8$ K		

$$\delta_r v^g = \delta_r(\Delta H_v) + \delta_r(dP/dT) + \delta_r T \quad (5)$$

resp.

$$\delta_r B = K(\delta_r v^g + \delta_r T) + \delta_r v^g, \quad (6)$$

where $K = v^*/|B|$, $v^* = RT/P$. Relation (6) was analyzed by Voňka⁷, who found that the accuracy of the calculation is affected above all by the stability coefficient K whose magnitude depends on the region of the saturated vapour pressure curve in which the calculation is being performed. It follows from his analysis that at equilibrium pressures lower than 50 kPa, the value of K does not offer any hope for a realistic prediction of the second virial coefficient. For equilibrium pressures higher than 50 kPa, the results depend on the accuracy of equilibrium data. If, as a typical value of the second virial coefficient, $B = -1000 \text{ cm}^3 \text{ mol}^{-1}$ is considered, then, for a 10% error in the value of B , the error in the input data must not exceed approximately 0.5%. It also follows from our analysis of errors of separate steps during our measurements of the heat of vaporization and from the reproducibility of parallel measurements that we have achieved approximately 0.1% error in the heat of vaporization. Higher attention must be above all paid to the value of the temperature derivative of the saturated vapour pressure. It might be assumed in our case that both the experimental technique and the correlation of the data enable to determine the value of dP/dT with a 0.5% error. Therefore we believe that our values of the second virial coefficient are loaded with a $\pm 15\%$ error. Since direct experimental data on the state behaviour in a wider temperature range are rather scarce, our method thus indicates a possibility of the adequate estimate.

REFERENCES

1. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.
2. Svoboda V., Hynek V., Veselý F., Pick J.: *This Journal* 37, 3165 (1972).
3. Cihlář J., Hynek V., Svoboda V., Holub R.: *This Journal* 41, 1 (1975).
4. Strubl K., Svoboda V., Holub R., Pick J.: *This Journal* 35, 3004 (1970).
5. Kudchadker A. P., Alani G. H., Zwolinski B. J.: *Chem. Rev.* 68, 659 (1968).
6. Lydersen A. I.: *Estimation of Critical Properties of Organic Compounds*. Coll. Eng., Univ. Wisconsin, Eng. Expt. Sta. Rept. 3, Madison, Wis., April 1955.
7. Voňka P.: *Thesis*. Prague Institute of Chemical Technology, Prague 1976.

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