during the transformation. x-Ray pictures, made at our request by Dr. E. J. W. Verwey[3] at the University of Groningen (Holland), revealed that a precipitate less than fifteen minutes old gave the same pattern as a well aged lead sulfate. The lines in the fresh precipitate, however, were very diffuse and it was roughly estimated that the amicroscopic particles within the microscopic crystals contained at least 1000 to 10,000 molecules.

From the above it is evident that the freshly formed microscopic crystals of lead sulfate have a spongy structure. They consist of primary particles separated by fine capillaries with a diameter of the order of molecular dimensions, which allow a diffusion of thorium B (lead) ions to the internal surface. On aging, a perfection process occurs in the interior of the crystals, resulting in a growth of the primary particles and a decrease of the internal surface. At present it is impossible to approximate these changes of the internal surface with any degree of accuracy, since it may be expected that the capillaries will be filled up with lattice material during the perfection process. It is planned to make an extensive study of the changes of the x-ray pattern during the aging, in order to approximate the magnitude of the internal surface at various stages of the process.

The most important conclusion which may be drawn from the present study is that *lead ions can move freely through the primary amicroscopic crystals and cause a homogeneous distribution of thorium B throughout the entire system.*

The lead ions in the primary particles are not bound to a definite position but have a free mobility, thus allowing all of them to reach the surface at various times and take part in the kinetic exchange process. The present studies are being continued and we hope to be able to throw more light upon the nature of the internal structural changes taking place on aging of freshly prepared lead sulfate.

Summary

1. The exchange phenomena between aging inactive lead sulfate and a radioactive lead solution are identical with those between radioactive lead sulfate and an inactive lead solution.

2. A large excess of lead nitrate in the supernatant liquid diminishes the speed of exchange between the precipitate and the solution.

3. The lead ions in the primary amicroscopic crystals of lead sulfate, even in a precipitate fifty minutes old, can move freely, thus explaining the homogeneous distribution of thorium B throughout the entire system.

MINNEAPOLIS, MINN. RECEIVED MARCH 9, 1934

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[3] At this place we wish to thank Dr. Verwey for his kind assistance.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium and Potassium Dissolved in Gallium

BY E. S. GILFILLAN, JR., AND H. E. BENT

A great many organic reactions of alkali metals or alkali metal amalgams have been studied. One of us has been interested for some time in the addition of alkali metals to organic free radicals.[1] A quantitative thermodynamic treatment of these reactions is possible providing the activity of the alkali metal has been determined in the amalgam used in the investigation. The use of sodium amalgams puts certain limitations on such experiments due to the fact that over most of the concentration range sodium amalgams are solid at temperatures suitable for organic reactions. In the hope of discovering alloys which would have quite different activities of sodium and which would be liquid at room temperature the following investigation was carried out on gallium.

Materials Used

The methods of preparing the various materials have been described elsewhere, with the exception of the gallium.[2] This was purchased from Charles Hardy, 415 Lexington Ave., New York City, at four dollars a gram. The best method of handling the material seemed to be to melt it under a solution of one molar sulfuric acid, then to supercool the vessel with ice water and while still liquid to cut the viscous metal with a glass rod. The pellets were then seeded with solid gallium. Solution of the metal in the acid is very slow. The pellets so prepared were clean and bright and

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(1) Bent, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); Bent and Dorfman, *ibid.*, **54**, 1393 (1932); Bent, Dorfman and Bruce, *ibid.*, **54**, 3250 (1932).

(2) Bent and Gilfillan, *ibid.*, **55**, 24, 3989 (1933).

after washing were dried in a desiccator. Pellets prepared in this manner were used in the early experiments involving large amounts of metal. In the final experiments with galvanic cells it was found necessary to further purify the metal in order to obtain a clean bright surface. Before this treatment the gallium was found to wet glass, not to flow readily, and to give a concave surface in glass tubing. After purification the surface was more convex than a similar volume of mercury, somewhat whiter than mercury and would flow cleanly through glass tubing. The purification consisted in heating the gallium above 800° in a quartz tube in an atmosphere of carefully purified hydrogen. This removed part of the scum which appeared during the heating. The metal was then further heated at a temperature of 1000° and at a pressure of less than 10^{-4} mm. which caused some vaporization of impurities. After cooling, the metal appeared to be perfectly clean. It was found possible to distil the metal slowly in quartz apparatus. However, the quartz sublimed with the metal sufficiently rapidly to prevent the product from coalescing into globules. Gallium was also shaken vigorously with carefully dried ethylamine in order to test for any reaction. Although the solution became dark due to finely divided particles of gallium, most of which settled on standing, there was little indication of reaction.

Sodium Gallium Alloys

These alloys were prepared in an evacuated system. The gallium used was in the form of pellets, and the sodium was run through a constriction to remove surface impurities. The gallium was weighed before the beginning of the experiment. The weight of sodium was obtained as the increase in weight after the apparatus had been sealed off from the line, a ground joint being used in order to give a definite weight of glass. In one experiment 1.9261 g. of sodium was added to 2.9990 g. of gallium. At first the metals seemed to mix without evolution of heat to form a homogeneous liquid. On warming to about 100°, however, the tube suddenly became very hot, the glass turning brown as a result of the high temperature. On cooling a solid crystalline mass was obtained which did not melt on strong heating of the tube in an air–gas flame. The conclusion is that the reaction gave out enough heat to raise the temperature of the mixture to about 400° and that the resulting material was solid at this temperature. The product reacted very slowly with hot 6 *N* sulfuric acid, remaining solid for several days in this solution.

A second experiment with direct mixing also produced a solid which broke the glass tube due to expansion. In this experiment 6.0400 g. of gallium was mixed with 0.0537 g. of sodium.

These experiments indicate that sodium is so insoluble in gallium as to make the alloy of no value for the purposes of organic chemistry. It seemed worth while, however, to determine the minimum amount of sodium which would give a saturated solution and to determine the activity of the sodium in such an alloy.

Two cells, therefore, were prepared using gallium as one electrode and sodium as the other electrode. The gallium was carefully treated as described above in order to give a perfectly clean surface. The electrolyte was sodium iodide in ethylamine. Sodium was electrolyzed into the gallium, the current being measured by placing the total resistance of the potentiometer in the circuit and noting the reading on the potentiometer necessary to balance the standard cell which was placed on the terminals for the unknown. The results are indicated in Table I. After the second addition of sodium the gallium showed a metallic scum on the surface which suggested the formation of a solid phase. The corresponding e. m. f. was found to be 0.702 ±0.001 volt. Addition of more sodium seemed to increase the amount of solid on the surface but did not alter materially the e. m. f. After the fourth day the sodium appeared to be reacting seriously with the ethylamine and on the following day the cell blew up. A second cell prepared in a similar manner gave practically the same results. In order to refer all measurements to 30° the temperature coefficient of the e. m. f. was determined. At 37.8, 31.0 and 25.2° the observed values for the e. m. f. were 0.6971, 0.7100 and 0.7187, respectively. Neglecting the slight change in concentration resulting from the change in temperature this gives for $\overline{H}$ for sodium in gallium the large value of −28 kg. cal.

TABLE I

SODIUM GALLIUM CELLS AT 30°

	Mole fraction of sodium	E. m. f., volts
First cell	0	1.2890
	5.68×10^{-6}	0.7116
After standing overnight		1.23
Metallic scum	3.493×10^{-5}	0.7025
	7.96×10^{-5}	.7012
	1.3×10^{-4}	.7001
Second cell	0	1.2352
Gallium liquid		1.0082
	2.4×10^{-7}	0.787
	4.0×10^{-6}	.7035
	2.4×10^{-5}	.705

TABLE II

POTASSIUM GALLIUM CELL AT 32°

	Mole fraction of potassium	E. m. f. volts
Gallium solid	0	1.248
Gallium liquid		0.926
Metallic scum	6.7×10^{-8}	.767
	3.6×10^{-7}	.756
	9.6×10^{-7}	.758
	3.8×10^{-6}	.686
	2.0×10^{-5}	.653

Much larger currents were then passed through the cell. A very thick scum was produced which partially disappeared on pouring off the ethylamine and heating to

300°. On cooling the scum again appeared and the e. m. f. was the same as that obtained before heating. Large currents were then passed through the cell and the potential measured as quickly as possible after electrolysis. It seemed to be a matter of chance whether a value of about 0.7, 0.3 or 0.0 volt was obtained. These results suggest that perhaps a second compound exists giving the value of 0.3 volt and that in some cases the rapid electrolysis gave a sodium surface. During these experiments the cell was very sensitive to mechanical disturbance.

Potassium Gallium Alloy

Only one cell containing potassium was constructed. The gallium was carefully purified and the potassium was distilled before being admitted to the cell. The results are given in Table II. A scum was visible after the first electrolysis. These data indicate that the solubility of potassium in gallium is probably not more than 6.7×10^{-8} mole of potassium per mole of gallium and that the activity of the potassium corresponds to an e. m. f. of 0.76 volt. The two-phase alloy did not give as constant an e. m. f. as in the case of the sodium as shown by Table II. This may be due to the fact that the concentration of this alloy is much smaller. Some caution is necessary in interpreting the data as one cannot be certain that the alloy is of uniform concentration throughout. This would seem to be the case, however, as agitation had no effect on the e. m. f. Assuming the smallest concentration of alkali metal which first produced a scum to be the concentration of the saturated alloy a value of log a_2/N_2 is obtained equal to about -5 in the case of potassium and -7 in the case of sodium.

Mercury Gallium Alloy

The extremely small solubility of the alkali metals in gallium suggested the desirability of determining roughly the mutual solubility of gallium and mercury. Above 30° two liquid phases were present. Due to the tendency of gallium to supercool an accurate determination of the freezing point is not easy. No lowering of the freezing point of the gallium could be detected although the method used would not have been sensitive to more than three or four degrees. Using a pentane thermometer a definite depression of 0.8° in the freezing point of mercury was detected with a probable error of 0.2°. The thallium-mercury diagram gives a value for the freezing point constant of mercury of 218° per mole fraction. This gives for the concentration of the saturated solution of gallium a mole fraction of 0.004 or expressing the solubility in weight per cent. 0.13. The most concentrated amalgam reported in the literature contained 0.2436% gallium at 19°.[3]

These data may be interpreted in terms of the internal pressures of the metals as described by Hildebrand.[4] A table of internal pressures, as shown by Hildebrand, enables one to predict that two elements having very nearly the same internal pressure will not form two immiscible phases. One cannot, however, from internal pressures predict the existence of compounds. The formation of a compound between sodium and gallium prevents one from drawing any conclusions regarding the mutual solubility of the metals. The insolubility of mercury and gallium in each other, however, should follow from the position of gallium in the table of internal pressures.

There are many ways of estimating the internal pressures of metals. In the case of gallium, however, the various methods do not agree well. Taking the physical constants as determined by Richards and Boyer[5] we find that gallium comes next to sodium in a list of the metals arranged according to internal pressure when the coefficient of expansion and the compressibility are used as a measure of this property. If surface tension is used for placing gallium in such a series we find that it comes next to mercury. Both of these measures of internal pressure would lead to the prediction that gallium would dissolve in mercury. A much better location for gallium in the series is obtained, however, by placing gallium in the table given by Hildebrand, Hogness and Taylor by dividing the boiling point by the atomic volume.[6] Although the boiling point is not known accurately this places gallium between tin and aluminum.

This position for gallium is quite in accord not only with the insolubility of gallium in mercury but with the mutual solubility of gallium and tin. The difficulty in determining the internal pressure of gallium by compressibility[7] or surface tension data may be accounted for by the assumption of association of gallium in the liquid state. The study of the scattering of x-rays from liquid gallium by Menke[8] indicates that such association is present in gallium.

Conclusions

1. The solubility of sodium in gallium at 30° is about 0.001 weight per cent. The activity of the sodium is given by an e. m. f. of 0.70 volt.

2. The solubility of potassium in gallium at 32° is about 4×10^{-6} weight per cent. The e. m. f. from potassium to this alloy is 0.76 volt.

3. The insolubility of gallium in mercury indicates that gallium has a rather high internal pressure, probably about the same as that of tin.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 13, 1934

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(3) Davies and Keeping, *Phil. Mag.*, [7] **7**, 145–153 (1929).

(4) Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, p. 181 *et seq.*

(5) Richards and Boyer, THIS JOURNAL, **43**, 274 (1921).

(6) Hildebrand, Hogness and Taylor, *ibid.*, **45**, 2830 (1923).

(7) Pushin, Stepanovic and Stajic, *Z. anorg. Chem.*, **209**, 329 (1932). These authors confirm our results on the insolubility of gallium in mercury and the formation of a high melting compound of sodium and gallium.

(8) Menke, *Physik. Z.*, **33**, 593 (1932).