that the components in these instances are iron sulfide and pyrite, iron and iron carbide and nephelite and albite. Further investigation is needed, however, to decide these points.

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ON THE HEAT OF FORMATION OF SOLID SOLUTIONS.

BY H. W. FOOTE AND BLAIR SAXTON.

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Ever since van't Hoff pointed out that isomorphous mixtures could be considered as solid solutions, the problem has been an interesting one as to what extent the properties of such mixtures are a linear function of composition. It is safe to say that, in general, the properties are much more nearly linear than are the properties of liquid solutions. For instance, probably no isomorphous mixtures diverge as widely in properties from a linear relation as solutions of water and nitric acid. This is because substances which are isomorphous are usually very closely related chemically, while liquids which are totally unrelated may dissolve each other readily. Some properties are so nearly linear that it has not been possible to measure any difference. Retgers has shown, for example, that the specific gravity of isomorphous mixtures is in general what would be calculated if they were considered as mechanical mixtures. This property, however, cannot be measured with very great accuracy and it is probable that a difference does exist but that it is small. Melting points and vapor pressures, so far as they are known, commonly show small variations from the linear relation. These small variations in properties are an expression of the fact that isomorphous mixtures contain a somewhat different amount of energy than mechanical mixtures of the same composition do and that isomorphous mixtures have what may be termed a heat of solid solution which, in general, is small. Ostwald[1] demonstrated this in a few cases before van't Hoff's work appeared, and the same has been shown since, notably by Sommerfeldt,[2] Beketoff,[3] Kurnakov and Zemcynznyj[4] and Wrzesnewski.[5] The results all show that there is a small positive or negative heat of formation.

Salts which are isomorphous with each other only to a limited extent are in some ways comparable with partially miscible liquids. The composition of each solid, when it has become saturated with the other, is a function of the temperature, as it is with liquids. With liquids, however,

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[1] *J. prakt. Chem.*, **25**, 1 (1882).

[2] *Jahrb. Mineral.*, Beibl., **13**, 435 (1899–1901).

[3] *Z. anorg. Chem.*, **40**, 355 (1904).

[4] *Ibid.*, **52**, 186 (1907).

[5] *J. Russ. Phys. Chem. Soc.*, **43**, 1364 (1911).

temperature usually, though not always, affects the solubility of each one in the other in the same way. Thus, rising temperature increases the solubility of aniline in water and of water in aniline. With solids, so far as we are aware, a change in temperature has opposite effects on the solubility of each solid in the other. For instance, silver and sodium chlorates each form a limited series of mixed crystals with the other.[1] As the temperature rises, the amount of sodium chlorate which silver chlorate can take up, forming tetragonal crystals, falls off, while the amount of silver chlorate increases which is taken up by sodium chlorate to form cubes. It appears from the principle of Le Chatelier that there should be a connection between the heat of solid solution and change in the mixing limits with temperature. Since the solubility of sodium chlorate in silver chlorate decreases as the temperature rises, the heat of solid solution should be positive while the reverse should hold for the other type of mixed crystals. Strictly, this would be true for the heat of solid solution only when the crystals are near their mixing limit, but there is evidence that this value does not change greatly with dilution.

In the present article, we shall give the results of an experimental determination of the heats of solid solution of sodium chlorate in silver chlorate and of silver chlorate in sodium chlorate. The same method has been used in obtaining the heats of solid solution that other investigators have used for a similar purpose. It consists essentially in determining the heats of solution in water of the mixed crystals and of mechanical mixtures having the same empirical composition. The heat of solution of the mechanical mixture minus that of the mixed crystals gives the heat of formation of the latter from the single salts.

The silver chlorate used in this work was prepared by treating precipitated silver carbonate in excess with a solution of chloric acid, filtering and evaporating to crystallization. It was recrystallized before use. The chloric acid required in making this salt was prepared by treating a solution of pure barium chlorate with a calculated amount of sulfuric acid. The solution gave no test for either barium or sulfuric acid. Sodium chlorate was prepared by recrystallizing the commercial product.

Four samples of mixed crystals were prepared, using the data given by Foote[2] as a guide in making up the solutions. Two of the samples were on the sodium chlorate side and crystallized as cubes. The others contained an excess of silver chlorate and were tetragonal. In their analysis, silver was determined as chloride and calculated to chlorate. Sodium chlorate was determined by difference. Following are the analyses of the four samples used:

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[1] Foote, *Am. Chem. J.*, **27**, 345 (1902).

[2] *Loc. cit.*

		$AgClO_3$. %.	$NaClO_3$. %.
1.	Isometric	15.02	84.98
2.	Isometric	30.31	69.69
3.	Tetrahedral	63.79	36.21
4.	Tetrahedral	73.84	26.16

All samples were finely ground and sifted before use. It was necessary to use bolting cloth in place of a metal sieve when silver chlorate was present.

The calorimeter was the one mentioned in the preceding article, and was described by Haigh.[1] The stirrer was made of glass instead of brass to prevent a reaction with the solution. The greatest care was taken to make the conditions in the different determinations as nearly alike as possible. The rate of stirring and the temperature of the water in containing vessel and outer jacket were so regulated that radiation corrections were minimized. The results obtained are given in Tables I–IV.

Table I.—Silver Chlorate in Sodium Chlorate.

15.02% $AgClO_3$. Isometric mixed crystals.

Material.	Weight. g.	t_2-t_1.	Heat capacity of calorimeter.	Heat effect.	Average heat effect. (Calories.)
Mechan. mixture	10.00	—0.929°	513.7	—477.3	—478.1 cal.
Mechan. mixture	10.00	—0.932	513.7	—478.8	
Mixed crystals	10.00	—0.916	513.7	—470.6	—470.1
Mixed crystals	10.00	—0.914	513.7	—469.5	

Table II.—Silver Chlorate in Sodium Chlorate.

30.31% $AgClO_3$. Isometric mixed crystals.

Material.	Weight. g.	t_2-t_1.	Heat capacity of calorimeter.	Heat effect.	Average heat effect. (Calories.)
Mechan. mixture	10.00	—0.893	515.6	—460.4	—462.2
Mechan. mixture	10.00	—0.896	514.6	—461.1	
Mechan. mixture	10.00	—0.902	514.6	—464.1	
Mechan. mixture	10.00	—0.900	514.6	—463.1	
Mixed crystals	10.00	—0.872	515.6	—449.6	—449.4
Mixed crystals	10.00	—0.871	515.6	—449.1	

Table III.—Sodium Chlorate in Silver Chlorate.

63.79% $AgClO_3$. Tetragonal mixed crystals.

Material.	Weight. g.	t_2-t_1.	Heat capacity of calorimeter.	Heat effect.	Average heat effect. (Calories.)
Mechan. mixture	10.00	—0.829°	515.6	—427.4	—429.3
Mechan. mixture	10.00	—0.835	515.6	—430.5	
Mechan. mixture	10.00	—0.834	515.6	—430.0	
Mixed crystals	10.00	—0.886	515.6	—456.8	—456.8
Mixed crystals	10.00	—0.886	515.6	—456.8	

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[1] This Journal, 34, 1144 (1912).

TABLE IV.—SODIUM CHLORATE IN SILVER CHLORATE.

73.84% $AgClO_3$. Tetragonal mixed crystals.

Material.	Weight.	t_2-t_1.	Heat capacity of calorimeter.	Heat effect.	Average heat effect. (Calories.)
Mechan. mixture	10.00	—0.818°	514.6	—420.9	—422.8
Mechan. mixture	10.00	—0.813	514.6	—418.3	
Mechan. mixture	10.00	—0.818	514.6	—420.9	
Mechan. mixture	10.00	—0.829	514.6	—426.6	
Mechan. mixture	10.00	—0.823	514.6	—423.5	
Mechan. mixture	10.00	—0.829	514.6	—426.6	
Mixed crystals	10.00	—0.859	514.6	—442.0	—441.5
Mixed crystals	10.00	—0.857	514.6	—440.9	

From the results given above, we have calculated the heat effect due to the formation of a solid solution by one mol of solute (Table V).

TABLE V.—MOLECULAR HEAT OF SOLUTION.

No.	Type of crystals.	Mols solvent: 1 mol solute.	Heat effect of 10 g.	Molecular heat of solution. (Calories.)
1.	Isometric	10.17 $NaClO_3$	— 8.0	—1019 ($AgClO_3$)
2.	Isometric	4.13 $NaClO_3$	—12.8	—1017 ($AgClO_3$)
3.	Tetragonal	0.98 $AgClO_3$	+27.5	+ 809 ($NaClO_3$)
4.	Tetragonal	1.57 $AgClO_3$	+18.7	+ 761 ($NaClO_3$)

Both molecular heats are small and of opposite sign. The values for the isometric crystals are practically constant, showing that in this case there is little or no heat of dilution. In the other case, the variation, though small, is probably greater than the errors of experiment, so there appears to be a small heat of dilution.

The solubility of each salt in the other at different temperatures, given by Foote,[1] is as follows:

Temp.	Isometric. Molec. per cent. $AgClO_3$ in $NaClO_3$.	Tetragonal. Molec. per cent. $NaClO_3$ in $AgClO_3$.
12°	14.33	50.04
25°	18.45	48.19
35°	21.73	47.92
50°	26.56	47.10

The amount of silver chlorate which can be taken up by the sodium salt to form mixed crystals increases with the temperature. As Table V shows, the process is accompanied by absorption of heat. The reverse is true in the case of the tetragonal crystals. In the relation of the heat of solution to the temperature coefficient of solubility, the law of Le Chatelier is, therefore, applicable to solid solutions as well as to solutions of other types. It may be well to add that, on the other hand, the van't Hoff equation

$$\frac{d \ln C}{dT} = \frac{Q}{2T^2},$$

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[1] *Loc. cit.*

which gives for dilute liquid solutions a quantitative connection between the temperature coefficient of solubility and the heat of solution, does not apply.

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THE DISSOCIATION OF HYDROGEN INTO ATOMS.

Part I. Experimental.

BY IRVING LANGMUIR AND G. M. J. MACKAY.

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Some early measurements[1] of the heat loss by convection from heated tungsten wires in hydrogen showed that the loss increased at an abnormally high rate when extremely high temperatures were reached.

A little later[2] a series of measurements on the heat convection from various kinds of wires in different gases led to a general theory of convection from hot bodies, which makes possible the approximate calculation of heat losses from a wire at any temperature in any gas which behaves normally.

With hydrogen, the theory led to results in close agreement with the experiments, up to temperatures of about 2300° K. Above this, however, the observed heat loss increased rapidly until at 3300° K., it was over four times the calculated value.

This fact suggested that the hydrogen was partly dissociated into atoms at these high temperatures.

In a subsequent paper,[3] the theory of heat conduction in a dissociating gas was developed to apply to this case.[4] It was shown that the power required to heat the wire could be expressed as the sum of two terms, thus:

$$W = W_C + W_D \qquad (1)$$

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[1] Langmuir, *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911).

[2] Langmuir, *Phys. Rev.*, **34**, 401 (1912).

[3] Langmuir, THIS JOURNAL, **34**, 860 (1912).

[4] At the time of publication of the above mentioned paper, I was unaware that Nernst had previously (Boltzman, *Festschrift*, **1904**, p. 904) developed a quantitative theory of the heat conduction in a dissociating gas, and had shown that the heat conductivity of nitrogen peroxide, determined by Magnanini, agreed well with that calculated by his equations from the known degree of dissociation of this substance. Nernst showed that the effect of the dissociation is to increase the heat conductivity of a gas by an amount equal to

$$Dq\frac{dc}{dT}.$$

He does not, however, show that this leads to the very simple and useful form of equation developed by the writer, namely,

$$W_D = SDq(C-C').$$

Nernst points out that the heat conductivity of gases may be used not only to detect dissociation qualitatively, as R. Goldschmidt (Thesis, Brussels, 1901) had shown, but in some cases to determine the degree of dissociation quantitatively. (I. LANGMUIR.)