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The Entropy of a Crystalline Solution of Silver Bromide and Silver Chloride in Relation to the Third Law of Thermodynamics

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With the object of testing experimentally the third law of thermodynamics as applied to crystalline solutions, the chief thermodynamic properties of such a solution of silver bromide and silver chloride have been studied. Measurements described and recorded include: the free energy of formation, obtained from measurements of the e.m.f. of appropriate silver-silver halide electrodes against hydrogen; the heat of formation, from measurements of heat absorbed in dissolving the various phases in a thiosulfate solution; the specific heats between 15°K and 298°K of the pure constituents and the solid solution. The entropy of silver bromide and of silver chloride is calculated from the specific heat curves. The entropy change in the formation of the solid solution at 298°K is calculated from the experimental data and is found to agree with the result calculated statistically. The latter is identical in form and

magnitude with the entropy as calculated thermodynamically for an ideal solution, though the heat content and free energy show that the solution is far from perfect. From the specific heat curves it appears that the entropy of mixing persists essentially unchanged in magnitude to the lowest temperature of the measurements, and presumably to the absolute zero. The existence of finite entropies, or entropy differences, at the absolute zero is regarded as established thermodynamically, and the requisite interpretation of statistical ideas to secure concordance with this result is discussed. Finally, although the existence of a valid but limited third law is accepted, and a concise general statement of it suggested, it is pointed out that the "principle of the unattainability of the absolute zero" must be regarded as extra-thermodynamic in character.

THE early formulations of the third law gave rise at once to questions concerning its application to solid solutions. Thus Nernst¹ expressed the opinion that the law, in the form that entropy changes are zero at the absolute zero, is strictly applicable to all condensed systems. Planck² and Einstein,³ however, in addition to adopting the concept of absolute entropy and assigning zero entropy to pure solids at 0°K, took the position that the entropy of mixing must persist to the lowest temperatures. They maintained, therefore, that solid solutions must possess finite positive entropy at the absolute zero.

Subsequently, a number of papers addressed to this question, and the essentially similar problem of the super-cooled liquid or glass, have appeared. A paper by Stern⁴ treats theoretically of *crystalline* solutions. Lewis and Gibson⁵ discuss

generally both solid solutions and glasses, and Pauling and Tolman⁶ give a detailed theory for glasses. On the experimental side Gibson and his collaborators⁷ have studied glassy solutions of ethyl and methyl alcohols, and pure glycerol glass. Simon and Lange⁸ also studied glycerol, carrying the measurements to liquid hydrogen temperatures. As far as we are aware, however, no crystalline solution has previously been investigated experimentally.

Although the essential problem is the same in all cases mentioned above, the crystalline solution presents it in its simplest form theoretically and experimentally. Such systems are clearly visualized as random distributions of the component molecules over the points of a lattice. There is little necessity, in simple cases, for special assumptions relating to the quantum states of the atoms or molecules, since these can

¹ Nernst, Sitzber. Kgl. Preuss. Akad. Wiss. 972 (1913).

² Planck, *Thermodynamik*, Veit and Co., Leipzig (1913).

³ Einstein, Second Solvay Congress, Brussels, 1913; *Rapports*, Paris (1921).

⁴ Stern, Ann. d. Physik 49, 823 (1916).

⁵ Lewis and Gibson, J. Am. Chem. Soc. 42, 1529 (1920).

⁶ Pauling and Tolman, J. Am. Chem. Soc. 47, 2148 (1925).

⁷ Gibson, Parks and Latimer, J. Am. Chem. Soc. 42, 1542 (1920); Gibson and Giauque, J. Am. Chem. Soc. 45, 93 (1923).

⁸ Simon and Lange, Zeits. f. Physik 38, 227 (1926).

scarcely differ in type from those of pure crystals. This comparative simplicity in physical state may be assumed to be reflected also in the simpler specific heat laws applicable to crystals. This is important practically since it renders the necessary extrapolations to absolute zero less open to question. These advantages seemed to us to warrant experiments designed to test the behavior of some typical crystalline solution with respect to the third law.

We have therefore determined the free energy and heat of formation of a crystalline solution of silver bromide and silver chloride from the pure compounds at 298°K. From these data the entropy of formation of the solution is calculated. We have also measured the specific heats of the pure compounds and the solution in the temperature range from 298°K to 15°K. By extrapolation of these data, in conjunction with the entropy value at 298°K, we have obtained an estimate of this entropy change at the absolute zero. The present paper comprises the results of these studies, together with a discussion of the differences of interpretation which still obtain in this field.

PREPARATION AND TESTS OF THE SOLID SOLUTION AND OTHER MATERIALS

The existence of a complete series of solid solutions of the bromide and chloride of silver is well established. Küster⁹ prepared such solutions by precipitation from silver nitrate and mixed halide solutions. Monkemeyer¹⁰ prepared them by fusion, and determined the freezing point—composition curve (which shows a minimum at 65 mole percent silver bromide). Wilsey¹¹ made x-ray photograms of various solutions prepared by fusion, and of each of the pure substances, in powder form. He found each substance to crystallize with the sodium chloride type of lattice, and that the lattice constants of the solutions lie linearly between those of the pure crystals when plotted against mole fraction.

In our own work it was established in numerous preliminary experiments that mixed-crystals of

reproducible composition and properties could be most conveniently prepared by precipitation from silver nitrate with mixtures of hydrochloric and hydrobromic acid. Mixtures of solutions of known concentration of these substances were made up by weight, and after shaking for various periods at 25° the weights of the precipitated solid solutions were determined. These data permit the calculation of the composition of the crystals and of the ratio HCl/HBr in the solutions in equilibrium with them. It was ascertained in these experiments that four days shaking at 25° is sufficient to establish equilibrium of the precipitate with the solution even in the extreme cases. For example, in precipitations involving the same quantities the product was the same after four days, whether silver chloride was first precipitated and then the hydrobromic acid added, or the reverse procedure followed.

The character of the material so obtained was further tested in qualitative experiments by comparing microscopically its index of refraction in sodium light with that of silver chloride and silver bromide by means of a series of sulfur-selenium melts of appropriate range. The refractive index of the solution lay between those of the pure substances. No indication of inhomogeneity was found.

The ability of the solid solution to withstand low temperature treatment without appreciable separation into its constituents was also established by tests of its refractive index after prolonged immersion in liquid air. These preliminary tests were fully substantiated in our later work when x-ray photograms¹² were obtained of the solid solution as finally prepared for our measurements and of a sample of the same material taken from the calorimeter after our specific heat measurements, extending to liquid hydrogen temperatures, had been completed. No detectable difference was present. Moreover, the lines of the pure crystals, exposures of which were also made, were entirely absent from the photograms of the solid solution, and the lattice constants of our solutions were closely calculable by interpolation from the constants of the pure substances, as was found by Wilsey with his samples.

⁹ Küster, *Zeits. f. anorg. allgem. Chem.* **19**, 81 (1899).

¹⁰ Monkemeyer, *Neues Jahrb. Mineral Geol. Beil.* **22**, 1 (1906).

¹¹ Wilsey, *J. Frank. Inst.* **200**, 739 (1925).

¹² We are indebted to Dr. W. H. Dore for placing apparatus at our disposal for the x-ray exposures.

The material used in all of our final measurements was prepared in a single batch of about 1.5 moles by precipitation from mixed acids, 1.7 *M* total concentration, with 0.1 *M* AgNO₃. The amounts used were calculated from the preliminary experiments to give a solid solution of about 73 mole percent silver bromide, with a concentration ratio (HCl/HBr) of the acids in equilibrium with it of 190. After slowly adding, with vigorous shaking, the silver nitrate to the solution of the acids, the precipitate was allowed to stand, with occasional shaking, for a week at 25° to establish equilibrium. It was then washed repeatedly for another week with 0.1 *M* acid of the equilibrium concentration ratio until freed from detectable amounts of nitrate. The precipitation of the mixed crystals (and the pure substances also) was carried out in dim red light. At no time in any of the subsequent operations or in the experiments themselves were the salts exposed to direct daylight, and only rarely to more than a subdued red light.

A part of the total quantity of the mixed crystals described above was set aside in contact with the equilibrium solution for use in the e.m.f. measurements described later. The remainder, after settling and draining, was dried by evacuation with a mercury vapor pump. Subsequent fusion of samples of material so dried showed a loss in weight of less than 0.03 percent. It is recognized that slight changes in surface composition of the crystals may have been caused by this method of drying. In view of the nearly complete removal of liquid before evacuation, and the rapidity of the evacuation itself, the amounts affected by these changes must have been very small.

The solid solution thus prepared was analyzed by conversion to the chloride by heating in a stream of dry chlorine. Four determinations gave 72.80 ± 0.08 mole percent silver bromide as a mean, in satisfactory agreement with the composition estimated in its preparation. From the standpoint of the entropy change, an equimolar mixture would be preferable. Departure from this ratio was made in order to avoid very large equilibrium ratios of the acids used as electrolytes in our e.m.f. measurements, as increased precautions are otherwise required for accurate work.

Pure silver chloride and silver bromide were prepared in about the same amount and under the same light conditions as the solid solution. The solutions used in these preparations were 0.1 *M*. The precipitated salts were washed with conductivity water until methyl red gave no test for acid. Portions of each were dried by evacuation as described above, the remainder being kept in water.

THE FREE ENERGY OF FORMATION OF THE SOLID SOLUTION

We have determined the free energy of formation of the mixed crystals described above from measurements of electromotive force. The cells employed were of the type Ag, AgBr·AgCl (mixed crystals), HCl+HBr (equilibrium ratio), H₂, together with similar cells employing the pure halides with the corresponding pure acids.

The cells and hydrogen generators were of the types described by Lewis, Brighton and Sebastian.¹³ The platinum electrodes were of the platinized platinum type with a fairly thin coating of platinum black. The silver electrodes were of spiral form, made in the way described by Randall and Young.¹⁴ It was found convenient to make them six at a time and place them in small glass tubes. These tubes were then heated, evacuated with a mercury vapor pump and sealed. In use, these electrodes were surrounded by the salts described above, instead of being plated with the halide.

Preliminary cells showed that it was necessary to remove oxygen completely from the silver electrode. This was done, following Güntelberg,¹⁵ by bubbling pure nitrogen through the cell electrolyte for three or four hours. The tube containing the silver electrode was broken under acid previously freed from oxygen. Electrical equilibrium in the cells was quickly reached after saturation with hydrogen. Usually, however, the cells were placed in the thermostat at night and the readings taken the next morning. Each cell contained two hydrogen electrodes and these usually agreed to 0.02 or 0.03 millivolt. The ther-

¹³ Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.* **39**, 2245 (1917).

¹⁴ Randall and Young, *J. Am. Chem. Soc.* **50**, 989 (1928).

¹⁵ Güntelberg, *Zeits. f. physik. Chemie* **123**, 199 (1926).

TABLE I. *Electromotive force of cells.*

Cell No.	Solid phase	Molality HCl	Molality HBr	Barometric pressure	Observed e.m.f.	Standard e.m.f.
1	solid sol.	0.5087	0.002677	754.0	0.2465	0.1018
2	solid sol.*	.5096	.002684	754.0	.2479	.1034
3	solid sol.*	.5093	.002681	756.0	.2466	.1020
4	solid sol.	.5088	.002679	756.0	.2476	.1029
5	solid sol.	.09994	.0005260	754.7	.3283	.1015
6	solid sol.	.09941	.0005232	754.7	.3284	.1014
7	AgCl	.5094	—	757.5	.2709	.2228
8	AgCl*	.5094	—	757.5	.2709	.2228
9	AgCl	.1151	—	748.6	.3450	.2228
10	AgCl	.1151	—	752.7	.3454	.2231
11	AgBr	—	0.5224	756.9	.1161	.0714
12	AgBr	—	.5229	756.9	.1162	.0715
13	AgBr	—	.1236	750.6	.1904	.0725
14	AgBr	—	.1240	750.6	.1900	.0722

* Material from calorimeter after specific heat runs.

mostat contained oil and was held at $25^{\circ}\text{C} \pm 0.02^{\circ}$. The electrical system was the same as that used by Lewis, Brighton and Sebastian¹³ except for the substitution of a Leeds and Northrup Type K potentiometer instead of the volt box. The concentration of acid used was determined after completion of the measurements, samples being taken from each side of the cell.

The experimental observations are recorded in Table I. In this table, the first column designates the cells by number. In column 2 are indicated the solid phases, prepared as described above, employed in the silver electrode. The molalities (moles per 1000 g H_2O) of the acids in the cell electrolytes, determined by analyses of samples drawn from each side of the cell, are given in columns 3 and 4. The barometric pressure in mm is shown in the fifth column. The observed electromotive forces in volts, recorded in column 6, are averages of readings taken over a period of several days after the cells had reached equilibrium, i.e., after variations were reduced to less than 0.2 mv. The cells generally became steady in about four hours, and were consistent and reproducible, within the limits required in this work.

For the comparison of the individual cells, and in the calculations of free energy, it is convenient to have the standard electromotive forces, E° . The values obtained for E° for each cell are listed in the last column of Table I. The formula employed in the calculations is

$$E = E^{\circ} - 0.05915 (A \log a_{\text{HBr}} + B \log a_{\text{HCl}} - \frac{1}{2} \log p_{\text{H}_2}).$$

In this equation, E and E° are, respectively, the observed and standard electromotive forces. The activity of the acids is represented by the symbol a with the appropriate subscript, and the partial pressure of hydrogen by p_{H_2} . The factors A and B represent the mole fraction of silver bromide and silver chloride, respectively, in the solid solution. The required activity values are obtainable from the determinations of activity coefficients by Scatchard¹⁶ for HCl and of Livingston¹⁷ for HBr, with the assistance of the principle of ionic strength¹⁸ in the case of the mixed electrolytes.

The average value of E° for the cells involving the solid solution, for which the individual values are given in Table I, is 0.1022 volt. For the cells containing pure silver chloride it is 0.2229 volt, and for the silver bromide cells 0.0719 volt. From these, the e.m.f. corresponding to the formation of one mole of our solid solution from 0.728 mole

¹⁶ Scatchard, J. Am. Chem. Soc. **47**, 641 (1925).

¹⁷ Livingston, J. Am. Chem. Soc. **48**, 45 (1926). As far as we have been able to ascertain, Livingston did not exclude oxygen from the electrolytes in his cells. This may have influenced his activity coefficients to some extent. We believe the uncertainty in these values to be in part responsible for the relatively large difference in E° for the silver bromide cells with 0.5 M and 0.1 M HBr. These inaccuracies are, however, not serious in the present connection.

¹⁸ Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., New York, 1924.

TABLE II. *Heats of solution of AgBr, AgCl, and the solid solution in a thiosulfate solution at 25°.*

Substance	Moles of substance used	Temperature rise of calorimeter, °C	Heat capacity of calorimeter, cal.	Heat of solution, cal./mole.
AgBr	0.05928	0.02607	1227.7 1230.6	
			Av. 1229.1	540.5
	0.05932	0.02589	1223.2 1224.5	
			Av. 1223.8	534.2
				Av. 537.4
AgCl	0.05929	0.2470	1227.5 1229.2	
			Av. 1228.4	5118
	0.05929	0.2484	1223.0 1221.3	
			Av. 1222.2	5120
				Av. 5119
Solid Solution	0.05931	0.09000	1226.6 1229.8	
AgBr _{0.728} Cl _{0.272}	0.05931	0.09004	Av. 1228.2	1863.7
			1228.5 1228.4	
			Av. 1228.4	1864.8
				Av. 1864.3
Mechanical Mixture 0.04311 AgBr + 0.01623 AgCl	0.05934	0.08663	1224.9	1788.1 Calc. 1791.5*

* From values found for pure substances.

AgBr and 0.272 mole AgCl may readily be calculated. It proves to be $0.728 \times 0.0719 + 0.272 \times 0.2229 - 0.1022 = 0.0110$ volt. This corresponds to a free energy change for the reaction of 254 cal. The uncertainty in this value we think is not greater than 1 millivolt, or about 20 cal.

THE HEAT OF FORMATION OF THE SOLID SOLUTION

The heat of formation of our solid solution was determined by measuring the heat effects when the mixed crystals and each of the pure constituents were dissolved in separate portions of a thiosulfate solution.

The apparatus and procedure used were those described by Randall and Rossini.¹⁹ The sodium thiosulfate solution, identical in each of the runs, was made up in the proportion of 1100 grams of water to 200 grams of recrystallized (and partially dehydrated) sodium thiosulfate, which were also the amounts used in the calorimeter. After each determination of a heat of solution, the heat capacity of the calorimeter and its contents was twice determined. Measurements were made on two samples each of the solid solution and the

¹⁹ Randall and Rossini, J. Am. Chem. Soc. **51**, 323 (1929). We express our thanks to Dr. Rossini for valued assistance in these measurements.

pure constituents, and on one sample of a mechanical mixture made up approximately in the proportion of the solid solution. The results are summarized in Table II, which is self-explanatory.

From these results it is found that the change in heat content in the formation of one mole of the solid solution is 80.7 cal. at 25°. This value we consider to be correct to ± 10 cal.

HEAT CAPACITY AND ENTROPY OF SILVER BROMIDE AND SILVER CHLORIDE AND THE SOLID SOLUTION

This portion of the experimental work consisted in the determination of the heat capacities of the two pure constituents and the solid solution between 298° and 15°K.²⁰ The apparatus used and procedure followed in the specific heat runs were, with minor exceptions, the same in type as generally employed in low temperature work in this laboratory at the time of these measurements (1928). The technique is so much standardized that detailed description is not required here.²¹ The amounts of the materials used in the measurements of heat capacity were as follows: 122.28 g = 0.6511 mole AgBr; 121.01 g = 0.8442 mole AgCl; 104.22 g = 0.5931 mole solid solution (weights corrected to vacuum). We show in Table III the results of the measurements. The temperatures and corresponding molal heat capacities there shown are means over intervals ranging from 2 to 5°.

From these data the entropy difference $S_{298} - S_0$ of each substance was obtained graphically on large scale plots of C_p against $\log T$. The necessary extrapolation to the absolute zero from the lowest temperatures of measurement was made with the assistance of Debye and Einstein functions combined in such a way as to fit the experimental points (within 0.08 cal.) up to 50°K.

²⁰ Since the completion of our specific heat work, other measurements for AgCl and AgBr have been published. Clusius and Harteck, *Zeits. f. physik. Chemie* **A134**, 243 (1928), studied AgCl from 10.5 to 126°K, and Eucken, Clusius and Wortinek (*Zeits. anorg. Chem.* **203**, 39 (1931)) AgBr between 11.8 and 273°K. These data are in general in good agreement with ours.

²¹ Our apparatus was designed following suggestions of Professor W. F. Glauque, whose cooperation in the specific heat measurements is much appreciated. A set-up similar in most essentials to ours is described by Latimer and Greensfelder, *J. Am. Chem. Soc.* **50**, 2202 (1928).

Entropies at the lowest measured point were then obtained from calculated values for these functions. The entropy terms resulting from these extrapolations amounted to 0.90, 0.43 and 0.50 cal./mol/deg. for the silver bromide, the silver chloride and the solid solution, respectively. The difference $S_{298} - S_0$ was found to be 25.62 for silver bromide, 22.97 for silver chloride, and 24.99 for the solid solution.

We estimate that the uncertainty in the values of these entropy differences is less than 0.1 cal./mol/deg., and consider that the differences among these quantities themselves are not less accurate than this because of the nearly identical treatment given each substance.

It is to be noted that $S_{298} - S_0$ for the solid solution as determined directly above does not differ significantly from that of a mechanical mixture of the same proportions. The value for the solid solution is 24.99, while that calculated for a mechanical mixture is 24.90.

It is also important to note the detailed behavior of the specific heats with respect to the additive law. For this purpose Table IV, showing values of ΔC_p in the formation of a mole of the solution from its constituents, as obtained by combining values from the smoothed curves at equal intervals in $\log T$, has been constructed.

It will be seen that the difference between the observed value of C_p for the solution from that of the components in the pure state is less than 0.1 percent in the higher temperature range, and therefore well within the experimental error. At the lowest temperatures of our measurements, however, the difference has increased, but is still less than 1 percent. This difference is slightly greater than we should attribute to experimental uncertainty, yet not enough to permit us to say that there are significant departures from the additive law. If any such departures occur they do so at temperatures outside the range of our measurements.

COLLECTED RESULTS

The reaction that we have studied may be written,

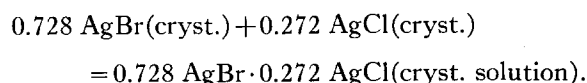


TABLE III. *Molal heat capacities of silver bromide, silver chloride, and the solid solution.*

<i>T</i>	AgBr <i>C_p</i> , cal./mole	<i>T</i>	AgCl <i>C_p</i> , cal./mole	<i>T</i>	Solid Solution <i>C_p</i> , cal./mole
24.04	3.520	15.00	1.122	16.04	1.643
28.31	4.516	18.09	1.767	19.94	2.468
32.81	5.417	21.07	2.259	24.32	3.385
37.43	6.226	24.71	2.878	29.26	4.469
41.69	7.086	28.70	3.623	34.62	5.468
45.87	7.562	32.60	4.273	39.68	6.240
50.54	8.006	37.37	4.941	44.22	6.933
55.28	8.508	43.04	5.735	48.37	7.418
60.19	8.924	48.33	6.405	52.51	7.883
69.34	9.689	53.65	6.926	56.68	8.334
74.42	9.972	58.32	7.390	60.46	8.635
83.65	10.305	62.42	7.788	64.39	9.027
93.09	10.658	75.17	8.779	68.25	9.293
101.56	10.982	79.39	9.019	73.35	9.600
108.35	11.164	88.56	9.501	76.99	9.780
115.49	11.293	97.29	9.865	80.92	9.959
124.17	11.439	105.91	10.230	85.12	10.106
134.97	11.497	114.16	10.493	89.09	10.276
142.72	11.621	122.66	10.682	92.84	10.396
150.67	11.749	130.58	10.834	96.89	10.514
158.16	11.810	138.45	10.988	101.16	10.682
166.78	11.945	140.65	11.021	105.22	10.807
175.62	11.964	149.13	11.203	110.64	10.984
183.93	12.088	157.90	11.401	114.65	11.080
192.05	12.240	166.07	11.548	119.05	11.109
200.34	12.155	174.28	11.582	123.31	11.201
212.26	12.332	183.13	11.640	127.50	11.223
222.71	12.297	191.01	11.760	135.85	11.353
235.33	12.222	200.24	11.876	143.02	11.471
246.17	12.326	209.80	11.993	144.83	11.544
258.95	12.300	210.54	12.030	152.53	11.658
269.70	12.406	220.82	12.048	160.55	11.608
279.24	12.452	230.73	12.083	168.72	11.825
289.29	12.375	240.40	12.061	176.80	11.861
		250.36	12.182	184.09	12.090
		260.54	12.137	191.64	11.945
		270.43	12.050	198.78	12.100
		284.97	12.135	206.36	12.140
		292.12	12.080	215.08	12.230
				231.99	12.228
				239.96	12.193
				247.81	12.189
				251.99	12.225
				261.20	12.302
				274.39	12.275
				287.13	12.228
				293.45	12.196

TABLE IV. ΔC_p in the formation of the solid solution from the pure constituents.

$\log T$	1.25	1.50	1.75	2.00	2.25
C_p solid solution	2.000	4.945	8.295	10.660	11.920
C_p pure constituents	1.982	4.899	8.240	10.679	11.921
ΔC_p	0.018	0.046	0.055	-0.019	-0.001

We have determined by standard methods of thermodynamics the values of ΔF and ΔH for this reaction at 298.1°K. The well-known relation, $\Delta S = (\Delta H - \Delta F)/T$, between these quantities and the entropy change permits the calculation of the latter. We have thus found;

$$\Delta F_{298} = -254 \pm 20 \text{ cal.};$$

$$\Delta H_{298} = 81 \pm 10 \text{ cal.};$$

$$\Delta S_{298} = 1.12 \pm 0.10 \text{ cal./deg.}$$

From the specific heat measurements we have obtained the change in heat capacity for this

reaction in the temperature interval 15–298°K. At no point within this range was the change in heat capacity significantly different from zero. That is

$$\Delta C_{p\ 15-298} = 0.$$

Making the assumption that this relation will remain true at all temperatures down to absolute zero, it follows that ΔS at the absolute zero is not zero, but is the same, within experimental error, as at 298°K, or about 1.1 e.u.

Stated in another way, we have found from the specific heat curves, with the assumption of zero entropy for each substance at the absolute zero, that for

$$\text{AgBr, } S_{298} = 25.62 \pm 0.1 \text{ cal./deg.,}$$

$$\text{AgCl, } S_{298} = 22.97 \pm 0.1 \text{ cal./deg.,}$$

$$\text{Solid solution, } S_{298} = 24.99 \pm 0.1 \text{ cal./deg.}$$

From which we find, allowing about the same accuracy for the entropy difference as for the "absolute" values,

$$\Delta S_{298} = 0.09 \pm 0.10 \text{ cal./deg.}$$

This last result does not differ from zero by more than the possible experimental error, and is in conflict with the result found above by established methods. From this angle, therefore, the apparent result of our measurements is this: if the entropies of the pure salts at the absolute zero are taken as zero, the solid solution at this temperature must be assigned a value of about 1.1 units of entropy.

We believe these results to be typical and shall in the following section discuss their interpretation.

INTERPRETATION OF RESULTS

The entropy change at the absolute zero obtained above depends in part upon an extrapolation of the specific heat measurements. It is possible to claim, therefore, that departure from the accepted curves may occur at very low temperatures in such a way as to make $\Delta S_0 = 0$. The systems we have studied seem to us very unlikely to exhibit specific heats near the absolute zero that would not be predictable from the experimental curves at higher temperatures. It appears still less likely that any abnormalities that may exist at very low temperatures will make the

additive law ($\Delta C_p = 0$) untrue. We consider, therefore, that objections to the experiments from this standpoint are invalid in the present case.

A further objection that has been strongly urged²² against experiments of this type arises from the fact that in the lower temperature range the solid solution becomes thermodynamically unstable, and, if equilibrium were maintained, would separate into two phases. With approach to the absolute zero these would approach the pure salts in composition. Even at temperatures where no separation of phases tends to occur, the establishment of the ultimately stable condition may be a very slow process. Long annealing may be expected to produce phases differing in properties from those not allowed to come to equilibrium, and the heat capacities of the latter will depend upon their age at the time of measurement. The argument then is that no ideally reversible isothermal process, and no reversible heating or cooling, involving a phase slowly shifting through a series of unstable states is possible. Since reversible processes are essential to the measurement of entropy differences, unstable "frozen" phases must be excluded from thermodynamic consideration. From this standpoint, it is meaningless to speak of the entropy difference between the solid solution and the pure substances at the same (low) temperature, since none can be ideally determined.

The practical difficulty attending a reversible isothermal process involving a frozen phase must be at once admitted. It is also true that the ordinary process of reversible heating to a temperature permitting the isothermal change, followed by reversible cooling of the products to the original temperature, cannot be carried out in the strictly idealized fashion. In real processes of this kind, however, very close approach to reversibility, in the sense that the total entropy change of system and surroundings is insignificantly small, can be attained. In such processes the materials may be transferred successively between a series of heat reservoirs differing from each other in temperature by a small, but finite, amount, remaining in each for a finite time long enough for close approach to temperature equalization but

²² See for example the able review by Simon, *Ergebnisse d. exakten Wissenschaften* 9, 222 (1930).

not for equilibrium of any other sort. Such a process is essentially reversible; as much so, for example, as many "reversible" galvanic cells operating with finite currents. Moreover, failure of complete reversibility does not invalidate the calculation of entropy changes. It merely limits the exactness of the result.²³ The inaccuracy in many cases may be made very small in the real process. Moreover, by appropriate extrapolation of results to zero times (of contact) and zero temperature differences between reservoirs in suitably conceived real processes, the result of an ideal process of the same sort could no doubt be obtained with high accuracy. As the strictly reversible process is an idealized one in any event, it is perhaps simpler to invoke the aid of ideal catalysts, infinitely accelerating the desired processes, or excluding the undesired. The difficulties attending realization of ideal reversibility then vanish. These difficulties, regardless of what method may be chosen for overcoming them, are connected solely with rate effects and are extraneous to thermodynamics. In the light of these considerations we see little force to the objections discussed above, and claim that the calculation of $(S_T - S_0)$ as $\int_0^T C_p d \ln T$ for frozen phases is amply justified.

Quite different and perhaps more subtle questions arise when the problem is viewed statistically. As is well known,²⁴ the concepts of statistical mechanics and thermodynamics can, in general, be brought into correct relationship by the assumption that the entropy of a system²⁵ in a given state is $S = k \ln Z$. In this equation Z is the number of distinguishable configurations or

detailed states comprising the macroscopic state in question. Adopting this view, the entropy change in the formation of our crystalline solution can be calculated. Effects resulting from mixing of isotopes, and nuclear spin effects, are without interest in the present connection and may be ignored. In the pure substances, then, only one distinguishable state, in the sense first used by Bose and Einstein, appears to be possible at the absolute zero. In the solid solution, however, each interchange of a bromide with a chloride ion gives rise to a new state. The number of physically different possible exemplars of the solution is therefore the number of distributions of the two unlike negative ions over the corresponding positions in the lattice. It may be shown⁴ to be $N!/(X_1 N)!(X_2 N)!$. This is the factor by which Z for the solid solution exceeds Z for the pure substances. In it, N is Avogadro's number, and X_1 and X_2 are the mole fractions of the constituents. The usual application of Stirling's approximation leads to the relation,

$$\Delta S = -RX_1 \ln X_1 - RX_2 \ln X_2.$$

This equation is identical with that obtained thermodynamically for perfect solutions, and is closely substantiated by the measurements above, which yielded 1.12 ± 0.1 for the entropy of mixing, as compared with 1.16 calculated by the formula. The solution, of course, is not perfect since its molal heat content and free energy differ by 80 calories from the ideal values. It is of much interest to find that the equation of entropy of perfect solutions may nevertheless be applied. We believe the statistical and experimental verification of this point in the present example justify its acceptance in all similar cases, irrespective of the degree of perfection of the solution as judged by other standards.

The experimental measurements at 298°K were made under conditions permitting an interchange of the atoms of the solid solution upon the crystal lattice. Under such circumstances there can be little question that the number of states in the solid solution is greater than in the pure substances by the factor obtained above. Under other conditions, however, an apparent difficulty arises.

Thus, as the temperature is lowered during the specific heat measurements the interchange of

²³ A small error is of course unavoidably introduced in calculations like ours. This arises from the fact that some part of the unstable material must undergo a change during the measurement of heat capacities in certain temperature ranges. The measured values therefore do not all correspond to absolutely identical phases. This error we consider trivial in the present instance. It is similar in type to that in the analogous cases of monoclinic sulfur or finely divided white tin below their transition points, and perhaps not so difficult to eliminate.

²⁴ Cf. Lewis and Mayer, *Proc. Nat. Acad. Sci.* **14**, 569 (1928).

²⁵ The controversy concerning the merits of absolute as opposed to relative entropy is of no interest here. In our opinion it involves only questions of convenience and taste. We have used throughout either language without distinction.

atoms is effectively prohibited. Throughout these measurements, and at the absolute zero, a single configuration of the crystalline solution is represented. Its entropy, therefore, in quantum statistics as ordinarily applied, apparently should be taken as zero at the absolute zero. If it is so taken, some portion of the thermodynamic argument is invalidated. It is obviously necessary, therefore, to modify the thermodynamic or the statistical interpretation.

If the first course is chosen, the point of attack is again sought in the change from the condition of complete equilibrium in the e.m.f. measurements to the "frozen" system in the specific heat work. It may be claimed that the reduction from $N!/(X_1N)!(X_2N)!$ to one in the number of configurations accessible to the solid solution represents a change in thermodynamic as well as statistical constraints, equivalent to a complete change in the nature of the system. Correspondingly and automatically, the entropy of the solid solution in the constrained state should be reduced relative to that of the unconstrained system by the amount of the entropy of mixing. This term should then be included in the entropy of the solid solution or not, depending upon the ability or inability of the atoms (or molecules) to make frequent interchanges in times comparable to the duration of the phase in the intended application. In other words, allowing time for interchange introduces, and "freezing" excludes, an irreversible process, in which, effectively, a pure "compound" is converted into a solution of the same composition, and which is accompanied by the entropy increase $-2RX \ln X$.

This position, however, is tenable only if the validity of thermodynamics applied to phases of this type is denied. Otherwise, no latitude in the assignment of entropy is possible, no irreversible process may be assumed in the passage between the frozen and the unconstrained system. For, as previously outlined, a cycle involving these states can be completed without significant increase in entropy of the surroundings. A change of entropy of the kind claimed is therefore not demonstrable. As we see it, the constraints operative in the frozen system act solely to maintain the unstable systems in preference to the stable. They introduce no ambiguity in the entropy of the phase as it actually occurs. To reject this conclusion would

seriously damage the structure of thermodynamics. The severe and unnecessary limitations that would be imposed by such a course could be compensated only through detailed knowledge respecting the presence and nature of frozen equilibria in all systems treated by either the third or the second law. We think, therefore, that the conflict in ideas is best resolved by modifying the statistical interpretation.

Such a modification has been proposed by Lewis.²⁶ According to him, Z in the equation defining entropy represents the total number of states which, so far as the observers information extends, are possible configurations of the system. The ease or speed with which the system may pass from one to another of the permitted configurations is in this view unimportant. Thus, in the present case, when the atoms of the crystalline solution become frozen in fixed positions the particular pattern is unknown. The number of configurations in doubt (not excluded by information possessed by the observer) is as great as if free interchange of the atoms on the lattice were occurring. At the absolute zero this situation still obtains. To the solution, therefore, is to be assigned positive entropy, in amount calculated above, representing the observers lack of information. For any *specified* configuration of the solution, the entropy again becomes zero.

The statement of the situation most acceptable to us may be outlined somewhat as follows. The entropy change of a system is thermodynamically determined by the definition of the initial and final states. In considering a particular entropy change statistically, the definitions of the states of the system must be made to conform to the thermodynamic ones. In the crystalline solution near the absolute zero the state as ordinarily defined is not restricted to a single detailed pattern. It is indefinite in the sense that it may consist of any one of a large number of detailed states, lying within a band of energies, each of which states falls within the thermodynamic definition, and might be regarded as an exemplar of the system. This indefiniteness, which is imposed by the non-selective character of the process of formation, must be embodied in the statistical definition by taking Z as equal to the number of different permitted exemplars. If a process could be invented

²⁶ Lewis, *Science* **71**, 569 (1930).

by which some one configuration could be reversibly obtained at will to the exclusion of all others, the definition of the state would be correspondingly narrowed, and the entropy would be zero. In the absence of ability of the observer thus to work with a single detailed state, multiplicity must be admitted in fixing Z . This position seems to us to meet adequately the present requirements, without undue strain in the accepted ideas of statistics.

The distinction between the opposed viewpoints sketched above impresses us as in no sense trivial. Practically, perhaps, it is unimportant, since the advocates of either argument will in general achieve correct results in applications. In its larger aspects the controversy, which is still an active one, involves rather fundamental ideas. On this account we have given in detail, at the risk of obviousness, the reasons supporting the retention of the thermodynamic conclusion as to the finite entropy at 0°K of the solution, and the interpretation of statistical ideas to agree with it.

We wish to make it clear, however, that the arguments advanced here are not directed against the existence of a generally valid thermodynamic and statistical theorem relating to entropy at the absolute zero. We cannot, therefore, endorse the "ruthless" attitude adopted by Fowler and Sterne.²⁷ These authors would abandon the third law because entropy changes in real systems do not always become zero with approach to the absolute zero, and because it is not always easy in practice to tell when they do. It has, of course, become increasingly clear in recent years that blind application of the law, even to "pure" crystals, must often result badly. The various cases discovered and explained by Giauque and his coworkers,²⁸ and the statistical work of Fowler and Sterne, are conclusive on this point. Nevertheless, a substantial number of systems of diverse types²² may be handled in the ordinary way. The exceptional cases deviate through a uniform cause discussed below. Already much

progress has been made toward the prediction of the occurrence and extent of deviations. There is every reason to expect that such predictions will in the future be pretty generally possible. The doubt expressed by Fowler and Sterne regarding the utility of the third law is, we should state, the only feature of their work bearing on the present question to which we cannot subscribe. We should mention particularly that their device in the treatment of the entropy of mixing in frozen phases leads to the inclusion of the mixing term as part of the entropy, as we have claimed here.

Although the fundamental basis and the limitations of the third law are very generally understood, a concise formulation of it proves a little elusive. The statements in most general use associate zero entropy with the perfect crystalline²⁹ (perfectly ordered) condition, or with the condition of lowest energy (lowest quantum state),³⁰ usually assumed to be "ordered" also. The attempt to define a "perfect crystal" encounters various difficulties not originally contemplated, such as the possibility of mosaic crystals, which are not perfect in the ordinary sense, but must be included in the law. More serious is the frequent occurrence of crystalline solutions of various types (including random distributions on the lattice of isotopic atoms, random orientations of nuclear spins, etc.), which may be quite perfect crystallographically, but do not conform to the law. These difficulties may be met by resorting to the requirement of perfect order. We believe, however, that while the condition of complete order is a sufficient criterion, it is not a necessary one. We see no necessity or support, for example, for the assumption of perfect order of the molecules of degenerate gases, or of the electrons in metals (if they obey Fermi statistics) at the absolute zero, although the entropy of such phases apparently must be taken as zero. Even the atoms of a perfect crystal are, according to the ideas of quantum mechanics, in vibratory motion at the absolute zero. This, and also the uncertainty principle, clouds the concept of perfect order of the atoms but is without necessary effect upon the entropy. The criteria of lowest energy and lowest quantum state avoid any necessary

²⁷ Fowler and Sterne, *Rev. Mod. Phys.* **4**, 635 (1932).

²⁸ See for example (a) Giauque and Johnston, *J. Am. Chem. Soc.* **50**, 3221 (1929); (b) Johnston and Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929); (c) Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930); (d) Clayton and Giauque, *J. Am. Chem. Soc.* **54**, 2610 (1932); (e) Giauque and Ashley, *Phys. Rev.* **43**, 81 (1933).

²⁹ Lewis and Randall, reference 18, 444-448.

³⁰ Simon, reference 22, 231, and other authors there cited.

implication of order, but are themselves either unnecessary or insufficient. Thus, unstable crystals, like diamond, are of zero entropy but not lowest energy,³¹ and the atoms of crystalline solutions are presumably all in their lowest vibrational levels, though the entropy cannot be taken as zero.

The goal in the search for an adequate formulation is, of course, to find some property, preferably a thermodynamic one, which can be rigidly correlated with statistical singleness of state, and therefore with zero entropy. The conspicuous examples of substances that do not have zero entropy at the absolute zero are glasses and solutions. These differ significantly from other phases at the absolute zero only in the fact that the exemplars of a given system differ among themselves, and comprise a large group of distinguishable states. We believe that these states cover a "band" of energies, which may often be very narrow but never absolutely sharp. We suggest, therefore, as a simple, comprehensive, and sufficiently restrictive statement of the third law that *the entropy of any phase of sharply specifiable energy is zero at the absolute zero*. All systems in states of lowest energy or perfect order conform to the limitation in this statement, which thus includes the formulations based on these criteria. In addition, certain other phases unnecessarily

excluded by the other statements are included by the preceding one, which seems to us therefore more appropriate.

The reason for ascribing a characteristic energy to each isomer of a crystal of a solid solution lies in the assumption that the interaction of the molecules differs to a significant, though very small, extent among the different arrangements, however close the similarity of the individual molecules may be. In the absence of exact specification of energy (exact within the meaning of the uncertainty principle), limiting the system to some one of the possible arrangements, a multiplicity, and therefore a finite entropy, for the loosely defined macrostate ensues. In many cases, of course, entropy changes in ordinary reactions involving such states (for example, mixtures of isotopes) will be zero, making it possible to take the "practical" entropy as zero at 0°K, for these phases.

Every known deviation from zero entropy by "pure" crystalline phases at 0°K may be connected with a random distribution of two or more distinguishable types of molecules or atoms over the crystal lattice. In illustration, we would recall that even a difference in orientation may distinguish otherwise similar molecules in a lattice, as proposed by Clayton and Giauque^{28d} to explain the entropy, $\frac{1}{2} R \ln 2$, of their crystals of carbon monoxide at the absolute zero. As a further example, we cite "ordinary" crystalline hydrogen, which we define as a solution of para-hydrogen molecules, of fixed mole fraction equal to $\frac{1}{4}$, with nine kinds of ortho-hydrogen molecules, whose individual mole fractions may vary between $\frac{3}{4}$ and 0. The enumeration of the accessible states for this phase gives

$$Z = 9^{3N/4} N! / (N/4)! (3N/4)!,$$

as found by Fowler and Sterne.²⁷ The entropy then proves to be³² $R(\frac{3}{4} \ln 3 + \ln 4)$, in agreement

³¹ The attempt to rescue the lowest energy formulation (compare Simon, reference 22, 231) by invoking as an additional criterion the presence of potential crests between crystal forms of different stability is unsatisfactory because such crests exist between the exemplars of all glasses, or glassy or crystalline solutions. It is worth while, we think, to emphasize the close analogy between various exemplars of an unstable crystalline solution and a series of different forms of unstable pure crystals of a single substance. In each there is a potential crest separating the various possible states. Every atom in either type of crystal is presumably in a position of minimum energy. Exchanges in position of atoms on the lattice of the crystalline solution, which result in the production of stabler "isomers," require an activation energy comparable in type and magnitude with the similar quantity in transitions between the forms of the pure crystals. The energy difference between the forms of highest and lowest energy is also comparable in magnitude in the two sets. The crystalline solutions of ordinary type differ from pure crystals primarily in the greater number of forms or isomers intermediate between those of highest and of lowest energy, and the consequent smaller difference in total energy between successive forms.

³² It is interesting to note that without the specification of a fixed mole fraction for the para form, it would be necessary to assume $Z = 10^N$ and $S_0 = R \ln 10$. There is perhaps some question as to whether ordinary gaseous hydrogen might not be defined in such a way as to require this value of S_0 for the "frozen" crystal at 0°K. We consider it legitimate, however, if not indeed necessary to include a specification of the energy of the sample which would narrow the proportion of ortho to para practically to 3 to 1.

with Giauque's result.^{28c} These substances and the other "irregular" ones are therefore actually crystalline solutions. The results obtained by direct measurement in the very simple system we have studied seem to us to offer important confirmation of the treatment which has been given these less obvious cases, which cannot be so directly studied.

The limitations we have discussed above apply with equal force to the "principle of the unattainability of the absolute zero," which is often allied

or identified with the third law. This principle, insofar as it is regarded as a thermodynamic law, is violated by the recognition of entropy changes that remain finite as the absolute zero is approached. In its unrestricted form, it may very well be universally true, for reasons connected with rate effects. In this form, however, some of its thermodynamic conclusions are incorrect. In limited form it adds nothing to the third law. It therefore seems to us advisable to eliminate it from the list of thermodynamic tenets.