

### Summary

1. As a first approximation the electron affinity in the gaseous state of the four free radicals studied is 60 kilogram calories.
2. The substitution of larger groups for phenyl slightly increases the electron affinity. The effect of substituting two groups is approximately the sum of the effects of the groups individually.
3. The fact that the larger free radicals have the greater electron affinity and the smaller tendency to form ethanes suggests that due to steric hindrance the carbon atoms cannot approach each other as closely and, therefore, the energy liberated is smaller.
4. The effect of the solvent on the equilibrium is considered and found to be essentially the same for the four free radicals studied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## THERMODYNAMIC PROPERTIES OF FUSED SOLUTIONS OF SODIUM BROMIDE IN SILVER BROMIDE

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RECEIVED MARCH 2, 1931

PUBLISHED MAY 6, 1931

The following investigation represents a contribution to the general program begun by Hildebrand and Ruhle<sup>1</sup> of gathering data upon the free energy of dilution of fused salt solutions. The system selected, solutions of sodium bromide in silver bromide, is a continuation of the more recent study by Salstrom and Hildebrand<sup>2</sup> of investigating the influence of the size of the cation of the diluting salt upon the activity of the solvent. The freezing point-composition diagram obtained for this system by Sandonini and Scarpa<sup>3</sup> shows no evidence of complex salt formations which might add complexity to any interpretation of the results.

### Experimental Part

The sodium bromide was from commercial sources of high purity. The remaining materials, apparatus and procedure involved in this investigation were essentially the same as those described for the previous study of lithium bromide in silver bromide.<sup>2,4</sup> In short, the method consists of removing hydrolysis and oxidation products from the cell by bubbling a stream of dry hydrogen bromide gas through the fused salts for at least two hours. Bromine gas generated by electrolysis of fused lead bromide

<sup>1</sup> Hildebrand and Ruhle, *THIS JOURNAL*, **49**, 722 (1927).

<sup>2</sup> Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).

<sup>3</sup> Sandonini and Scarpa, *Atti. accad. Lincei*, II, **22**, 517 (1913)

<sup>4</sup> Salstrom and Hildebrand, *THIS JOURNAL*, **52**, 4641 (1930).

was then bubbled through the melt over a graphite rod dipping into the solution. Equilibrium was attained in about two hours. Readings were then taken at certain temperature intervals over the whole permitted temperature range several times. Ascending and descending series were in complete agreement.

TABLE I

Mole fraction of AgBr	Temp., °C.	Ag/AgBr, NaBr/Br <sub>2</sub>		Temp., °C.	E. m. f. obsd., volt
		E. m. f. obsd., volt	Mole fraction of AgBr		
1.000 A	442.3	0.8031	0.6045 C	569.3	0.7955
1.000 A	453.6	.8000	.6045 C	577.0	.7936
1.000 A	456.0	.7989	.6045 C	588.9	.7910
1.000 A	467.0	.7956	.6045 C	597.9	.7889
1.000 A	490.9	.7887	.6045 C	598.4	.7888
1.000 A	499.9	.7866	.6045 C	598.5	.7887
1.000 A	521.4	.7803	.6045 C	604.3	.7874
1.000 A	524.4	.7795	.6045 C	604.4	.7873
1.000 A	531.7	.7769	.6045 C	616.3	.7844
1.000 A	538.3	.7751	.6045 C	618.0	.7840
1.000 A	556.2	.7702	.5130 D	605.8	.7966
1.000 A	565.0	.7680	.5130 D	608.3	.7960
0.7486 B	481.6	.8056	.5130 D	609.7	.7957
.7486 B	507.3	.7985	.5130 D	611.8	.7953
.7486 B	526.4	.7936	.5130 D	613.0	.7950
.7486 B	526.7	.7935	.5130 D	613.3	.7949
.7486 B	527.2	.7934	.5130 D	614.3	.7948
.7486 B	551.7	.7874	.5130 D	615.5	.7945
.7486 B	553.1	.7869	.5130 D	616.5	.7944
.7486 B	605.8	.7735	.5130 D	617.7	.7942
.7486 B	607.0	.7732	.5130 D	618.7	.7940
.7486 B	607.9	.7730	.5130 D	618.8	.7939
.7486 B	615.8	.7711	.5130 D	621.3	.7934
			.5130 D	621.7	.7933

The results of the e. m. f. measurements of the cell, Ag(s)/AgBr(l), NaBr(l)/Br<sub>2</sub>(g), are given in Table I and plotted in Fig. 1. The values for pure silver bromide are those obtained in the silver bromide-lithium bromide investigation.<sup>2</sup> Because of the high melting point of solutions rich in sodium bromide, measurements on cells beyond a half mole fraction of this salt could not be obtained with the Pyrex containers used. The study of cells containing increasing fractions of sodium bromide was also increasingly limited as to temperature range. The extreme deviations of the observed values from the straight lines drawn through them in Fig. 1 is 0.4 millivolt, and the average deviation is less than 0.15 millivolt.

Since the theoretical treatment of the results will ultimately require a knowledge of the interionic distances, it was considered desirable to measure the density of a solution containing a half mole fraction of each salt. The method consisted in weighing a tungsten-weighted quartz bulb in

air, in water and then at various temperatures in the fused salt solution, correcting<sup>5</sup> each time for the expansion of quartz. The bulb was sharply

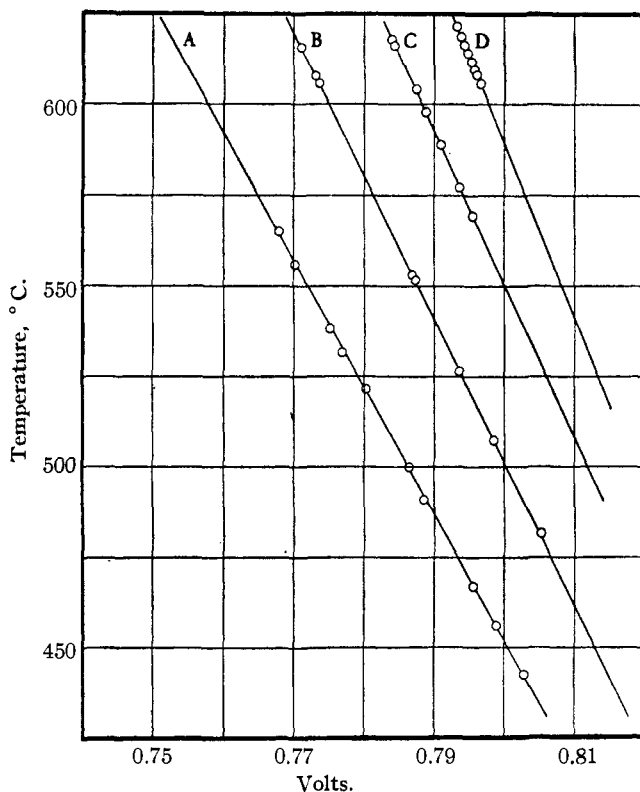


Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag/AgBr, NaBr/Br<sub>2</sub>. Mole fraction of silver bromide in A is 1.000, B is 0.7486, C is 0.6045 and D is 0.5130.

tapped before each reading to remove any adhering bubbles of gas. The densities observed are given in Table II.

TABLE II  
DENSITIES OF 0.5 MOLE FRACTION OF NaBr IN AgBr

Temp., °C.	619.3	616.0	615.0	613.2	612.0	609.5	607.4
Density	3.754	3.757	3.758	3.759	3.760	3.762	3.764

The observed values yield the equation for the density of 0.5 mole fraction of sodium bromide in silver bromide,  $d^t = 4.311 - 0.0009 t$ . Using the density values for silver bromide obtained by Lorenz and Höchberg<sup>6</sup>

<sup>5</sup> Data are not available for calculating the effect of surface tension of the fused solution upon the suspending wire but, because of the fineness of the platinum wire employed, it is believed that such corrections would prove negligible.

<sup>6</sup> Lorenz and Höchberg, *Z. anorg. allgem. Chem.*, **94**, 288 (1916).

and for sodium bromide obtained by Jaeger,<sup>7</sup> we have calculated the molal volumes of silver bromide and sodium bromide at 600° as 34.74 cc. and 42.01 cc., respectively. A 50 mole per cent. solution at this temperature has a molal volume of 38.53 cc., which is 0.15 cc. more than additive.

### Discussion of Results

Since our main interest lies in the relation of free energy to composition at constant temperature, we obtained from Fig. 1 plotted on a large scale the values of the e. m. f.,  $E$ , determined for each solution at the temperatures 550 and 600°, together with their values of  $dE/dt$ . These temperature coefficients fall off almost linearly with the mole fraction of silver bromide,  $N_1$ . From these values we have obtained by the aid of the usual formulas, values of the entropy,  $\Delta S_1$ , and partial molal entropy,  $\bar{S}_1$ , the free energy of formation,  $\Delta F_1$ , and the partial molal free energy or free energy of dilution,  $\bar{F}_1$ , the molal heat of formation,  $\Delta H_1$ , and the heat of dilution,  $\bar{H}_1$ , the activity,  $a_1$ , and the activity coefficient,  $a_1/N_1$ .

TABLE III

ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH SODIUM BROMIDE				
$N_1$	1.0000	0.7486	0.6045	0.5130
$dE/dT \times 10^6$ (volts/deg.)	-290	-256	-238	-218
$\Delta S_1$ (cal./deg.)	-6.69	-5.91	-5.49	-5.03
$\bar{S}_1$ (cal./deg.)	0.00	0.78	1.20	1.66
550°, $E$ (volt)	.7720	.7877	0.8002	0.8088
550°, $\Delta F_1$ (cal.)	-17810	-18180	-18460	-18660
550°, $\bar{F}_1$ (cal.)	0	-370	-650	-850
550°, $\Delta H_1$ (cal.)	-23320	-23040	-22980	-22800
550°, $\bar{H}_1$ (cal.)	0	280	340	520
550°, $a_1$	1.0000	0.8014	0.6719	0.5952
550°, $a_1/N_1$	1.000	1.071	1.112	1.160
600°, $E$ (volt)	0.7577	0.7749	0.7883	0.7979
600°, $\Delta F_1$ (cal.)	-17480	-17880	-18190	-18410
600°, $\bar{F}_1$ (cal.)	0	-400	-710	-930
600°, $a_1$	1.000	0.7956	0.6658	0.5861
600°, $a_1/N_1$	1.000	1.063	1.101	1.142

These values are given in Table III and Fig. 2; Curve A shows  $-\bar{F}_1$  plotted against  $\log(1/N_1)$  where  $N_1$  is the mole fraction of silver bromide. If we attempt to calculate  $-\bar{F}_1$  by assuming the activity to be equal to the mole fraction we find that the simple assumption of complete ionization of both salts or of no ionization yield the same result, namely  $a_1 = N_1$ . This is evident when it is considered that dilution with sodium bromide would, if both salts were completely ionized, make no change in the proportion of bromide ion, but merely substitute sodium ion for silver ion, thus reducing the activity of the latter and hence of silver bromide in proportion to  $N_1$ , the

<sup>7</sup> Jaeger, *Z. anorg. allgem. Chem.*, **101**, 16 (1917).

same as for the case of no ionization. Such calculations are represented by curve B, Fig. 2, slightly higher than the observed. There is therefore a positive deviation of the activity from Raoult's law since  $a_1/N_1$  is greater than unity. However, the deviation is not nearly so marked as that found for solutions of lithium bromide and silver bromide.<sup>2</sup>

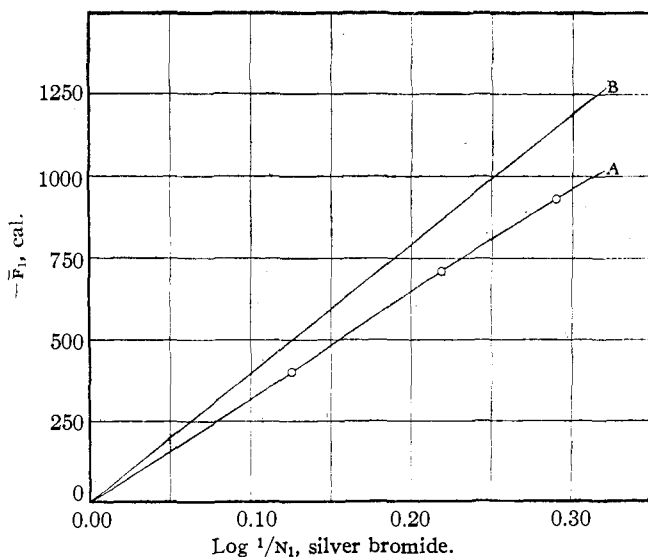


Fig. 2.—Change in free energy of silver bromide at 600° upon dilution with sodium bromide: A, observed; B, calculated.

It is of interest to note that dilution of silver bromide by lithium bromide,<sup>2</sup> which on the basis of complete ionization assumption simply means a substitution of the small lithium ion for the silver ion of more than double its size, lowers the activity of silver bromide far less than a similar dilution by sodium bromide where the substituted silver ion is only about four-thirds the size of the substituting ion. It therefore seems evident that the change in interionic forces due to the substitution of ions of varying size should be considered. This phase of the investigation is being carried further by studying the change in activity of silver bromide upon dilution with potassium bromide and rubidium bromide where the substituting cations are even larger. When data for these systems are at hand we expect to make a more comprehensive study of the whole subject.

### Summary

1. E. m. f. measurements have been made of the cell,  $\text{Ag(s)}/\text{AgBr(l)}, \text{NaBr(l)}/\text{Br}_2(\text{g})$  at mole fractions of silver bromide varying from 1.00 to 0.513 between the temperatures 450 and 620°.
2. Calculations have been made of the free energy of dilution, the heat

of dilution, entropy, activity and activity coefficients of these solutions at the temperatures of 550 and 600°.

3. Density determinations of 0.5 mole fraction sodium bromide in silver bromide were made between 600 and 620° and may be expressed by the equation,  $d^t = 4.311 - 0.0009 t$ .

4. It is pointed out that the positive deviation of the results from Raoult's law seem to indicate that changes in interionic forces upon dilution should be considered.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]  
**DEFORMATION OF ELECTRON SHELLS. III. THE MAGNETIC  
SUSCEPTIBILITY OF NEODYMIUM NITRATE**

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RECEIVED MARCH 4, 1931

PUBLISHED MAY 6, 1931

The object of this work, as pointed out in previous papers,<sup>2</sup> was to investigate the relations existing between the absorption spectra and other properties of certain rare earth salts. It has already been shown that in the case of aqueous solutions of neodymium salts a shift toward the red of the absorption bands with increasing concentration is attended with an increase in the ionic refraction of the neodymium. The purpose of the work here reported was to see whether the magnetic susceptibility of neodymium nitrate suffered a perceptible change as the changes in absorption and refraction were taking place.

### Experimental

The magnetic apparatus used resembled the Bauer and Piccard<sup>3</sup> modification of Quinckes' capillary rise method. As shown in Fig. 1 the capillary tube C, which was 1 mm. in internal diameter, was placed between the truncated poles of a Weiss electromagnet. The interspace between the poles was 3 mm. During the course of readings the meniscus was always returned to the same position both while the field was applied and while it was off. It was, therefore, not necessary that the field should be uniform, although an investigation showed that it was uniform over a considerable region. The meniscus was observed by means of the telescope A. The magnet was operated with a current of 5.2 amperes, which was sufficient nearly to saturate the iron pole-pieces as is shown in Fig. 2. This procedure is essential if error is not to be introduced from the hysteresis characteristics of the iron.<sup>4</sup> It also reduces the proportionate error from slight deviations in the current through the magnet.

<sup>1</sup> National Research Fellow.

<sup>2</sup> Selwood, *THIS JOURNAL*, **52**, 3112, 4308 (1930).

<sup>3</sup> Bauer and Piccard, *J. Phys.*, **1**, 97 (1920).

<sup>4</sup> Sève, *Ann. chim. phys.*, **27**, 425 (1912).