

considerations since Dushman's theory certainly has some promise. A more complete theory of monomolecular reaction rate which would allow for the fact that the molecules which react are activated by radiant energy of a whole range of frequencies, and would at the same time introduce something equivalent to the fundamental Dushman hypothesis  $s = \nu$  would be an interesting development.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

### FURTHER STUDIES CONCERNING GALLIUM.

**Its Electrolytic Behavior, Purification, Melting Point, Density, Coefficient of Expansion, Compressibility, Surface Tension, and Latent Heat of Fusion.**

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#### I. Electrolytic Behavior.

**Introduction.**—The study of the electrolytic behavior of gallium naturally had precedence in this investigation, because this behavior had an important bearing on the preparation of the material needed for the rest of the work. The earlier experimenters upon gallium commonly used electrolysis rather as a means of precipitating the metal from purified salts than as a means of purification. In a recent paper, Dennis and Bridgman<sup>1</sup> have pointed out the value of electrolysis for the latter purpose. Independently, we also had simultaneously thus used electrolysis.<sup>2</sup> Whereas the earlier experimenters commonly used alkaline solutions, Dennis and Bridgman, as well as ourselves, worked with more or less acid ones, free from alkali salts, thus eliminating the danger of contamination with alkali metals.

Although in the main the verdicts of the recent researches agree, several obscure points need elucidation before the matter is entirely consistent and comprehensible. The points especially to be investigated were the following: first, the single electrode potential of gallium, and secondly, the order of precipitation of indium, zinc and gallium, with several different current densities from solutions of several different acidities.

**The Single Electrode Potential of Gallium.**—No adequate measurements of this potential appear in the literature, but the element is usually considered as coming between zinc (0.52) and aluminum (1.0), being

<sup>1</sup> Dennis and Bridgman, *THIS JOURNAL*, 40, 1540 (1918). On p. 1537 references to earlier work are given.

<sup>2</sup> Richards and Boyer, *ibid.*, 41, 133 (1919).

nearer to that of zinc.<sup>1</sup> This conclusion is based upon the earlier work of Lecoq de Boisbaudran.

For our measurements an accurate potentiometer, standardized by means of a Weston cell, was used. Cadmium and zinc were also measured against a calomel electrode in order to be certain that the apparatus was functioning properly. The single potential difference of cadmium in normal solution of its sulfate was found to be 0.176, and that of zinc in normal solution of its sulfate, 0.521. Hence the apparatus was adequate. Care was taken, in many of the trials, to have solutions of gallium sulfate neither basic nor with excess of acid, by converting weighed amounts of gallium (through the nitrate and weighed amounts of sulfuric acid) into sulfate. These precautions were, however, probably not necessary, because a small concentration of free acid does not usually much affect a single electrode potential. With amalgamated zinc, for example, 3 *N* sulfuric acid was found by rough measurements to affect the potential by less than 0.05 volt. The potential of the decinormal electrode was assumed to be +0.56 volt. No allowance was made for the unknown solution-solution e. m. f.

In every case gallium showed at first a much smaller negative potential than the final value. With metal which had been exposed for a long time to the air the initial value was even positive (as much as 0.2 volt). In the course of 2 or 3 days the gallium potential gradually attained the maximum value  $-0.297$  in 0.1 *N* solutions; somewhat less ( $-0.25$ ) in *N* solutions, and even less when excess of sulfuric acid was present. 0.1 *N* gallium alum as electrolyte gave about the same potential ( $-0.294$  volt) as pure 0.1 *N* gallium sulfate.

Adequate comparison of the effects of ion concentration, corresponding to the Nernst equation, can hardly be made, because the ion-concentration of gallium sulfate has never been determined. The substance is much hydrolyzed and probably hydrolysis diminishes the concentration of the gallium ion in dilute solution, making a colloidal hydroxide.

Liquid gallium *decreased* in potential with the time of immersion, to a lower value ( $-0.18$ ) than the solid. Resolidification reversed this effect, but the gallium thus liquefied never assumed the value it would have had if its potential had been first determined as a crystalline solid. The decrease was hardly consistent enough to substantiate Rudorf's<sup>2</sup> conclusions concerning the free energy of the liquid, based on Regnault's measurements.<sup>3</sup>

Whichever final value is chosen from the above mentioned results, the

<sup>1</sup> See for example, Abegg's "Handbuch der anorg. Chem.," 3, [1] p. 367 (1906); *Compt. rend.*, 81, 493 (1875).

<sup>2</sup> Rudorf, Abegg's "Handbuch," *loc. cit.*, p. 366.

<sup>3</sup> J. Regnault, *Compt. rend.*, 86, 1457 (1878) (not Regnault, as Abegg gives the name).

single electrode potential of gallium thus measured stands between that of indium ( $-0.10$ ) and that of zinc ( $-0.52$ ). This was one reason for the statement to that effect in our earlier paper, because preliminary measurements of the electrode potential had been made before that paper was published. It will be seen, however, that this outcome gives an incomplete picture of the situation.

Another method of attacking qualitatively the problem of relative electrode-potential is by placing one metal in the solution of the salt of another, in order to determine if the second metal is precipitated at the expense of the first. De Boisbaudran's description of his result in this direction is not easily interpreted, but the simple experiment seemed worth repeating. Accordingly small amounts of fresh electrolytically precipitated zinc were placed in 2 portions of 5 cc. each of *N* gallium-sulfate solution. After 15 hours most of the gallium was precipitated in the form of a voluminous semigelatinous, white basic precipitate. In one case the slight metallic residue (after thorough washing, and the solution of the zinc in very dilute acid), gave spectroscopic evidence of gallium—but the amount was only a very small fraction of the whole, and may have been due to inclusion. Evidently zinc does not precipitate metallic gallium in the definite fashion in which, for example, it precipitates cadmium.

The contrasting experiment of placing gallium in a nearly neutral zinc-sulfate solution was likewise made. After standing for 24 hours, the nugget of gallium showed no sign of a "tree," even in the microscope, and its surface appeared almost, if not quite, as bright as at first. Evidently gallium does not precipitate zinc.

When a solid alloy of gallium and zinc is treated with a little dil. sulfuric acid, both zinc and gallium are dissolved until the acid is exhausted, and no "tree" of either metal forms on the etched and pitted button.

These qualitative experiments leave one still largely at a loss with regard to the electrode potential of gallium. They seem to indicate that this quantity may be nearly the same as that of zinc.

A clue to the answer to the puzzle was afforded by the following experiments. Small fragments of the purest gallium, freshly cut, were placed in solutions of cadmium sulfate and of copper sulfate. Neither fragment showed more than a very slight tendency to precipitate these metals, each of which (especially copper), must have a lower solution tension than gallium. After 6 hours no evidence of precipitation at all was manifest, and even after several days only a few minute spots of copper could be seen.<sup>1</sup> Clearly gallium, like its analogue aluminum,<sup>2</sup>

<sup>1</sup> Afterward, following a suggestion by A. B. Lamb, copper chloride was tried. Here also the precipitation of copper was very slow in starting, but when once started it proceeded more rapidly with the chloride than with the sulfate.

<sup>2</sup> See for example v. Deventer and v. Lummel, *Z. physik. Chem.*, **69**, 136 (1909).

has a distinct tendency to become passive (or "ennobled"), which must vitiate all attempts to determine its true active electrode potential by the methods heretofore recounted. Accordingly, another line of attack was begun.

**The Electrolytic Precipitation of Gallium, Indium and Zinc from Solutions of Varying Acidity and Concentration.**—The outcome of electrolytic precipitation depends, at least in part, of course, upon the electrode potentials of the substances concerned; but it depends also on at least 3 other conditions of electrolysis, namely, on the relative concentrations of the ions, on the current density at the cathode, and on "over-voltage" phenomena.

The effect of the concentration on the cation, as expressed by the Nernst equation, is well known. The solution tension of the solid metal is assumed to remain constant, but the effect of the opposing osmotic pressure of the cation increases with its logarithm; hence the single electrode potential decreases when the cation becomes more concentrated. For a trivalent ion such as indium or gallium, the theoretical increase in electromotive force is about 0.02 volt for each 10-fold dilution at room temperatures. In order to change the electrode potential by as much as 0.1 volt, the solution must obviously be diluted to at least one hundred thousand times its original volume (or possess a concentration of 0.00001 of its original concentration). Hence this effect cannot play a very important rôle in causing 2 metals 0.2 or 0.3 volt apart in the electrochemical series to appear together.

As an example of the combined effect of changing current density and "over-voltage," the following fact may be cited. Zinc, although commonly possessing a far greater solution potential than hydrogen, can be precipitated in part from normal solution of the sulfate in the presence of 2 *N* sulfuric acid by a current density of 0.4 amp./cm<sup>2</sup>, whereas this precipitate will redissolve while the current is running if the current density is reduced to 0.2 amp./cm<sup>2</sup>. In brief, there is a fairly definite relation between the current density, the concentration of the acid and the concentration of the metal which remains in solution after long-continued electrolysis. These considerations are of importance in interpreting the separation of metals electrolytically, especially if conclusions concerning relative electrode-potentials are sought.

The following experiments upon the electrolytic deposition of gallium, indium and zinc, separately and together, were comprehensive, but will be summarized as briefly as possible. In all of these experiments sulfuric acid was present in definite, but not always identical, excess over the amount corresponding to the bases present. As the electrolysis proceeded, sodium hydroxide was added in amounts needed to neutralize the acid formed and keep the hydrogen-ion concentration about constant.

The nature of the electrolytic precipitate was determined partly by its melting point, but usually by spectrum analysis. The 3 metals chiefly concerned (gallium, indium and zinc) give clear spark- and arc-spectra, alone or together; our experience agrees with that of Dennis and Bridgman in showing that very small traces of each metal may be detected in the presence of the others. The characteristic lines, being in the blue and violet, are all easily photographed. Our comparisons were made almost entirely in this way with a good glass-prism spectrometer. The metals were volatilized by an arc-spark obtained from a half kilowatt transformer from the 110 volt, 60 cycle, alternating current of the laboratory. The spark was intensified by a suitable condenser in parallel with the transformer, and the air lines were cut out by adequate inductance. Platinum points about 2 mm. in diameter were used as terminals of the spark gap and the metals to be analyzed were precipitated electrolytically directly upon the terminals, although these were not the electrodes of the fractional precipitation. Blank tests were frequent.

To recount first experiments upon the metals taken separately:

Comparable results were obtained with platinum foil electrodes of 8 sq. cm. area and 0.3 ampere current (that is, an approximate current density of 0.04 amp. per sq. cm.). The volume of the solution in each case was about 100 cc. or less, and during the electrolysis each was continuously and thoroughly stirred by a mechanical stirrer. The amounts of indium, zinc and gallium originally present were respectively about 0.4 g.; 0.2 g. and 0.1 g. The precipitated metal was completely transferred electrolytically from time to time to the spark gap terminals. With solutions of 0.2 *N* acidity, about 0.6 mg. of indium remained per 100 cc. solution after 12 hours' electrolysis, 4 times as much zinc and almost all the gallium present. Electrolyzed in solutions of 0.1 *N* acidity, all the indium was precipitated in 16 hours, about 1.2 mg. of zinc remained per 100 cc. solution after similar treatment, and distinctly more (90 mg. per 100 cc.) of the gallium. Zinc in a new trial was very nearly all precipitated in 8 hours from a solution of 0.05 *N* acidity, whereas 0.025 g. of gallium remained per 100 cc. of such solution after 13 hours. In a fourth trial, after 17 hours even from a 0.04 *N* acid solution, gallium was not fully precipitated, one mg. remaining per 100 cc. of electrolyte.

The results with more concentrated acid pointed in the same direction and need not be recounted in detail. No metal at all was precipitated by this low current density from a solution containing 0.4 g. per 100 cc. and 1.7 *N* in sulfuric acid; very little indium, less zinc and no gallium from such a solution normal in sulfuric acid; and nearly all the indium, most of the zinc and very little gallium even from a solution 0.5 *N* in sulfuric acid.

These results are all consistent; they point indubitably to the following order of precipitation: indium, zinc, gallium, and indicate that, whatever the cause, gallium has a considerably higher deposition-potential than zinc in these acid solutions. But this result is inconsistent with the direct potential—measurements already recounted—for these placed gallium between indium and zinc.

Turning now to the electrolysis of mixtures, the following methods were used and results obtained.

The volume was in each case about 0.5 liter; the same current density as before (namely 0.04 amperes per sq. cm.) was maintained; and the acidity was initially 0.15 *N*. When precipitation was almost finished the acidity was reduced in order to recover all of the gallium. Six successive electrolyses of mixtures were conducted. In every case zinc was detected in the first precipitate (which was chiefly indium) and it was found at every stage of the electrolysis, successive portions of the precipitate being taken out and examined spectroscopically. Evidently indium and zinc are too near together to allow easy electrolytic separation, although theoretically their electromotive ranges should not seriously overlap; and the same is true of gallium and zinc. But in every case gallium began gradually to appear only after most of the indium had been precipitated. Hence these two metals are far enough apart to be easily separated.

Similar results were obtained with platinum points giving much greater current density, in strongly acid solutions. When a platinum point is used for deposition instead of a foil, the current density is so great that the ionized hydrogen in the immediate vicinity of the electrode is not enough to carry the current even when the solution is strongly acid. Hence other cations of greater solution potential may come down with the hydrogen. By preference, of course, those with smallest negative solution potential come out first. Thus with a platinum point in 5 *N* sulfuric acid, we found that almost pure indium with melting point 155° came first out of a mixture of the 3 metals under consideration, if sufficient current density were used to precipitate anything besides hydrogen.

When only a small amount of zinc was present in the electrolysis conducted in this way, most of it appeared in the final deposit obtained after neutralizing the free acid. This fact is in accord with the results obtained with zinc alone, in which it was shown that this metal cannot be precipitated completely by current density 0.04 from a solution 0.1 *N* in acid.

Thus there is no real inconsistency between our results and those of Dennis and Bridgman. Different conditions produced different results. The amount of zinc in the specimen involved in our early trials was so small that little of it could be deposited by the current density and with the acidity then employed. Hence most of the zinc remained in the electrolyte to the end and the order of deposition in this case was gallium, indium, zinc, as stated. The fact that most of the zinc was deposited in the early part of the electrolysis of Dennis and Bridgman is easily explained if their solution (as is probable from their description) was decidedly less strongly acid than ours.

The explanation of the apparent inconsistency between the relative magnitude of the electrode-potentials and the order of actual deposition seems to indicate that gallium possesses a larger negative electrode-potential in the act of depositing from a solution than it possesses when actually deposited. In other words, it probably possesses some degree of "passivity" when in a metallic state, as already indicated by other tests. This conclusion is supported by the fact that gallium is markedly passive toward dil. nitric acid, although it dissolves in conc. nitric acid. It seems to occupy a place, in this respect, between indium, which dissolves easily in nitric acid of any concentration, on the one hand, and aluminum, which is passive towards dilute sulfuric and conc. nitric acid, on the other hand.

Our experiments on electrode-potential indicated that liquid gallium is even more passive than the solid. This agrees with the fact that liquid gallium is less easily attacked by acids than solid gallium, although this fact may be due, as Rudorf has pointed out,<sup>1</sup> merely to the possession of more points of attack in the solid. All these questions will receive more detailed examination here in the near future. An answer to the vexed question as to the cause of passivity in general, or of this case in particular, is left in abeyance for the present.

## II. Purification of Gallium.

The foregoing statements make clear the advantage of electrolysis as a first step in purification. The elimination of indium and all metals of lower solution tension is easy by this means. Accordingly this method was used as an initial step in the purification of the large quantity of gallium needed later for determining the properties of this substance.

The choice of electrodes for electrolysis was made with care. The liquid metal alloys with silver, making it brittle; and the deposited gallium contains dissolved silver. Hence this metal is entirely unsuitable. Iron seems to show in less degree a similar effect, except that the solid alloy is soft instead of being brittle. Gallium alloys slightly even with platinum foil, which is blackened afterwards by acid. Moreover, the liquid gallium removed from this platinum foil may contain traces of platinum.

A point of wire is evidently safer than a large piece of foil, since the action of one metal upon the other can take place only on the surfaces where they adjoin. Thus gallium from an iron point was found to contain no appreciable iron. That from a platinum point is even safer, since platinum is attacked less than iron is. Finally, in preparing our purest material we used as the electrode a gallium cathode contained in a cup and making contact beneath its surface with a platinum point of minimum dimensions.

During the electrolysis of a solution of the raw material (a crude gallium indium alloy) the hydrogen evolved was found to give a mirror in the Berzelius-Marsh apparatus. Part of this sublimate was shown to be arsenic, and germanium was indicated by the line 4033, although the two more prominent lines, 4227 and 4180, were often absent. A line very close to 4058 was likewise found. This was most probably due to lead, although this metal does not ordinarily form a volatile compound with hydrogen on electrolysis. It is true that Panett and Fürth<sup>2</sup> state that they have found such a compound (the particulars to be given later) but we have not been able to reproduce it. Whether the apparent presence of lead and also trace of zinc in the Marsh-Berzelius mirror were due merely to the spattering (which, however, had been carefully guarded

<sup>1</sup> Rudorf, Abegg's "Handbuch," *loc. cit.*

<sup>2</sup> Panett and Fürth, *Ber.*, 52, 2020 (1919).

against) or to traces of volatile compounds we do not pretend to decide. That arsenic was present there could be no doubt. The spectrum was compared with the spectrum of pure arsenic in a Plücker tube at 220° to 230°, taking the helpful precautions of Herpertz.<sup>1</sup> The suitable vacuum was obtained by a Langmuir pump.

Incidentally, mention may be made of a black precipitate consisting chiefly of gallium, and of a spongy aggregation which appears at the cathode under some conditions, the latter especially when the solution is almost neutral. It was easy to prove that both consisted of metallic gallium mixed with a trace of basic salt and bubbles of hydrogen which prevent its complete coherence.

Gallium deposited from the solution of the crude liquid alloy, when most of the indium had been separated electrolytically, contained considerable zinc. This could be, in part, eliminated by fractional electrolysis, but the process is slow, as may be inferred from the foregoing account.

Two methods were therefore employed which were found to be effectual in removing the last trace of this metal, namely, ignition at a red heat in a vacuum (when zinc distils by virtue of its lower boiling point) and fractional crystallization of the gallium with centrifugal draining (when all heteromorphous materials remain in the liquid).

The purification by heating in vacuum is most conveniently carried out by placing the electrolytic metal in a silica boat enclosed in a silica tube and heating for several hours in a good vacuum until the boat-load remains almost constant in weight. Complete constancy is not attained, since gallium itself is slightly volatile at 800°. The sublimate was shown by suitable qualitative tests to consist chiefly of zinc. The residue from this treatment must still have contained a trace of some unknown impurity since its melting point was still not quite constant.

Fractional crystallization of the metal was the method used to complete the purification. Liquid gallium, supercooled to a temperature slightly below its true freezing point, was inoculated with a trace of the solid phase, introduced on a platinum point. Crystals of gallium 4 to 6 mm. in length were allowed to form slowly. Consisting of the purer gallium, these crystals were removed, but upon their surface they carried some of the less pure liquid. This was removed by means of a hand centrifuge, the inner vessel of which consisted essentially of a test-tube with a much constricted place near the bottom. The crystals of gallium rested upon the constriction, and the liquid was driven by centrifugal force through the narrow opening, while the test-tube, resting upon a pad of cotton wool in a hollow wooden cylinder attached to a stout leather strap, was whirled in a 2-meter circle. Before the slightly warm glass vessel was placed in the wooden receptacle the latter had been warmed to 32° in order to prevent solidification of the adhering liquid before the centrifuging was complete. Two or 3 successive recrystallizations were enough to bring the purest fraction to a constant melting point, but in order to economize the small amount of fairly pure electrolytic material at our disposal as much as possible, many systematic recrystallizations from the mother liquors were conducted, thus purifying more of the gallium.

In all 10.4 g. of pure gallium of constant melting point (that is, showing no change in melting point from the beginning to the end of liquefaction)

<sup>1</sup>Herpertz. *Dissertation*, Bonn, 1906.



was separated from about 15 g. of the less pure electrolytic metal. This specimen was called Sample E.

### III. The Melting Point of Gallium.

De Boisbaudran, in successive trials, at first found the melting point of gallium to be  $29.5^{\circ}$  and later  $30.15^{\circ}$ , with very small amounts of material.<sup>1</sup> More recently Browning and Uhler<sup>2</sup> found the value  $29.7^{\circ}$  by reading the temperature at which globules of solid gallium fell through a slightly smaller platinum ring. Neither experimenter mentions the precautions taken with regard to standardizing the thermometers; and judging from our experience, probably neither had perfectly pure gallium.

Our own preliminary experiments, made by watching a crystal of the metal (either at the bottom of a small test-tube or suspended in a ring immersed beneath a slowly changing bath) usually gave too high results because of convection currents, and the lag in temperature of the metal. Methods of this sort led to the value  $30.8^{\circ}$  (which we found subsequently to be about a degree too high) for the melting point of our best gallium. An accurate determination of a melting point can hardly be made unless enough of the substance is at hand wholly to surround the registering instrument with a mixture of the 2 phases whose equilibrium is concerned. Therefore we did not succeed in obtaining satisfactory values until we used a much larger quantity of the metal.

Two methods were finally employed. First, the gallium was melted in a small air-jacketed test-tube in an easily adjustable thermostat, after the fashion of the Beckmann freezing-point apparatus, or that so often used by one of us for taking transition temperatures.<sup>3</sup>

In this apparatus about 10 g. of the best gallium was used. Its melting point remained constant until only a very few crystals remained.

Another method which gave precisely the same result consisted in determining the temperature at which a glass-stoppered dilatometer, filled with a mixture of crystallized and liquid gallium under water, showed neither decrease nor increase in the volume of its contents with time. About 8.5 g. of crystallized gallium was used. The water was pure and was freshly boiled and quickly cooled; so prepared it does not oxidize gallium seriously in a few hours. The scale on the capillary of the dilatometer showed change of about 0.4 mm. during the melting of 0.01 g. of gallium. The dilatometer was immersed to the beginning of the index tube in a thermostat at  $29^{\circ}$ , and the temperature was slowly raised until melting was indicated by the sinking of the water level in the capillary. After perhaps a quarter of the metal had melted, the temperature was slowly lowered until the column remained stationary.

The small thermometer used with each method was very carefully standardized with reference to the Parisian hydrogen scale through one of the Harvard Baudin thermometers, both being read with a cathetometer to within perhaps  $0.002^{\circ}$ .

The direct determination of the melting point in the small Beckmann

<sup>1</sup> *Compt. rend.*, **82**, 1036 (1876); **83**, 611 (1876).

<sup>2</sup> *Am. J. Sci.*, [4] **42**, 389 (1916).

<sup>3</sup> See for example, Richards and Wells, *Proc. Am. Acad.*, **38**, 431 (1902); *Z. physik. Chem.*, **43**, 465 (1903).

apparatus gave the value  $29.752^\circ$  for the melting point. With the dilatometer method, at  $29.755^\circ$ , the column slowly descended, whereas at  $29.745$  it slowly rose, indicating the value  $29.75^\circ$  as the true melting point. Since the 2 methods agreed, this value ( $29.75^\circ$ ) may be taken as correct for the purest gallium which we have thus far prepared.

#### IV. Density of Solid and Liquid Gallium.

The striking expansion of gallium upon solidifying is of peculiar interest, since this property is possessed by so few substances. Some previous investigators have ascribed it to the presence of impurities.<sup>1</sup> The work which follows shows, however, that undoubtedly the purest gallium behaves in the same way as the somewhat impure metal first studied.

The form of pycnometer employed was that used recently in the determination of the density of lead isotopes.<sup>2</sup> All the usual precautions were taken to insure constancy and definiteness of temperature, absence of air bubbles (the pycnometer was filled in a vacuum) and protection from evaporation. Both the solid and liquid gallium were weighed under freshly boiled and quickly cooled pure water. Without precautions, gallium on solidifying in a pycnometer invariably breaks it by the expansion which then occurs; but if the pycnometer is constantly agitated during slow cooling the crystalline mass does not attach itself to the vessel, nor subject the walls to outward pressure. If solidification against the walls begins to take place, it is easily overcome by partial melting and resolidification. When the density of the liquid was determined after that of the solid, the pycnometer was placed in an evacuated vessel in order to remove any trace of hydrogen which might have been formed by the long standing under water. Promptness is advisable since even with the purest water a slight action takes place after a number of hours and, of course, both bubbles of gas and the film of oxide cause a decrease in the observed density of the metal.

The densities of a number of samples were determined. The first sample, A, contained several per cent. of indium and a trace of zinc. It was obtained from the hydroxide dissolved in sodium hydroxide, which carries with it indium hydroxide. From Sample B most of the indium had been removed by fractional electrolysis. Sample C had been refractionated electrolytically from a solution 2 *N* in free sulfuric acid and the metal had been heated in a vacuum for 3 hours to expel zinc. Sample C<sub>2</sub> was another preparation of the same kind. Neither was entirely free from impurities. Therefore Sample D was prepared with much greater care by fractional electrolysis, but it began to melt on the surface  $0.2^\circ$  below the true melting point of gallium. Sample E, the purest, has already been described above.

The results for the density of the less pure material need not be given in full, but will be summarized.

Sample A (containing indium) was found, as an average of a number of determinations, to have the density of 6.162 as liquid at  $29^\circ$  and 5.975 as solid at  $20^\circ$ . No great difference was observed between the metal thus solidified in the pycnometer or solidified in air a little below the melting point on a block of paraffin. On the other hand, this impure gallium when solidified by dropping into cold water from a pipet, was found to give a lower result, about 5.90, probably due to included water, but possibly to be referred to the sudden solidification of a more bulky unstable alloy, which may not appear when the cooling is slow. Correcting the values for the solid to  $29^\circ$  by means of the coefficient of expansion, mentioned later, the value at  $29^\circ$  is found to be 5.974.

<sup>1</sup> See Rudorf, Abegg's "Handbuch," *loc. cit.*

<sup>2</sup> Richards and Wadsworth, *THIS JOURNAL*, 38, 222 (1916).

The change in specific gravity of this impure sample on melting is therefore found to be 0.188; of Sample B, considerably purer, the change at 29°, corrected in the same fashion, was from 5.893 to 6.084, or 0.191; for Sample C (several preparations) the average for 4 determinations of the solid was found to be 5.889, whereas 4 determinations of the liquid gave the value 6.079, a difference of 0.190.

Sample D, which was very nearly, but not perfectly, pure, gave, with 3 different preparations, the following values (2 apiece) for the liquid at 29.8°, 6.090, 6.094, 6.093, 6.097, 6.098, 6.099; an average of 6.095, whereas for the solid at 29.6°, the following 5 values were found: 5.907, 5.908, 5.907, 5.905, 5.903, an average of 5.906, and a difference of 0.189.

The last and purest sample, E, gave essentially identical results, which are given in full in the following table. In these cases, the gallium was introduced into the pycnometer in the liquid state and solidified there under pure boiled water. The density of the solid was determined at 29.65° and that of the liquid at 29.8° on the hydrogen scale.

## DENSITY OF GALLIUM.

(Liquid.)							
No.	Obs. wt. Ga.	Wt. in vac.	Wt. H <sub>2</sub> O in vac. not displ.	Corrected. vol. H <sub>2</sub> O.	Vol. pyc.	Vol. H <sub>2</sub> O displ.	Dens. W/V.
1.....	9.0447	9.0452	5.8956	5.9209	7.4056	1.4847	6.092
2.....	9.0447	9.0452	5.8959	5.9211	7.4056	1.4845	6.093
3.....	10.1864	10.1870	5.7104	5.7348	7.4056	1.6708	6.097
4.....	10.1864	10.1870	5.7103	5.7347	7.4056	1.6709	6.097
							Av., 6.0947
(Solid.)							
1.....	9.0447	9.0452	5.8493	5.8740	7.4056	1.5316	5.905
2.....	9.0447	9.0452	5.8487	5.8734	7.4056	1.5322	5.903
3.....	10.1864	10.1870	5.6563	5.6802	7.4056	1.7254	5.904
4.....	10.1864	10.1870	5.6558	5.6797	7.4056	1.7259	5.903
							Av., 5.9037

The respective densities of pure liquid and solid at the melting point are, therefore, 6.0947 and 5.9037, the difference being 0.191; and the respective specific volumes of the 2 states of the metal are 0.16408 and 0.16939 cc., the difference being 0.00531 cc. Allowing for its coefficient of expansion, the density of the solid at 20° may be taken as 5.907 and its atomic volume as 11.85, if the atomic weight is 70.1.

Evidently, since the further purification between D and E produced no essential change in the density of either solid or liquid, and since the substance last measured had been heated for a long time in vacuum and purified by crystallization, the densities recorded above for the gallium in the 2 states cannot be far from the truth. The following table, reiterating the change of density on crystallization in the several specimens of increasing purity, shows conclusively that the impurities have nothing to do with the change of volume, since the variations are not greater than the possible variation due to experimental error.

Sample.	Average density. Solid.	Average density. Liquid.		Difference between density of solid and liquid.
A.....	5.974	6.162	} More or less	{ 0.188
B.....	5.893	6.084		
C.....	5.889	6.079	} impure	{ 0.190
D.....	5.906	6.095		
E.....	5.904	6.095	Fairly pure	0.189
			Very pure	0.191

Supposing that no great contraction or expansion takes place when indium is dissolved in gallium (which seems reasonable because of the similarity of the 2 metals), the percentage of indium in Sample A (its specific gravity being 7.31), is easily calculated approximately from the liquid to be 5.6% and from the solid to be 4.8%. Evidently, Sample A must have contained about 5% of indium. If contraction occurred on the solution of one metal in the other, the percentage thus calculated would be higher than the true value, and *vice versa*.

### V. The Cubical Coefficient of Expansion of Gallium.

The direct measurement of the linear expansion of solid gallium was not easily made with the small amount of metal at hand, and, therefore, the cubical coefficient of expansion was found by determining the density of solid gallium at 0.1° and 29.65°. The volume of the pycnometer also was determined at 0.1° in order that any errors due to manipulation, to possible condensation of moisture on, or evaporation from, the pycnometer, etc., should be equalized. In this way in 5 experiments (from which the danger of condensation was excluded by warming the pycnometer before drying and weighing) the density varied between the extremes, 5.912 and 5.915, in average 5.9134 at 0.10° C., whereas the density at 29.65° had been found to be 5.9037. The increase in density is thus 0.0097, which corresponds to a cubical coefficient of expansion of 0.000055 or a linear coefficient of expansion of 0.000018.

Of course any value obtained in this way has a large probable error, but it is better than nothing. This value is about  $\frac{1}{3}$  that for sodium, somewhat less than that for magnesium, aluminum, cadmium, thallium or zinc, but not far from that for copper and silver. It is about midway between the values for zinc and arsenic, as would be expected from the fact that the atomic volume of gallium is also approximately midway between those of these 2 metals, near it on opposite sides in the periodic table.<sup>1</sup>

### VI. The Compressibility of Gallium.

The method and apparatus have already been described in detail.<sup>2</sup> The form of piezometer first used for the liquid was essentially like that

<sup>1</sup> Richards, "Concerning the Compressibilities of the Elements, and Their Relations to Other Properties," *THIS JOURNAL*, **37**, 1643 (1915); correction, **37**, 2696 (1915).

<sup>2</sup> For example, Richards and Jones, *ibid.*, **31**, 161 (1909).

employed for determining the compressibility of the rubidium-potassium alloy.<sup>1</sup> If solidified in this apparatus the gallium, of course, would have burst the containing tube. For this reason gallium was cast in a separate small glass tube, producing a cylinder of the metal from which the broken fragments of glass were wholly removed. This cylinder was placed in a slightly larger test-tube, and this latter tube was capped with a long glass cap. The whole was then placed in a still larger test-tube that came almost to the top of the cap, and a platinum wire held the combination together. In this way solid gallium could be compressed under mercury, but protected from this liquid by the toluene underneath the cap. The contrivance was less simple than that used later for determining the compressibility of indium,<sup>2</sup> but was adopted in this case for fear of melting the gallium accidentally, when it would have immediately amalgamated with the mercury.

The weighing of the toluene and mercury (which had been purified by usual methods) was effected as follows. The cylinder of the solid metal was placed in the inner test-tube and this tube was next filled with toluene in a vacuum. The cap (filled with toluene) was then placed over the test-tube while immersed in a larger vessel containing toluene, and the capped tube was placed in the larger test-tube while still under the liquid. After wiring the tubes together, a weighed quantity of mercury was finally added to the outer tube, replacing the toluene, and also holding the toluene beneath the cap. Enough toluene was displaced so as to make sure that no more would be liberated from the cap accidentally, and all the toluene was removed from the surface. Since the weights of the glass, gallium and mercury were known, that of the toluene was found very simply by the difference. It is necessary in such a case to know the weight of the toluene with great accuracy since its compressibility is thirty times as great as that of gallium.

The assembled apparatus was suspended in a piezometer, essentially like that used in earlier researches.<sup>3</sup> The samples of gallium of which the compressibility was determined have already been described as Sample C. The purest sample, E, could not be used for this work, since there was not enough of it; but the amount of impurities could not have been enough in Sample C to exceed the probable error of measurement in its effect.

Following are the complete data of 2 determinations of gallium, together with the measurements made with the piezometer alone. The figures in the last column, for the range 100 to 400 megabars,<sup>4</sup> were taken from curves carefully drawn through the points defined by the preceding data.

In order to apply the large correction due to the presence of the toluene, 26.538, 25.719, and 25.939 g. of this hydrocarbon were compressed separately in Piezometer II and found to need mercury additions of 11.105, 10.578 and 10.820 g., respectively, between 100 and 500 megabars. Subtracting from each the value which was obtained in this piezometer with mercury alone (0.249 g.) and dividing by the weight of toluene in each case, values for the difference in added mercury over this pressure range pro-

<sup>1</sup> Richards and Stull, *Carnegie Inst. Pub.*, **76**, 19 (1907).

<sup>2</sup> Richards and Sameshima, *THIS JOURNAL*, **42**, 49 (1920).

<sup>3</sup> Richards and Stull, *Carnegie Inst. Pub.*, **76**, p. 11, pattern V, Fig. 2.

<sup>4</sup> The megabar is the "absolute atmosphere," or 0.983 of the ordinary "atmosphere."

duced by one g. of toluene, 0.409, 0.402 and 0.408 are obtained, in mean 0.406. The presence of the additional glass had an effect (in the contrary direction) of 0.0032 per g. These values were substituted in the equations<sup>1</sup> already given.

DATA FOR COMPRESSIBILITY OF SOLID GALLIUM (AT 20°).

I. Piezometer I with 429.2 g. mercury alone.

Press. range.	Wt. Hg.	Press. range.	Wt. Hg.	Wt. Hg. for 400 megabars.
99.0-283.7	(0.1256)	283.7-478.7	(0.1263)	0.264
99.7-299.9	(0.1334)	299.9-495.9	(0.1245)	0.261
90.6-305.6	(0.1412)	305.6-499.0	(0.1236)	0.259

Av., 0.261

II. Piezometer I with 23.42 g. solid gallium, 0.871 g. toluene and 5.86 g. glass test-tube container.<sup>a</sup>

88.0-359.3	(0.2397)	357.3-496.3	(0.5428)	0.560
115.0-275.0	(0.2397)	275.0-505.3	(0.5428)	0.561
130.6-302.8	(0.2505)	302.8-513.5	(0.5299)	0.564

Av., 0.562

III. Piezometer I with 19.47 g. solid gallium, 0.858 g. toluene and 5.86 g. glass.

115.9-298.0	(0.2638)	298.0-510.1	(0.2716)	0.548
107.1-303.9	(0.2829)	303.9-494.1	(0.2472)	0.549

Av., 0.548

<sup>a</sup> One of these trials was rejected as obviously in error, probably from a mistake in weighing.

Thus 2 values for the compressibility of solid gallium are obtained: 0.0000024 and 0.0000016—in the mean 0.0000020. The comparatively poor agreement of the results is to be regretted; it is probably to be ascribed to the complication and consequent size of apparatus, adopted because of the low melting point of gallium. Although only preliminary, these results are, nevertheless, worth recording, since they are the only results for this constant which have been obtained.

Determinations of the compressibility of *liquid* gallium were less satisfactory and need not be recounted in detail; but they showed indubitably that liquid gallium is far more compressible than the solid, although it is more dense. The average of 2 determinations was nearly 0.000004—about the value for mercury. This is an interesting example of the rule to which no exceptions at moderate pressures have as yet been found: that liquids are more compressible than their solids.

### VII. The Surface Tension of Liquid Gallium.

Mention has already been made, in brief extracts,<sup>2</sup> of the work on the surface tension of gallium; the work is now to be described. For the

<sup>1</sup> The most convenient for this purpose have the form given in THIS JOURNAL, 37, 471 (1915), with the addition of another term,  $0.0032 \times 5.86$  in the parenthesis in the numerator to account for the glass container within the piezometer.

<sup>2</sup> See *Carnegie Inst. Year Book*, No. 18, 327 (1919).

present purpose the flat-drop method often used for mercury<sup>1</sup> is the most suitable, since, because of the property of adhering to glass possessed by gallium, the capillary-rise method could not be conveniently employed.

The flat-drop method consists in measuring the height between the greatest diameter of a large, flat drop resting on a horizontal surface and the highest level of the top of the drop, which must be large enough to have a perfectly flat surface in the middle. The drop, of course, must rest upon a surface which it does not "wet."

The mathematical expression for the computation of the surface tension reduces from a very complicated form to the simple equation  $2\gamma = SA^2$ , where  $\gamma$  is the surface tension,  $S$  the density of the substance at the temperature employed, and  $A$  the height in millimeters above the maximum diameter.

The work of Laplace,<sup>2</sup> Quincke<sup>3</sup> and Meyer<sup>4</sup> may be merely mentioned. Heydweiller,<sup>5</sup> like Quincke, called attention to the necessity of a large drop and further proved that the form of a solidified drop was of little use in determining the surface tension of a solid. Stöckle<sup>6</sup> showed that after remaining for hours in contact with a gas, the liquid usually showed a smaller surface tension than at first, the final values agreeing essentially with those observed in a vacuum. Evidently, then, one must wait until constancy is attained.

In our own experiments the gallium of which the surface tension was to be determined was supported on a plane surface at the bottom of a small box immersed under the water of an accurate thermostat and fed with an atmosphere of pure carbon dioxide. The box was of iron about  $15 \times 8 \times 10$  cm. On its front side was cemented a small plane window of optical glass and in the rear a somewhat larger window pane was secured. Both were sealed into place by a water-tight paste made from litharge and glycerine, protected by a thin coating of paraffin. The top of the metal container was closed with a piece of mica with a small hole for introducing the metal.

The plane surface employed for supporting the liquid metal was at first a block of paraffin, later a block of hard wood and finally, when contamination from this substance was feared, a small block of gas carbon. Paraffin becoming somewhat softened at  $30^\circ$  adheres slightly to the gallium, and even hard wood was not wholly free from this difficulty, but carefully smoothed and polished gas carbon proved to a wholly satisfactory support. The box was coated both inside and out with paraffin to preserve the gallium should it be accidentally displaced, and to prevent rusting and leaking. The carbon dioxide was passed through a U-tube immersed in the thermostat in order that it might enter at the constant temperature. The thermostat itself, consisting of a large square metal box, had a window of plane optical glass both in the front and the rear. Very great care was taken to have the front pane and that of the container box

<sup>1</sup> See for example, Chwoison, *Lehrb. Phys.*, 1, 602 (1902).

<sup>2</sup> Laplace, *Mec. Cel.*, 4, 538 (1845).

<sup>3</sup> Quincke, *Pogg. Ann.*, 105, 38 (1858).

<sup>4</sup> Meyer, *Wied. Ann.*, 53, 845 (1894).

<sup>5</sup> Heydweiller, *Ann. Phys. Chem.* 65, 311 (1898); see also Gnadenwitz, 67, 467 (1899).

<sup>6</sup> Stöckle, *Wied. Ann.*, 66, 499 (1898).

vertical and exactly parallel in order that there might be no error from refraction. This was accomplished optically by measuring by means of a perfectly horizontal telescope (that of the cathetometer used later for measuring the height of the drop), the position of a distant spot of light (on a level with the telescope), as reflected in these glasses. The carbon dioxide employed was made from pure marble and purified by a saturated solution of sodium hydrogen carbonate (the water having been boiled to free it from dissolved oxygen) and conc. sulfuric acid. Air must be excluded wholly in order to prevent oxidation of the gallium. The purest sample of gallium employed was Sample E already described; melting at  $29.75^{\circ}$  it must have been very nearly, if not quite, chemically pure.

Mercury also was measured, to serve as a check. Several samples were employed, the best having remained for sometime under sulfuric acid with agitation and also having been sprayed 6 times through a tower containing dil. nitric acid as well as finally through one containing water to remove the acid. The mercury was subsequently dried in a large evaporating dish, distilled in a partial vacuum, and filtered.

Before reading the height of the drop the liquid metal was allowed to remain on its carefully levelled platform in the small thermostatted container with the perfectly vertical window until constancy was surely reached. No change was observed with gallium after 20 or 30 minutes, although usually at least an hour was allowed. Mercury attained constancy even more promptly than gallium. The drop of the latter metal must be occasionally shaken and even stirred on top with a glass rod introduced through a tube from the top, otherwise inconstant values, above the final constant one, are obtained. Perhaps a very thin quite invisible film of oxide sometimes formed and exerted a disturbing influence, in spite of the great pains taken to exclude oxygen. Of course the drop must be perfectly dry and wholly free from acids.

The measurement of the height of the drop above the point of maximum diameter was usually made by locating the latter with the help of a small carbon-filament lamp on the level with the telescope. A brilliant point of light obviously appears on the desired level and it is easy (especially if the aperture of the object glass of the telescope is much reduced in diameter) to measure the distance between this point of light and the flat top of the drop. The measurement was made by an accurate eye-piece micrometer which was standardized by moving the telescope exactly 1 mm. and counting the number of turns of the micrometer head necessary to bring the image back to the cross hair once more, or by actually measuring a metal rule in the thermostat at the same distance from the telescope as the drop of metal to be measured. Both methods gave essentially the same result for the standardization of the micrometer.

In order to test the size of drop necessary to give the maximum height, drops of mercury varying from 1.6 to 23 g. in weight were measured, and of gallium varying from 3 g. to 10 g. At least 15 g. of mercury (producing a flat drop with a diameter of 15 mm.) was needed to give an approximately constant value. 8 g. of gallium giving a drop of the same diameter was apparently enough to give nearly constant results with this less dense substance. Probably in order to attain the highest accuracy, even larger drops should be used.

The final determinations for mercury and gallium follow. The large letters designate the purity of the samples according to the descriptions already given; the small subscript letters indicate different fillings and settings of the apparatus. Each figure given consists of the average of 18 to 20 readings. Preliminary experiments with impure materials in which the various conditions of experimentation were developed, are omitted. All of the final results are given in each case.



## THE SURFACE TENSION OF MERCURY AT 30°.

## Final Determinations.

Setting.	No.	Wt. sub.	Height drop mm. from max. diam.	Surface tension. Mg./Mm.	Resting on
<i>b</i> .....	1	18.132	2.5501	43.97	Wood
	2	20.446	2.5532	44.08	Wood
	3	23.384	2.5548	44.12	Wood
<i>c</i> .....	1	17.968	2.5509	44.00	Wood
	2	21.762	2.5493	43.94	Wood
	3	27.837	2.5532	44.07	Wood
<i>e</i> .....	1	15.7	2.579	44.96	Carbon
	2	20.7	2.580	45.02	Carbon
	3	15.2	2.572	44.73	Carbon
<i>f</i> .....	1	12.31	2.542	43.69	Carbon
	2	16.84	2.544	43.74	Carbon
<i>g</i> .....	1	12.65	2.528	43.21	Carbon
	2	15.24	2.531	43.31	Carbon
				Av.,	44.06

## THE SURFACE TENSION OF GALLIUM AT 30°.

## Final Determinations.

Sample and setting.	No.	Wt. ga.	Height drop mm. from max. diam.	$\gamma$ , Mg./Mm.	Resting on
<i>Ee</i> .....	1	8.11	3.467	36.61	Carbon
	2	10.05	3.463	36.54	Carbon
	3	10.05	3.458	36.43	Carbon
<i>Ef</i> .....	1	7.97	3.470	36.69	Carbon
	2	10.04	3.473	36.75	Carbon
	3	10.04	3.473	36.75	Carbon
<i>Eg</i> .....	1	8.35	3.461	36.50	Carbon
	2	9.96	3.470	36.67	Carbon
<i>Ek</i> .....	1	8.54	3.454	36.36	Carbon
	2	10.00	3.458	36.43	Carbon
<i>El</i> .....	1	8.30	3.458	36.44	Carbon
	2	9.92	3.461	36.41	Carbon
<i>Elj</i> .....	1	8.94	3.463	36.44	Carbon
	2	9.88	3.464	36.55	Carbon
				Av.,	36.54

The rather wide range in the case of mercury from 43.2 to 45.0 is greater than is desirable; it is doubtless due to the difficulty of adjusting all the optical requirements of the system to perfect uniformity. Since a great many different settings of the apparatus were made it seems fair to conclude that the average has almost, if not quite, eliminated uncertainty from this source.

In the case of gallium the range is much smaller, probably because of increased experience and dexterity. The earlier experiments where the metal rested on paraffin and contained considerable indium were somewhat higher than the final ones made with purer substances and more satisfactory supports. These latter seem to leave little to be desired. In

brief, then, we find the surface tension of mercury at  $30^\circ$  to be 44.06 mg./mm. (which is very near that of Stöckle and other accurate experimenters) and that of liquid gallium to be 36.54 mg./mm. In terms of dynes/cm. the values become, respectively, 432.0 and 358.2, since  $g = 980.4$  in Cambridge. Thus the surface tension of liquid gallium is about 5 times that of water.

### VIII. The Latent Heat of Fusion of Gallium.

Berthelot determined the latent heat of fusion of gallium calorimetrically in the usual way, obtaining a value 19.08 calories per g.<sup>1</sup> We have used the somewhat preferable method, based upon the familiar equation of Clapeyron. The values in the equation  $Q = T (V_l - V_s) dp/dT$  are easily determined with accuracy. In this equation, of course,  $T$  represents the absolute temperature,  $V_l - V_s$  the change of volume of a gram of substance on melting, and  $p$ , pressure. Of course, since  $Q$  is always positive (that is, heat is always absorbed on melting), an increase in volume on solidification necessitates a negative temperature coefficient. The experimentation is most conveniently carried out according to the method used by Demerliac,<sup>2</sup> which consists in establishing the pressure required to maintain equilibrium in a mixture of the solid and liquid phase at a fixed temperature.

Our apparatus consisted of a piezometer similar to that used in the compressibility experiments, but of only quarter the size and with a narrower capillary. Within this piezometer the gallium was contained in a small open test-tube protected from the mercury on top by an inert liquid. Neither the gallium nor the surrounding liquids need be weighed. The thermostat was arranged so that it could be adjusted quickly at any desired temperature over the range of  $2^\circ$  or  $3^\circ$  and was provided with an adequate heating arrangement which could be regulated with great nicety. In detail the operations were as follows.

The piezometer (having been cleansed thoroughly and dried in a current of air) was partly filled with mercury and placed in a larger vessel which was evacuated in order to remove air. The little test-tube containing a cylinder of gallium (cast as before) was then placed in the piezometer, covered with either toluene or water and again partly evacuated to remove air. After the piezometer had been completely filled with toluene (or water) and the stopper (without lubricant) placed in position, a portion of the gallium was melted, and sufficient mercury was placed in the side arm of the piezometer so as to make contact at the platinum point when equilibrium had been reached at the desired pressure. Since the piezometer was used at practically constant volume, the respective amounts of the 2 phases of gallium had to be adjusted to this volume by cautious melting or freezing, accomplished by temporarily altering either pressure or temperature.

The melting point of gallium was thus determined at various pressures between 200 and 450 megabars, by finding the pressure at which equilibrium was reached at a

<sup>1</sup> Berthelot, *Compt. rend.*, **86**, 786 (1878).

<sup>2</sup> Demerliac, *ibid.*, **122**, 1117 (1896); **124**, 75 (1897).

definite long maintained temperature. The pressures were measured by the absolute gage already mentioned and the temperatures were referred exactly to the international hydrogen standard. The first 3 trials were rejected as merely preliminary, although essentially like the later ones. All the others are given below.

## CHANGE OF MELTING POINT WITH PRESSURE.

No.	Press. in megabars.	Centigrade melting pt.	$\Delta P.$	$\Delta T.$	$\Delta P/\Delta T.$
(A).....	1.0	29.752	..	...	...
4.....	348.9	29.047	347.9	-0.705	-496
5.....	441.1	28.859	440.1	-0.893	-495
6.....	248.2	29.242	247.2	-0.510	-485
7.....	248.7	29.242	247.7	-0.510	-486
8.....	443.2	28.842	442.2	-0.910	-485
9.....	349.7	29.045	348.7	-0.708	-493
			Av., 346		490

These figures naturally fall into 3 groups when classified according to pressure, but it is evident upon comparing Expts. 5 and 8 at the highest pressure that the possible error of experimentation is as great as the total range in the values of  $\Delta p/\Delta T$ . Therefore these figures are not accurate enough (because of the comparatively small pressure range) to determine the change of  $dp/dT$  with pressure. The best method of utilizing the results is to assume that their average applies to an average pressure, which must be taken as one-half of the average  $\Delta p$ , because  $\Delta p/\Delta T$  is approximately equal to  $dp/dT$  at about the average pressure involved in the range  $\Delta p$ .

One other point must be taken into account before applying the Clapeyron equation, namely, the change of  $V_l - V_s$  with change of pressure. Since the solid is less compressible than the liquid, although more bulky, this change of volume on melting will increase as the pressure increases. Ordinarily this correction has been left out of account in the application of this equation, but it was properly heeded by Bridgman in his paper on "Water, Liquid and Solid, under Pressure."<sup>1</sup> The case of water is, of course, similar to that of gallium. Since the cubic compressibility of the liquid per megabar is about 0.000004 and that of the solid about half as great, the correction to be applied to the volume change over 173 megabars will be 0.00034 cc. per cc. of the metal or 0.00006 per g. The value for  $V_l - V_s$  at the atmospheric pressure is -0.00531. Hence at a pressure of 173 atmospheres it must be -0.00537.

We have now all the data needed by the Clapeyron equation:

$$Q = T (V_l - V_s) dp/dT = 302.5 (-0.00537)(-490) \\ = 79.6 \text{ joules} = 19.04 \text{ cal. per g. (at 173 megabars pressure).}$$

This value is very nearly the same as Berthelot's 19.08, but since the latent heat of melting of gallium, like that of ice, probably changes with

<sup>1</sup> P. W. Bridgman, *Proc. Am. Acad.*, **47**, 471 (1912).

pressure, the identity is perhaps not as close as it appears to be. Nevertheless the 2 figures cannot be widely discrepant, even applying the as yet unknown correction for pressure. Probably  $dp/dT$  also changes with pressure, as Bridgman found in the case of ice; and if so, it probably changes in such a direction as to counteract, or perhaps, even reverse the effect of the change in  $V_l - V_s$ . The decision concerning this matter must be left to future investigations. Unless a much wider pressure range is employed, the measurements of both  $\Delta P$  and  $\Delta T$  will have to be made with the utmost accuracy in order to solve the problem.

The value of  $\Delta P/\Delta T$  given in the foregoing table is equivalent to a change in the melting point of  $0.00204^\circ$  per megabar or nearly  $0.00207^\circ$  per atmosphere.<sup>1</sup> This change in the melting point is more than twice that produced upon ice under the same conditions.

We are indebted to the Carnegie Institution of Washington, as well as to an anonymous fund, for generous support in this investigation, and also to Mr. F. G. McCutcheon, of the Bartlesville Zinc Company, for his courteous presentation of part of the material used as the source of gallium.

#### Summary.

This paper contains a description of experiments leading to the following conclusions.

I. (a) The observed single electrode potential of gallium was not easily reproducible at a constant value. It reached in maximum only about  $-0.30$  volt in  $0.1 N$  solution (if the calomel electrode is taken as  $+0.56$  volt), apparently placing gallium between indium and zinc in the electrochemical series.

(b) On the other hand, gallium is distinctly more difficult to precipitate electrolytically from acid solutions than zinc. According to repeated experiments, gallium might be expected from this behavior to have a single electrode potential of at least  $-0.7$ . It can be precipitated in weakly acid solutions if sufficient current density is employed, however.

(c) A possible explanation of this apparent inconsistency is to ascribe a mild degree of passivity to gallium—an explanation borne out by the fact that this metal when pure precipitates copper only very slowly from its solutions.

II. After preliminary purification by electrolysis, which easily eliminates indium and many other metals, pure gallium was freed from zinc by ignition in a high vacuum and especially by crystallization, giving material of constant melting point.

<sup>1</sup> P. W. Bridgman, in a research of which a description is now in press, found the nearly equal quantity  $0.00203^\circ$  per  $\text{kg./cm}^2$ , with a small quantity of our gallium. The megabar is  $0.987$  atmosphere or  $1.02 \text{ kg./cm}^2$ .

III. The melting point of gallium was found by 2 methods to be  $29.75^{\circ}$  C. on the international hydrogen scale.

IV. The density of the purest gallium was found to be 5.904 and that of liquid gallium 6.095, both at the melting point. The expansion on solidification (0.00531 cc. per g.) was proved not to be due to impurities.

V. The cubic coefficient of expansion of solid gallium was found to be about 0.000055. Hence the density of the solid at  $20^{\circ}$  is 5.907, and its atomic volume 11.85.

VI. The compressibility of solid gallium was found to be 0.0000020 and that of the liquid about twice as great.

VII. The surface tension of liquid gallium in carbon dioxide at  $30^{\circ}$  was found to be 36.54 mg./mm. In control experiments with the same apparatus, that of mercury at the same temperature was found to be 44.06.

VIII. The latent heat of fusion calculated from the Clapeyron equation and the change of melting point with pressure was found to be 19.04 calories per g. at 173 megabars pressure; that is, the melting point is lowered  $0.00207^{\circ}$  by the increase of pressure of one atmosphere.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 128.]

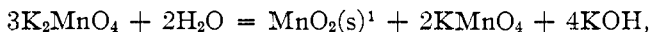
## THE EQUILIBRIUM CONDITIONS OF THE REACTION BETWEEN MANGANATE, PERMANGANATE AND MANGANESE DIOXIDE.

BY CHARLES E. RUBY.

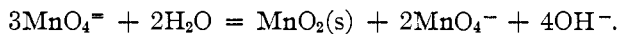
Received December 6, 1920.

### I. Introduction.

The immediate object of this research was to study the equilibrium conditions of the reaction



or more properly, those of the corresponding ionic reaction:



The ultimate purpose in view was to derive from the equilibrium constant of this reaction, by combining it with the fairly well known electrode-potential of the reaction  $MnO_4^= + \oplus = MnO_4^-$ , the electrode-potential of the reaction  $MnO_2(s) + 4OH^- + 2\oplus = MnO_4^= + 2H_2O$ , and of other related reactions, thus contributing to our knowledge of the quantitative relations between the different stages of oxidation of manganese.

This research was undertaken at the suggestion of Prof. A. A. Noyes, and was carried out with the aid of a grant made to him by the Carnegie

<sup>1</sup> A formula followed by (s) denotes that the substance is present as a solid phase.