The partial molal volumes computed from these equations and given in Table III with a probable error of ±0.05 ml./mole decrease continuously with increasing dilution of each component. This decrease between the mole fractions 1.0 and 0.0 amounts to 4.7% for BrF_3 and 2.7% for BrF_5. However, the volume contraction which occurs on mixing is always less than one per cent.

TABLE III

PARTIAL MOLAL VOLUMES OF BrF_3 AND BrF_5 AT 25.0°

Mole fraction of BrF_5	$\overline{V}_{BrF_3}$, ml./mole	$\overline{V}_{BrF_5}$ ml./mole	Mole fraction of BrF_5	$\overline{V}_{BrF_3}$ ml./mole	$\overline{V}_{BrF_5}$ ml./mole
0.0	48.85	69.17	0.6	48.15	70.72
.1	48.83	69.50	.7	47.86	70.87
.2	48.78	69.80	.8	47.50	70.99
.3	48.69	70.07	.9	47.07	71.07
.4	48.56	70.31	1.0	46.54	71.09
.5	48.38	70.53			

The experimental molar refractions were computed from the Lorenz–Lorentz expression 6, using values of n and d obtained from equations 2 and 3

$$R_{\text{exp}} = \frac{n^2 - 1}{n^2 + 2}\left(\frac{N_1M_1 + N_2M_2}{d}\right) \qquad (6)$$

The R values are given in Table IV with a probable error of ±0.02 cc. In an ideal system, R would be a linear function of N_2; in the present system, R is linear within experimental error for N_2 between 0.0 and 0.4, then exhibits a negative deviation from linearity which is greatest (0.06 cc.) at N_2 = 0.75. This maximum deviation is no larger than that commonly found in a mixture of neutral molecules, such as carbon tetrachloride and benzene.[4] Although bromine trifluoride is known to contain (BrF_2^+) and (BrF_4^-) ions,[8] its equivalent conductance decreases upon dilution with bromine pentafluoride, and the effect of the ions becomes progressively less important. The molar refractions of the binary solutions are therefore chiefly characteristic of the undissociated molecules.

TABLE IV

MOLAR REFRACTIONS OF BrF_3–BrF_5 SOLUTIONS

Mole fraction of BrF_5	$d^{25}{}_4$, g./ml.	$n^{25}{}_D$	R_{Exp}, cc./mole	R_{Ideal}, cc./mole
0.0	2.8030	1.4536	13.22	13.22
.1	2.7648	1.4413	13.45	13.44
.2	2.7277	1.4293	13.67	13.66
.3	2.6918	1.4177	13.87	13.88
.4	2.6567	1.4066	14.08	14.10
.5	2.6225	1.3959	14.28	14.32
.6	2.5891	1.3859	14.48	14.53
.7	2.5562	1.3765	14.69	14.75
.8	2.5239	1.3677	14.91	14.97
.9	2.4920	1.3599	15.15	15.19
1.0	2.4604	1.3529	15.41	15.41

The atomic refractions of fluorine and bromine cannot be computed with any certainty from the above data. Bromine in particular must have different R values in the two compounds, since it has two more unshared electrons in the trifluoride than in the pentafluoride. Any R value ascribed to fluorine may be expected to vary also, but to a lesser extent. The interaction between bromine and fluorine probably has an effect upon the molar refractions of these compounds analogous to that which occurs in the alkali fluorides.[9,10] The molar refractions of the alkali fluorides are larger in the solid state than in solution, due to the loosening of the cation electronic system by the intense force field of the fluoride ion. Although in the bromine fluorides the bonding is largely covalent, similar loosening of the bromine electronic system by fluorine can be expected.

Acknowledgment.—The authors wish to thank Dr. Robert K. Steunenberg and Mr. Warren Z. Wade for their suggestions and technical assistance.

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[8] A. A. Banks, H. J. Emeleus and A. A. Woolf, *J. Chem. Soc.*, 2861 (1949).

[9] K. Fajans and G. Joos, *Z. Physik*, **23**, 26 (1924).

[10] N. Bauer and K. Fajans, THIS JOURNAL, **64**, 3023 (1942).

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MANITOBA]

Heat of Neutralization Studies at High Acid–Base Concentration. II. Sodium Hydroxide–Hydrobromic Acid[1,2]

BY WENDELL J. BIERMANN AND NEILL WEBER

RECEIVED MARCH 29, 1954

The heats of neutralization of sodium hydroxide and hydrobromic acid solutions have been measured at 25° for reactant concentrations from 3 to 16 molal, with an accuracy of 0.1%. The results have been used to calculate the relative enthalpies of hydrobromic acid solutions from 3 to 16 molal.

The chemical similarity between hydrochloric acid and hydrobromic acid makes it desirable that some studies be made of the thermodynamic properties of hydrobromic acid for comparison with the established properties of hydrochloric acid. The relative enthalpies of hydrobromic acid solutions can be determined by heat of neutralization measurements of the system hydrobromic acid–sodium hydroxide since all supplementary data are available and reasonably reliable.

Experimental Details

The apparatus was very similar to that described in a previous paper.[3] A second stirrer was placed in the calorimeter can to reduce the time required for equilibration, and the hollow lid of the calorimeter well was eliminated because of the mechanical difficulties in maintaining water-tightness. Instead, the well was closed with a brass plate which seated

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[1] Aided by a grant from the National Research Council, Canada.

[2] Paper I, ref. (3).

[3] P. Bender and W. J. Biermann, THIS JOURNAL, **74**, 322 (1952).

on a gasket and the thermostat water level was raised by addition of water from a reservoir. Access to the well was made by pumping sufficient thermostat water back to the reservoir to expose the well closure.

The GSAP camera was replaced by a Robot II camera for recording time–temperature data. The twenty-four frames obtained from one winding of the camera spring motor were adequate, and the 1" × 1" negative is more easily read than 16-mm. film strips.

Temperature measurements were made with a Leeds and Northrup type 8160 metallic sheathed platinum resistance thermometer calibrated by the makers and checked with a glass sheathed type made and calibrated by the National Research Council of Canada, who also calibrated the standard cells used in the electrical calibration of the calorimeter. Conventional calibrations were made of the Mueller bridge, potentiometer, weights, etc., used in the measurements.

Determination of the heat of neutralization of hydrobromic acid and sodium hydroxide had been done at several concentrations in the earlier calorimeter, and when these were compared with the series done in the present calorimeter all deviations noted were substantially smaller than the accuracy claimed in this work.

Solutions.—The sodium hydroxide solution was prepared and analyzed as noted previously.[3]

Below 11 molal hydrobromic acid solutions were prepared by distilling reagent grade 48% hydrobromic acid over tin to remove free bromine, collecting only the constant boiling middle fraction of the distillate and diluting as required. Higher concentrations were prepared by cooling the constant boiling solution and passing in hydrogen bromide. Hydrogen bromide was generated by suspending red phosphorus in 48% hydrobromic acid and dropping bromine into the cooled suspension until the liquid was almost saturated with hydrogen bromide. Gentle warming then liberated much of the hydrogen bromide with no visible bromine present. The hydrobromic acid was analyzed by the gravimetric silver bromide method.

Both silver bromide and silver chloride were collected in sintered glass crucibles and dried overnight at 170°. It was reported[4] that silver chloride dried in this manner retained up to 1% water. A chloride analysis carried out on fused reagent grade potassium chloride, with the silver chloride dried as above, reproduced the original sample weight to within 0.02%, provided that the silver chloride had been "aged" before filtering for at least six hours at room temperature. The retention of significant amounts of water was observed only in the case of freshly precipitated material.

Calculations and Results

Because the heat capacities of concentrated solutions of hydrobromic acid are uncertain it was desirable to avoid calculation of the temperature coefficient of the calorimeter reaction. The starting temperature of the reaction was therefore adjusted to within a few hundredths of a degree of 25°. Correction for concentration differences of the reactants, or thermal effects due to dilution of excess acid, would have involved a successive approximations method in the calculations, so that the reactant concentrations were adjusted carefully and the excess hydrobromic acid kept negligible in amount. These corrections, when evaluated after calculation of the relative enthalpies of hydrobromic acid solutions, proved to be insignificant.

When the heat of reaction was computed with the heat capacity of the product sodium bromide solution, which data were supplied by Bender and Kaiser,[5] the result was the heat of reaction at 25° for the process

$$\left[\mathrm{NaOH} + \frac{55.51}{m}\,\mathrm{H_2O}\right] + \left[\mathrm{HBr} + \frac{55.51}{m}\,\mathrm{H_2O}\right] = \left[\mathrm{NaBr} + \frac{55.51}{m'}\,\mathrm{H_2O}\right]$$

where $m' = 55.51\, m/(111.02 + m)$. The experimental data are presented in Table I and are estimated to be accurate to better than 0.1%.

TABLE I

EXPERIMENTAL VALUES FOR THE HEAT OF NEUTRALIZATION OF SODIUM HYDROXIDE AND HYDROBROMIC ACID SOLUTIONS AT 25°

m	$-\Delta H_N$, def. cal. per mole	m	$-\Delta H_N$, def. cal. per mole
2.930	14,084	9.775	16,802
3.961	14,368	11.079	17,488
4.997	14,703	13.015	18,570
6.005	15,085	14.427	19,442
6.935	15,476	16.029	20,385
8.470	16,150		

Computation of the relative enthalpies of hydrobromic acid solutions is made through the following expression for the heat of neutralization

$$\Delta H_N = \Delta H_N^0 + \phi_L(\mathrm{NaBr},m') - \phi_L(\mathrm{NaOH},m) - \phi_L(\mathrm{HBr},m)$$

The apparent relative enthalpy of sodium bromide solutions is taken from Hammerschmid and Robinson's[6] recalculation of the data of Wüst and Lange.[7] The apparent relative enthalpies of the sodium hydroxide solutions are taken from Bertetti and McCabe's[8] heat of dilution data, corrected to 25° by means of their specific heat values, and $\bar{C}^0_{p_2}$ and $\bar{C}^0_p$, values given by Gucker and Schminke,[9] and Osborne and Ginnings,[10] respectively. An additional 27 calories was added to each of these values of the relative enthalpies of sodium hydroxide solutions to correct the extrapolational error introduced by inclusion of Richards and Gucker's[11] low concentra-

TABLE II

THE HEAT OF NEUTRALIZATION OF HYDROBROMIC ACID AND SODIUM HYDROXIDE AND THE APPARENT RELATIVE ENTHALPY AND THE RELATIVE PARTIAL MOLAL ENTHALPY OF HYDROBROMIC ACID SOLUTIONS IN DEFINED CALORIES AT 25°

m	m'	$-\Delta H_N$	ϕ_L(NaOH, m)	ϕ_L(NaBr, m')	ϕ_L(HBr, m)	$\bar{L}_2$ (HBr, m)
3	1.460	14,096	−20	−120	675	1272
4	1.930	14,386	+3	200	862	1660
5	2.392	14,705	64	272	1048	2054
6	2.846	15,085	163	336	1265	2494
7	3 292	15,489	297	395	1476	2942
8	3.731	15,925	470	449	1685	3411
9	4.162	16,411	675	493	1922	3944
10	4.586	16,920	910	536	2154	4491
11	5.004	17,443	1167	572	2383	5069
12	5.414	17,984	1438	606	2619	5692
13	5.818	18,563	1722	637	2883	6386
14	6.216	19,200	2028	663	3187	7167
15	6.607	19,795	2334	682	3458	7964
16	6.992	20,361	2590[a]	695	3755	8843

[a] Extrapolated.

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(4) J. E. Willard, *Record. Chem. Prog.*, Fall, p. 163 (1951).

(5) P. Bender and A. Kaiser, private communication.

(6) H. Hammerschmid and A. L. Robinson, THIS JOURNAL, **54**, 3120 (1932).

(7) K. Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925).

(8) J. W. Bertetti and W. L. McCabe, *Ind. Eng. Chem.*, **28**, 247 (1936).

(9) F. T. Gucker, Jr., and K. M. Schminke, THIS JOURNAL, **55**, 1033 (1933).

(10) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

(11) T. W. Richards and F. T. Gucker, Jr., THIS JOURNAL, **51**, 712 (1929).

tion heat of dilution work by Bertetti and McCabe. The heat of neutralization at standard conditions was taken as −13,321 defined calories per mole.[3]

To obtain relative enthalpies at round concentrations the heats of neutralization at these concentrations were interpolated from the experimental data. These heats of neutralization are given in Table II. Table II also includes the values of ϕ_L and $\bar{L}_2$ for hydrobromic acid, together with the sodium bromide and sodium hydroxide enthalpy data used in their computation. $\bar{L}_2$ was computed in the conventional fashion by the expression of ϕ_L(HBr) as a function of molality. Combination of the several sets of data limits the accuracy of the apparent relative enthalpies of hydrobromic acid to about ±30 calories/mole.

Discussion

Comparison of the apparent relative enthalpies of hydrobromic acid solutions with equivalent values for hydrochloric acid solutions computed from the data of Akerlof and Teare[12] shows the close resemblance anticipated. If the relative enthalpies of the two solutions are plotted against molality the hydrobromic acid plot shows somewhat greater curvature, and the relative enthalpy curve of hydrobromic acid is displaced from a few calories at lower concentrations to a maximum of about 250 calories lower at higher concentrations. Interpretation of this comparison will be deferred until a later paper.

[12] G. C. Akerlof and J. Teare, THIS JOURNAL, **59**, 1855 (1937).

WINNIPEG, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

On Physical Adsorption. VI. Two-dimensional Critical Phenomena of Xenon, Methane and Ethane Adsorbed Separately on Sodium Chloride[1]

BY SYDNEY ROSS AND HADDEN CLARK

RECEIVED APRIL 27, 1954

Xenon, methane and ethane when adsorbed separately on {100} surface planes of sodium chloride show two-dimensional condensation and typical critical temperature phenomena as the temperature is raised. The two-dimensional critical temperatures are observed at *ca.* 104°K. for xenon, *ca.* 90°K. for methane, and *ca.* 132°K. for ethane. The isosteric heats of adsorption are calculated from the isotherms, and their variation with degree of surface coverage is interpreted.

The previous paper of this series[2] reported the two-dimensional condensation of ethane when adsorbed as a monolayer on a variety of homotattic solid surfaces, and set forth the conditions required for two-dimensional condensation of an adsorbate. These conditions were used to discover suitable adsorbates that would demonstrate this phenomenon on the uniform crystallographic surface, the {100} planes, of sodium chloride. The phenomenon was investigated, however, only at a single temperature, and hence its interpretation as a genuine monolayer condensation did not carry the authority that could be conferred on it, if it were shown (by observing the behavior of the system at different temperatures) to have a heat of transition and a critical temperature for the transition. The present paper reports the results obtained with xenon, methane and ethane adsorbed separately on the same sample of sodium chloride at different temperatures. These systems were selected, according to the principles stated by Ross and Winkler,[2] as likely to display the phenomenon of two-dimensional condensation on a solid surface. The predicted effects were actually observed, and it was found that, for each system, there exists a critical temperature, analogous to the normal critical temperature of liquefaction of a gas, above which the condensation does not occur. The purpose of this paper is to find the region of the two-dimensional critical temperature, as an important step in elucidating the mechanism of adsorption of non-polar adsorbates on an ionic adsorbent.

Apparatus and Materials

The adsorption system is a volumetric type, generally similar to that of Wooten and Brown,[3] using mercury stock valves to avoid the presence of stopcock grease in the system. The stock-valves and the buret are surrounded by an ice–water-bath while the apparatus is in use. The pressures are read with a cathetometer and a mercury manometer of 12-mm. internal diameter.

The cryostat consists of an aluminum block, hollowed out to hold the adsorption bulb and the bulb of the vapor pressure thermometer. The block is wound with electrical heating coils of constantan wire, which are used to balance the cooling of the liquid nitrogen bath and so provide temperature control. This assembly is suspended inside a brass can, which is evacuated during the determination of an adsorption isotherm. A large Dewar flask containing liquid nitrogen encloses the brass can. Figure 1 is a diagram of the arrangement of the cryostat.

The glass tubing that is not enclosed by the aluminum block would be cooler than the adsorption bulb were it not provided with a heater, the lead heater of Fig. 1. Two copper–constantan thermocouples are placed in the cryostat; one measures the stability of the temperature of the aluminum block, and the other detects any differences in temperature between the leads and the block, which difference need not be made to disappear since it is enough to make sure that the lead heater is warmer than the block, by adjusting the current through the heater.

The authors are indebted to Dr. J. A. Morrison, National Research Council, Ottawa, for the original design of the cryostat.[4] In its present slightly modified form, temperature fluctuations are restrained to within 0.02°.

The temperature of adsorption is obtained from the vapor-pressure thermometer, which has its bulb inside the cryo-

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[1] This paper is based on a portion of a Thesis submitted by Hadden Clark to the faculty of Rensselaer Polytechnic Institute, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1954.

[2] S. Ross and W. Winkler, THIS JOURNAL, **76**, 2637 (1954).

[3] L. A. Wooten and J. R. C. Brown, *ibid.*, **65**, 113 (1943).

[4] Dr. J. A. Morrison intends to publish a more extensive account of this cryostat, which makes a fuller description in this place unnecessary.