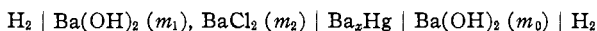


The fifth and sixth columns of Table IV contain the values of  $m_w = m_H = m_{OH}$  computed by equation (8). The next two columns contain the values of  $\gamma_H \gamma_{OH}$  computed by multiplying  $K_\gamma$  by  $a_{H_2O}$ , and the last two columns  $\gamma$  or  $\sqrt{\gamma_H \gamma_{OH}}$ . The values of  $\gamma$  obtained by the two methods rarely differ by more than 1% or  $\pm 0.5\%$  from their mean.

### Summary

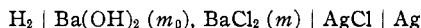
1. Measurements of the electromotive forces of the cells



have been made, and the activity coefficient of barium hydroxide in aqueous barium chloride solutions has been computed.

2. From these and other suitable results previously determined, the ionic activity coefficient of water in barium chloride solutions has been computed.

3. The cells



have been measured and the ionic activity coefficient of water has been computed from the results, and compared with the values obtained from the amalgam cells.

4. The dissociation of water in barium chloride solutions increases, passes through a maximum and then decreases with increasing ionic strength, a behavior similar to that observed in solutions of the alkaline halides. The maximum dissociation occurs at  $1.5\mu$ .

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, CHEMICAL LABORATORY OF THE BAVARIAN ACADEMY OF SCIENCES, MUNICH, GERMANY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA]

## INTEGRAL HEATS OF DILUTION AND RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM BROMIDE AND POTASSIUM BROMIDE SOLUTIONS AT TWENTY-FIVE DEGREES\*

BY H. HAMMERSCHMID AND A. L. ROBINSON

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### Introduction

The measurement of heats of dilution of strong electrolytes at concentrations low enough to permit an unambiguous extrapolation of the results to infinite dilution makes possible a combination of such measurements with data obtained at higher concentrations to calculate the relative partial molal heat contents of the components of the solutions. These are the partial molal heat contents referred to the molal heat contents of

\* Communication Number 37 on Thermochemical Investigations by E. Lange and co-workers.

the reference state, the infinitely dilute solution.<sup>1</sup> A knowledge of the partial molal heat contents and the partial molal specific heats of the components of solutions is necessary for the calculation of thermochemical and thermodynamic properties of solutions, such as heats of reaction and their temperature coefficients, temperature coefficients of activity coefficients and partial molal free energies, temperature coefficients of solubility and ionic entropies.

Measurements are presented here of the heats of dilution of aqueous sodium bromide and potassium bromide solutions from 0.1 *M* to infinite dilution at 25° and these measurements are combined with data of Wüst and Lange<sup>2</sup> to calculate relative partial molal heat contents from infinite dilution to saturation.

### Experimental

A differential adiabatic calorimeter, developed by Lange and co-workers, already described<sup>3</sup> was employed. All details of manipulation and calculation were the same as in previous investigations.

The potassium bromide was a guaranteed preparation of de Haën, several times recrystallized. For the sodium bromide measurements two different 0.1 *M* stock solutions were used; one was a solution prepared by Dr. W. Geffken for density determinations and kindly furnished by him, which contained sodium bromide prepared from pure sodium carbonate,<sup>4</sup> and solution two was made from a Kahlbaum preparation that had been recrystallized twice. Both solutions were standardized by titration with two different silver nitrate solutions using phenosafranine as an indicator.<sup>5</sup>

The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The third column of the table gives the heat effects of individual measurements (negative values of  $\Delta H$  indicate heat evolved) in this concentration interval calculated per mole of salt, and the fourth column gives the average of the individual measurements and the probable error, exclusive of any systematic errors. The reproducibility of the measurements is better than two per cent.

### Discussion

The data of Table I are plotted against the square root of the molality (weight and volume concentrations differ inappreciably in this concen-

<sup>1</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 88.

<sup>2</sup> Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

<sup>3</sup> Lange and Monheim, *ibid.*, **149A**, 51 (1930); Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

<sup>4</sup> Baxter, *THIS JOURNAL*, **38**, 70 (1916).

<sup>5</sup> Fajans and Wolff, *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

TABLE I  
MEASURED HEATS OF DILUTION AT 25°

Initial concn., mole/liter	End concn., mole/liter	$\Delta H$ , calories/mole				Average $\Delta H$ , calories/mole
		Prep. 1		Prep. 2		
Sodium Bromide						
0.1	0.0026	-51.3	49.7	51.9	52.3	-51.3 $\pm$ 0.3
.1	.0052	-45.5	45.9	45.3	46.3	-45.8 $\pm$ .15
.05	.0013	-49.9	49.4	49.3	50.0	-49.7 $\pm$ .1
.05	.0026	-44.1	44.1	44.0	43.9	-44.0 $\pm$ .0
.025	.00065	-43.0	43.1	43.6		-43.2 $\pm$ .1
.025	.0013	-38.5	38.4	39.2		-38.7 $\pm$ .2
.0125	.00065	-31.5	32.3	30.2	30.6	-31.4 $\pm$ .3
.0125	.000328	-34.4	35.0	33.6	34.7	-34.4 $\pm$ .2
.00627	.000164	-22.4	24.3	24.4		-23.7 $\pm$ .4
.00627	.000325	-21.7	22.7	22.6		-22.3 $\pm$ .2
Potassium Bromide						
0.1	0.0026	-44.6	43.0	43.5	43.5	-43.7 $\pm$ 0.2
.1	.0052	-37.0	36.0	37.0		-36.7 $\pm$ .2
.05	.0013	-40.5	41.0	41.1		-40.9 $\pm$ .1
.05	.0026	-35.7	35.9	37.2	36.2	-36.3 $\pm$ .2
.025	.00065	-38.1	41.0	37.9	38.7	-38.9 $\pm$ .3
.025	.0013	-33.8	33.2	33.8		-33.6 $\pm$ .2
.0125	.000329	-30.9	31.1	31.4	30.6	-31.0 $\pm$ .1
.0125	.00065	-28.9	29.0			-29.0 $\pm$ .05

tration range) in Fig. 1. Below 0.01 *M* the integral heats of dilution are proportional to  $m^{1/2}$  within the limit of experimental error and can be

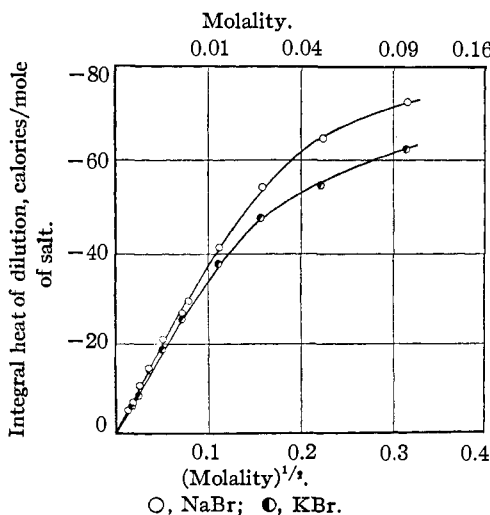
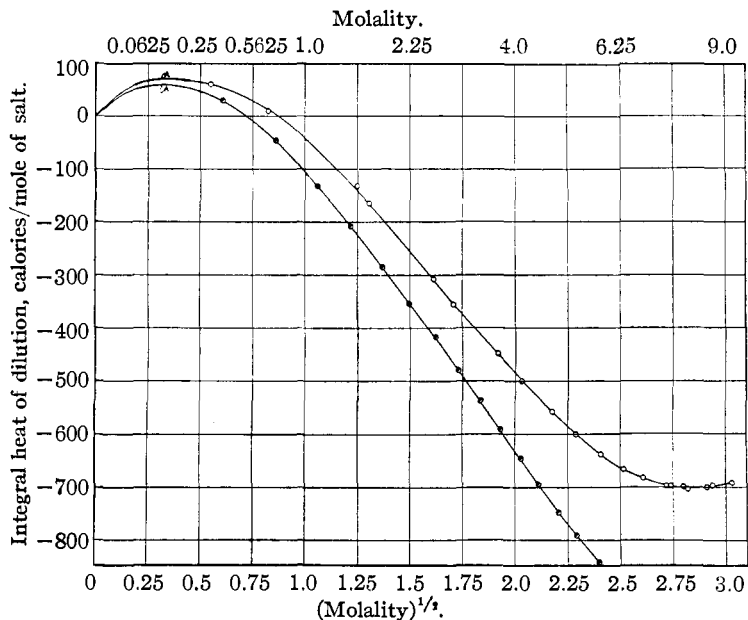


Fig. 1.—Integral heats of dilution at 25°.

0.01 *M* the integral heat of dilution (heat absorbed when a solution containing one mole of the salt is diluted with an infinite amount of water)

extrapolated to infinite dilution with an uncertainty of not more than one calorie. In Fig. 2 the results below 0.1 *M* have been combined with the data of Wüst and Lange which extend to saturation for both salts. The error involved in coördinating the two sets of measurements is not more than five calories and is probably less. In Table II are given the integral heats of dilution for the two salts at various concentrations from infinite dilution up to saturation; these values have been interpolated from Figs. 1 and 2. Up to

of sodium bromide is represented by  $\Delta H_{\text{int.}} = -359 m^{1/2}$ ; for potassium bromide  $\Delta H_{\text{int.}} = -350 m^{1/2}$ . The individual nature of these curves for salts of the same valence type has been discussed before.<sup>6</sup>



○, NaBr; ●, KBr. Curves to A, these measurements.

Fig. 2.—Integral heats of dilution at 25°.

TABLE II  
INTEGRAL HEATS OF DILUTION AT 25°

Concentration moles/1000 g. H <sub>2</sub> O	$\Delta H_{\text{int.}}$ calories/mole salt		Concentration moles/1000 g. H <sub>2</sub> O	$\Delta H_{\text{int.}}$ calories/mole salt	
	NaBr	KBr		NaBr	KBr
0.0000	0.0	0.0	1.00	39	106
.0001	- 3.5	- 3.5	1.44	116	201
.0004	- 7.0	- 7.0	2.25	256	353
.0016	-14.5	-14.0	3.24	396	521
.0025	-18	-17.6	4.00	484	633
.0064	-29	-28	4.84	566	743
.01	-36	-34	5.68 (satd.)		841
.04	-60	-52.8	5.76	636	
.09	-70.5	-61.3	6.25	664	
.16	-72	-61.5	7.29	695	
.25	-66	-52	7.84	701	
.64	-19.5	23.5	8.41	700	
			9.16 (satd.)	694	

<sup>6</sup> Lange, *Z. Elektrochem.*, **36**, 772 (1930); Lange and Robinson, *Chem. Rev.*, **9** 89 (1931).

The integral heat of dilution<sup>7</sup> is related to the relative partial molal heat contents of solute and solvent by  $-\Delta H_{\text{int.}} = \bar{L}_2 + n_1\bar{L}_1$ , where  $n_1$  moles of water are associated with one mole of salt at a given concentration. Values for  $\bar{L}_1$  and  $\bar{L}_2$  are most readily obtained from heat of dilution data by the method of Rossini,<sup>7</sup> using the slopes of the curves of Fig. 2. Figure 3 shows a plot of  $\bar{L}_1$  and  $\bar{L}_2$  for sodium bromide and potassium bromide

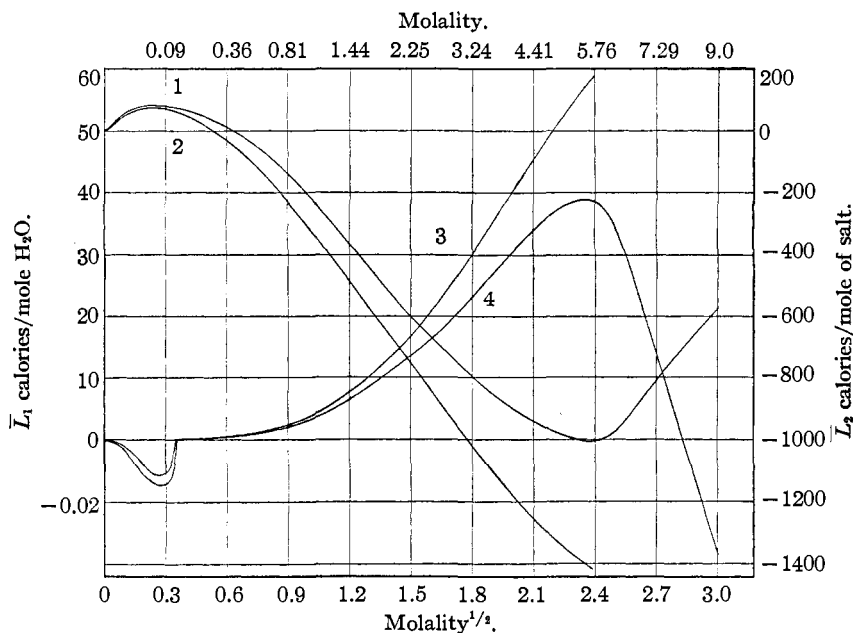


Fig. 3.—Relative partial molal heat contents at 25°.  $\bar{L}_1 = \bar{H}_1 - \bar{H}_1^\circ$ .  $\bar{L}_2 = \bar{H}_2 - \bar{H}_2^\circ$ . Curve 1,  $\bar{L}_2$  NaBr; Curve 2,  $\bar{L}_2$ , KBr; Curve 3,  $\bar{L}_1$  KBr; Curve 4,  $\bar{L}_1$  NaBr.

solutions so obtained and the values of Table III are interpolated from these curves.  $L_s$  is the relative molal heat content of the solid salt (referred to the standard state of infinite dilution) and is calculated from the data of Wüst and Lange on integral heats of solution;  $L_s$  for sodium bromide is for the anhydrous salt, although the saturated solution at 25° is of course in equilibrium with  $\text{NaBr} \cdot 2\text{H}_2\text{O}$ .

Rossini<sup>8</sup> has shown that at 25° up to concentrations of 2.5 *M* the partial molal specific heats of sodium bromide solutions are represented by  $\bar{c}_{p_2} = -24.3 + 20.4 m^{1/2}$  for the sodium bromide and  $\bar{c}_{p_1} = -0.123 m^{3/2}$  for the water and for potassium bromide solutions  $\bar{c}_{p_2} = -29.5 + 16.2 m^{1/2}$  and  $\bar{c}_{p_1} = -0.097 m^{3/2}$ . These values can probably be used up to saturation

<sup>7</sup> This is the negative of the function  $\phi_h - \phi_h^\circ$  used by Rossini [*Bur. Stand. J. Res.*, 6, 791 (1931)] and called by him the relative apparent molal heat content of the solute.

<sup>8</sup> Rossini, *Bur. Stand. J. Res.*, 7, 47 (1931).

TABLE III  
RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM BROMIDE AND  
POTASSIUM BROMIDE SOLUTIONS AT 25°

Concentration, moles/1000 g. H <sub>2</sub> O	$\bar{L}_1^a$ calories/mole H <sub>2</sub> O		$\bar{L}_2^a$ calories/mole salt	
	NaBr	KBr	NaBr	KBr
0.0	0.0	0.0	0.0	0.0
.001	-.0005	-.0004	11	9
.005	-.0016	-.001	38	30
.01	-.0031	-.0019	55	46
.05	-.0132	-.0104	79	71
.1	-.0138	-.0098	76	68
.2	.05	-.08	56	37
.5	.7	1.0	- 32	- 91
1.0	3.0	3.6	- 208	- 311
1.5	6.8	8.2	- 384	- 509
2.0	11.4	13.6	- 540	- 680
2.5	15.7	19.8	- 656	- 825
3.0	20.4	26.5	- 753	- 958
3.5	25.8	33.3	- 834	-1078
4.0	30.6	40.3	- 899	-1183
4.5	34.5	46.4	- 947	-1271
5.0	37.7	52.0	- 983	-1347
5.5	38.9	56.6	-1003	-1394
5.68 (satd.)		58.9		-1414
6.0	37.2		- 994	$L_s = -4727$
6.5	30.0		- 938	
7.0	20.3		- 858	
7.5	10.0		- 775	
8.0	0.8		- 706	
8.5	- 5.7		- 662	
9.16	-18.5		- 576	
			$L_s = 44$	

<sup>a</sup> Negative values indicate heat evolved.

concentrations<sup>9</sup> and are useful in conjunction with the values of the relative partial molal heat contents reported here.

The experimental portion of this work was kindly supported by the Notgemeinschaft der Deutschen Wissenschaft, the Kaiser Wilhelm Institute for Physics and the Munich Universitätsgesellschaft.

### Summary

The heats of dilution of aqueous sodium bromide and potassium bromide solutions have been measured at 25° from 0.1 *M* to 0.0002 *M* and extrapolated to infinite dilution. These measurements have been combined with the data of Wüst and Lange, which extend to saturation concentrations, to obtain values for the integral heats of dilution and relative partial molal heat contents of solvent and solute for the entire concentration range.

PITTSBURGH, PENNSYLVANIA

<sup>9</sup> For example see Harned and Nims, *THIS JOURNAL*, **54**, 423 (1932).