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

A THERMOCHEMICAL CONTRIBUTION TO THE STUDY OF THE SYSTEM CADMIUM-MERCURY*

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Many investigations concerning cadmium amalgams have already been undertaken, chiefly because these substances are used in the Weston standard cell. Early workers,[1] using mainly analytical methods, thought they had discovered a number of compounds of cadmium and mercury. Later workers[2] (especially Bijl), using chiefly the analysis of cooling curves, decided that only mix-crystals, or solid solutions, exist—the system cadmium-mercury apparently belonging to the fourth type described by Roozeboom.[3] In this type of amalgam or alloy, two or more continuous series of solid solutions are formed, the residual liquid in each case being richer than the solid in the lower melting constituent. Nevertheless, from several other lines of evidence[4] it seemed possible that there might be at least one compound of cadmium and mercury. Bibliographies of the subject (up to their respective dates) are given in the paper of Richards

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* Professor Richards prepared this communication for the press, but did not see it in proof.

[1] (a) Stromeyer ($CdHg_2$), *J. F. Chem. Phys.* (*Schweigger*), **22**, 362 ff. (1818); (b) Crookewitt (Cd_2Hg_5), *Jahresber.* (*Liebig*), **1847-8**, p. 392; *J. prakt. Chem.*, **45**, 87 (1848); (c) König (Cd_5Hg_8), *J. prakt. Chem.*, **69**, 466 (1856); (d) Kerp and Böttger (Cd_2Hg_7), *Z. anorg. Chem.*, **25**, 59 (1900); H. Iggena, *Dissert.*, Göttingen, **1899**; (e) Tammann, *Z. physik. Chem.*, **3**, 445 (1889); (f) Heycock and Neville, *J. Chem. Soc.*, **61**, 888 (1892); (g) Frilley ($Hg_{12}Cd$, Hg_5Cd, Hg_7Cd_2, Hg_5Cd_2, Hg_5Cd_4, $HgCd_2$ and $HgCd_3$), *Rev. metal.*, **8**, 541 (1911); (h) Bachmetjeff, *J. Russ. Phys.-Chem. Soc.*, **26** (Phys. Abth.) I, 265 (1894); ($CdHg_4$ and Cd_4Hg_3) see note, *Z. anorg. Chem.*, **36**, 204 (1903).

[2] (a) E. de Souza, *Ber.*, **8**, 1616 (1875); V. Merz, *ibid.*, **9**, 1050 (1876); (b) Merz and Weith, *Ber.*, **14**, 1441 (1881); (c) Schumann, *Wied. Ann.*, **43**, 101 (1891); *Dissert.* (Erlangen), **1891**; (d) G. A. Hulett, *Z. physik. Chem.*, **33**, 618 (1900); (e) Mazzotto, *Estr. Atti Inst. Ven.*, **4**, Ser. 7 (1892–3); abstr. in *Z. physik. Chem.*, **13**, 571 (1893); also see *Wied. Ann. Beibl.*, **18**, 312 (1899); (f) Bachmetjeff and Wsharoff, *J. Russ. Phys.-Chem. Soc.*, **25** (Phys. Abth.) I, 237–255 (1893); also *Jahresber.* (*Liebig*), **1893**, I, 108–109; (g) Roozeboom, *Verslag Akad. Wetenschappen Amsterdam*, **4**, 1–5 (1901); abstr. in *J. Chem. Soc.*, [2] **80**, 507 (1901); (h) Bijl, *Z. physik. Chem.*, **41**, 641 (1902); (i) Puschin, *Z. anorg. Chem.*, **36**, 201 (1903); (j) Roozeboom, "Die heterogenen Gleichgewichte" (Binary Systems,) II, 1 (1904); (k) Jaenecke, *Z. physik. Chem.*, **60**, 409 (1907); (l) Börnemann and Rauschenplat, *Metallurgie*, **7**, 936 (1909); **9**, 472, 505 (1911); *J. Soc. Chem. Ind.*, 31, 991 (1911); (m) Maëy, *Z. physik. Chem.*, **50**, 200 (1905); (n) G. McPh. Smith, *Am. Chem. J.*, **36**, 135 (1906).

[3] Roozeboom (see Fig. 7, VI), *Z. physik. Chem.*, **30**, 399 (1899); G. Tammann, "Lehrbuch der heterogenen Gleichgewichte," 1924, p. 145.

[4] (a) Kerp and Böttger's work, cf. ref. 1 d, above; (b) Richards and Forbes, *Carnegie Inst. Publ.*, No. 56, 1906; (c) Hildebrand, Foster and Beebe, THIS JOURNAL, **42**, 545 (1920).

and Forbes,[4b] Gmelin-Kraut's "Handbuch der anorganischen Chemie,"[5] and the recent manuscript theses of two of the present authors.[6,7] Other references also are enumerated below (Refs. 8–11). Most of the references preceding 1908 are taken from the thesis of H. L. Frevert; more recent references are from the thesis of C. E. Teeter, Jr. (see references 6, 7).

In 1906, when the present research was begun, no systematic experiments had been carried out by anyone on the heats of solution of cadmium amalgams in mercury and, indeed, little has been done in this direction since. Nevertheless, such a line of work seemed likely to throw light on the nature of the amalgams; therefore it was undertaken.[12]

The apparatus at first employed was comparatively simple. Suitable quantities of mercury (1.5 to 2 kg.) were placed in a covered calorimeter of glass and the considerable falls of temperature produced by the introduction of the amalgams were measured by a good standardized mercury thermometer. The calorimeter was placed (with a surrounding air gap) in a water tight "submarine" which was immersed in a large bath. At first a correction was applied for the warming effect of the surrounding thermostat, according to Newton's law; later the determination was made adiabatically; the two methods essentially agreed. The amalgams were made with care from moderately pure metals; their compositions were inferred from the weights of the components. The inference was not entirely satisfactory since during the act of amalgamation some oxidation occurs; but it is accurate enough for the present purpose, and parallel results at any given concentration at first seemed very consistent. Typical figures are given in Table I.

After a few weeks, however, irregularities developed. These were soon attributed to differences in the mode of preparation of the amalgams and to the relative ages of the specimens. Evidently they must be due to a slow readjustment of the components of the somewhat heterogeneous mass.

The next experiments compared the heats of solution of pellets formed

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[5] Gmelin-Kraut, "Handbuch der anorganischen Chemie," Band 5, Abtheilung 2, 1189–1200 (1914).

[6] H. L. Frevert, *Thesis* for the degree of Ph.D., Harvard University, on file at the Harvard Library, 1908.

[7] C. E. Teeter, Jr., *Thesis* for the degree of Ph.D., Harvard University, 1927, pp. 9–55. Amalgams prepared by Teeter were used by R. F. Mehl, in the study of the Crystal Structure of the System Cadmium-Mercury, THIS JOURNAL, **50**, 381 (1928).

[8] Schulze, *Z. physik. Chem.*, **105**, 177 (1923).

[9] Smith, *Phil. Trans.*, **207**, 393 (1908).

[10] Smith, *Coll. Researches of Nat. Phys. Lab.* (*Teddington*), **6**, 137 (1910); *Phil. Mag.*, [6] **19**, 250 (1910).

[11] Cohen and Moesveld, *Z. physik. Chem.*, **95**, 285 (1920).

[12] H. L. Frevert carried out most of the early experimental work before 1909.

by slow, undisturbed cooling with those of finely granular samples which were stirred until solid. The negative heats of solution of the granular samples of about 25 atom per cent. composition were always at first greater than those of the slowly crystallized samples; both types showed increase with age, but the granular samples changed less, and ceased changing sooner than the large crystals. For example, certain granular specimens showed a 4% increase in 320 hours, whereas similar specimens slowly crystallized showed about a 17% increase in the same time. They tended toward the same maximum, but in the latter case it was still far off. This was to be expected if the change was due to readjustment of the concentrations of different layers of material, for stirring would tend to make finely divided crystals which would become equilibrated more quickly than large crystals.

In April, 1908, a new series of the heats of solution of the original samples, now two years old, was made. The thermochemical effects for amalgams of less than 16 and more than 33 atom per cent. of cadmium were essentially the same as before. On the other hand, aged samples between these limits, with less mercury or less cadmium, respectively, gave distinctly greater negative heat effects than before (see Table I). In other words, the amalgams which changed were those in which small amounts of liquid had filled the interstices of matted crystals. Closer investigation of contrasted samples showed the nature of the readjustment. Pellets containing 25 atom per cent. of cadmium made by fusion (apparently quite solid on the surface when cold) revealed, when freshly prepared, traces of liquid, on close scrutiny of a fresh fracture. After a few weeks or months the liquid phase disappeared entirely in amalgams containing more than 25 atom per cent. of cadmium. There was also an increase in the size of the individual crystals and an irregular change of total volume, shown by cracking of the surface of the casting. Moreover, on comparing the aged with fresh amalgams in regard to other physical properties, marked changes were noted; with age the amalgam became harder and tougher. It was evident that the solid phase gained mercury at the expense of the liquid, and therefore that at first the cadmium had been partially segregated in the first crystals.

A device for preventing this preliminary segregation of the components was the logical step to apply next. This device was used by Smith in his admirable discussion of the Weston cell[9,10] (of course unknown to us at the time). Doubtless others had applied it before. This device consists in plunging the melted homogeneous mass into a cold environment. The resulting crystallization is too rapid to allow much segregation. In the present case several amalgams (contained in thin glass test-tubes) were thus quickly solidified by being plunged when completely molten into frozen ether at −117°. Fresh samples thus prepared gave the same heats of solution as slowly cooled amalgams two years old. This is clear from the comparison of the data in Cols. 3 and 4 of Table I. The inference is obviously that the rapid quenching had accomplished in a few seconds the same extent of equilibration that had been attained in two years; or rather it had prevented original segregation, giving a product which had a degree of equilibration equal to that of the aged sample. Obviously the preceding argument is supported.

Thus there could be no reasonable doubt that the crystals first deposited on slow cooling contained more cadmium than those deposited later (as indeed was to be expected from Bijl's diagram), and that the effects of age were due to the gradual equilibration of the earlier and later deposited crystals—those earlier deposited taking mercury from those formed later and these taking mercury from the still less concentrated drops of remaining liquid. Perhaps the first clear statement of the existence of successive different layers of this kind was that made by Schumann[13] in 1891. Gore[14] had also suspected such a possibility. The phenomenon has, however, been recently denied, or at least has been declared to be so transitory as to be unimportant.[15] Cohen called it "Zonenbildung" (perhaps not a very good name, since the word "zone" has a different crystallographical meaning) and fully understood its importance.[11] The fact of deposition of a solid solution in successive layers of different composition is at present common knowledge in metallurgical practice, where it is called "coring" or "enveloping."[16]

There follows a table of the early Harvard results just detailed, to which is added another column (the last) containing recent figures shortly to be discussed. The table explains itself, except as regards this last column.

The results before 1910 given in this table, although furnishing much light on the crystallization of these solid solutions, evidently did not completely solve the problem. The round curve at 23 atom per cent. was not easily explicable. Hence, because the available time of one of the original investigators had come to an end, the work was not published, and was held in suspense until further experimental work could be performed. This opportunity did not arise until 1924, when the third of the present authors continued it under the direction of the first.

Careful study of the early results showed a number of important points. In the first place it was evident that the method involving the solution of an apparently solid amalgam in mercury is an excellent method of determining whether or not the whole mass is really solid. For a solid amalgam in the neighborhood of 25 atom per cent. of cadmium has a large

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[13] Schumann, *Wiedemann's Annalen*, **43**, 101 (1891).

[14] Gore, *Phil. Mag.*, [5] **30**, 228 (1890).

[15] Schulze, ref. 8.

[16] See, for example, C. H. Desch, "Metallography," London, 1918.

TABLE I

HEATS OF SOLUTION OF CADMIUM AMALGAMS IN MERCURY IN KILOJOULES PER GRAM ATOM OF Cd

Atom per cent. of cadmium	Fresh (Frevert, May, 1906)	Aged two years (Frevert, April, 1908)	Quenched in ether ice, (Frevert, April, 1908)	Quenched in liquid nitrogen (Teeter, 1924–26)
75.0	– 0.98	– 0.99	.....	....
66.7	....	– 2.43	.....	....
54.5	....	....	.....	−5.7
50.0	– 6.2	– 6.1	.....	....
39.9	....	....	.....	−9.5
33.3	−10.9	−10.8	.....	....
28.6	....	....	−12.6	....
27.3	−12.7	−13.2	.....	....
26.0	....	....	−13.7	....
25.0	−13.8	−14.3	−14.3[a]	−14.6
23.1	−13.3	−14.5	−14.4[b]	−15.4
22.2	....	....	−14.51	−15.8[c]
21.6	....	....	.....	−14.6
20.8	....	....	.....	−14.4
20.0	....	....	−13.93	−14.3
16.7	....	....	−12.11	....
5.0	....	....	– 0.001	....

[a] Mean of two determinations (14.20 and 14.45).

[b] Mean of two determinations (14.55 and 14.42).

[c] The atom per cent. in this experiment was 22.5. All the values in this last column are averages of several determinations. For example, this particular value was the mean of 4 parallel experiments, 16.4, 15.9, 15.3 and 15.6. This particular concentration gave the most trouble of all; hence the widely differing values, which were less consistent than in any other case. An explanation will be given shortly.

negative heat of solution in mercury, whereas the mercurial liquid which clings to it has almost no heat of dilution. The method, then, discriminates sharply between an amalgam which has no "mother liquor" and one containing "mother liquor." It throws, therefore, into sharp relief the effect of the "coring;" for an amalgam in which the first crystals contain an abnormal excess of cadmium must also contain minute drops of interspersed liquid, if that amalgam has the composition which would exactly and completely solidify when thoroughly equilibrated. Evidently, also, the only way to find the true "solidus point" is with a completely equilibrated specimen, since the different layers on a crystal cannot be analyzed separately, or in any way inferred as to their composition from the percentage proportions of the components; too much depends on the conditions of crystallization.

Further investigation involved, therefore, in the first place, the preparation of thoroughly equilibrated samples of solid amalgams. Two methods of accomplishing this suggested themselves. One of these was the crystallization of a very small proportion of solid amalgam from a large amount of liquid. The very small percentage change in the "mother liquor" due to this almost negligible deposition of solid would allow only a very small change in the composition of the layers on the deposited crystals. This scheme was therefore put into practice, and in order to separate the "mother liquor" (which would, of course, vitiate the outcome), the crystals were whirled in a powerful centrifuge kept almost at the liquidus temperature.

The device was fairly successful, but met with three difficulties: first, the tenacious clinging of liquid mercury, which could not be wholly eliminated; second, superficial oxidation of the crystals, which could be partly prevented by working wholly in an inert atmosphere in the centrifuge (a troublesome expedient) but vitiated the product; third, the difficulty of analyzing the crystals, because the exact determination of cadmium in the presence of mercury has not been quite satisfactorily solved. Hence, although on the whole these centrifuged crystals gave nearly the same heats of solution in mercury as the quenched samples of the earlier time, the outcome is hardly worth recording here.

Much better results were obtained from the device of quenching. Already in 1908 it had been shown that cooling by frozen ether produced a nearly equilibrated sample, but no evidence was given that this sample was fully equilibrated. It seemed well worth while, therefore, to carry out a new series of experiments with yet more efficient quenching. Hence in 1925 we used boiling nitrogen (−190°) instead of frozen ether. The lower temperature is, of course, only serviceable in causing more rapid cooling; it does not affect the product after solidification. As Tammann[17] has pointed out in the case of metals, the tendency to crystallize and the velocity of crystallization increase rapidly with increased undercooling. The object was to accelerate the speed of solidification so greatly as to prevent, to maximum extent, the segregation of the components. More important than very low temperature for this end was, perhaps, the device used for plunging the liquid amalgam into the cold environment. This consisted in a so-called deflagrating spoon (such as is used in beginners' experiments on oxygen, for example) in which was placed the large globule of hot liquid amalgam. On being plunged directly into liquid nitrogen the metal thus came into immediate contact with the intensely cold liquefied gas, and the rate of cooling must have been extremely great. Solid thus prepared is less rich in cadmium than the crystals which first separate from the same liquid solution on slow cooling. It is rather, of course, that which would be attained when the whole solidified mass is completely equilibrated after years, in other words a homogeneous solid solution of the same concentration as the liquid solution from which it was made.

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[17] For example in the "States of Aggregation," Tammann (Mehl), Van Nostrand, New York, 1925, Chapter IX, p. 226 ff.

The specimens of amalgams of different compositions quenched in this effective fashion must have been more thoroughly equilibrated than any such amalgams hitherto studied. They had been made from "chemically pure" cadmium of commerce (which was doubtless pure enough for the purpose) and carefully purified mercury. The respective percentage compositions were computed from the weighed components after correction for the weights of cadmium oxidized during amalgamation, and the latter found by dissolving the oxide formed in excess of very dilute acid and titrating the excess, using a comparative method. Melting under carbon dioxide, of course, diminishes the oxidation and the possible error.

Specimens of 4 g. each of the thoroughly equilibrated amalgams thus prepared were then dissolved with careful thermochemical measurement in a large excess of mercury, in order to obtain results which could be compared with the work done nearly two decades before. Hoping to attain greater accuracy, a more complicated calorimetric method was used. This method (an isothermal one) was essentially similar to that described briefly in a paper by Farrington Daniels and one of us,[18] although somewhat improved. Since cadmium amalgams absorb heat on dissolving in mercury, the thermal change can be measured electrically by keeping the system constant in temperature. The electrical energy used was measured by means of a silver coulometer and a potentiometer. A Dewar flask immersed in a deep thermostat served as calorimeter. The heating coil was of insulated constantan wire in a close fitting silver tube bent into the form of a helix. Asphaltum paint protected the silver from the mercury in which it was immersed. The temperature change was read on a good standardized Beckmann thermometer. A loop of heavy copper wire covered with asphaltum paint served as stirrer. The amalgams, which were all crystalline solids, were dropped into the mercury by means of a hopper, a small silvered box with hinged bottom that could be tripped from the outside. The tube supporting the hopper also served for the introduction of carbon dioxide into the calorimeter. This gas was generated in absence of air and was nearly oxygen free; its presence is essential for great accuracy, otherwise oxidation during the experiment causes accidental heat. The silver coulometer was nearly immersed in a large battery jar, well stirred, and cooled by a stream of water in order to eliminate fluctuations in resistance due to heating with the passage of current. Minor variations of voltage were compensated by changing the resistance of the circuit, a less sensitive galvanometer in the potentiometer circuit being used as indicator. Current was obtained from a 6-volt storage battery which was charged continuously at a low rate.

In each measurement of heat of solution, 800 g. of mercury and 4 g. of amalgam were used. The voltage (about 0.5 volt) corresponded to 0.4 ampere through the coil. Because of the rapid solution of the amalgam, the drop in temperature was too rapid for complete compensation; hence a correction was necessary for the heat gained from the calorimeter. Readings of time and temperature were taken and a correction (5–7% of the observed heat of dilution) was applied by the Regnault-Pfaundler method. The duration of the experiment was from 5 to 8 minutes.

The possible minor sources of error were numerous but they were avoided as far as practicable by forethought and care. The variations in their net effect is shown by the comparison of parallel experiments (a footnote under Table I gives the most divergent series). The most serious was probably that due to the oxidation of cadmium; but one possible source of irregu-

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[18] Richards and Daniels, THIS JOURNAL, 41, 1746 (1919).

larity not yet referred to should be mentioned. This is the fact that near the solidus point a very small change of temperature may change a completely solid mass to one containing an appreciable number of finely divided drops of liquid. Sufficient pains must always be taken to have the solid amalgam exactly at the right temperature at the moment of immersion in mercury. If the amalgam at the moment of mixing should be too cold, it would give a cooling effect slightly too large because of its heat capacity; if too warm, it would give a cooling effect distinctly too small because of its heat capacity and the presence in it of liquefied drops. Because of these difficulties, more determinations were required than would otherwise have been the case in order that the final results should have a reasonable degree of accuracy. That reasonable accuracy was attained is indicated by the fact that the results follow a consistent curve, which for amalgams above 30 atom per cent. of cadmium (where differences in quench ing could not appreciably affect the result) coincides very closely with the earlier results obtained by the other apparatus. No claim for highest accuracy is made—for the present purpose consistency is more important, and of that there can be no doubt.

These results are given in the last column of Table I, and the whole of this table is plotted in the three curves in Fig. 1. Evidently the intensive quenching which the last samples had received accomplished their purpose of equilibrating the material far more efficiently than the frozen ether had done. Evidently, too, the cooling effect of the amalgam on dilution per gram atom of cadmium is greatest at the concentration 22.5 atom per cent. of cadmium, which does not correspond to any definite simple chemical composition. The single cusp in the lowest curve is obviously due simply to the complete disappearance of the liquid phase (going from left to right); and the blunting of the cusp with less perfect equilibration in the upper curves must be referred primarily to "coring," which, by segregating excessive cadmium in the interior of the crystals, prevents the existence of the full amount of solid solution at 22.5°, although some oxidation of cadmium in the early experiments may have played a minor role.

The method just described furnishes one of the best ways of determining the "solidus" point (that is, the commencement of melting) with exactness. Bijl was not able to find this point at all by means of cooling curves; he was obliged to resort to the dilatometer, which happened to serve because of the considerable volume changes involved. In otherwise similar cases in which these volume changes are small, the present method would be particularly valuable. It is satisfactory that our value of 22.5 atom per cent. of cadmium thus found for this point is very close to Bijl's value 22.9 ± found by the dilatometer (both being at 25°). Evidently any method of determining the solidus point which does not eliminate, as ours does, the inhomogeneity due to "coring" is not to be trusted—for the exact composition of the solid at the liquid–solid interface could not then be inferred exactly from the total composition even if the distribution ratio were known, because so much would depend upon the particular circumstances of the crystallization. This caution does not, of course, apply to the liquidus point (the beginning-of-freezing) because there the great mass of the solution is liquid and mobile.

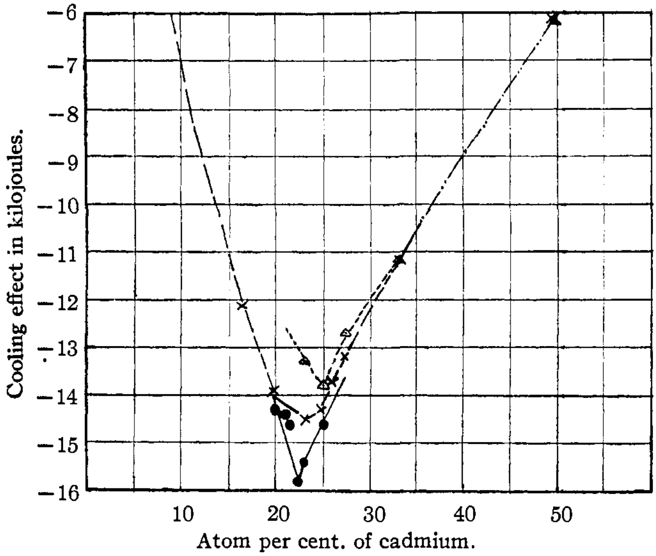

Fig. 1.—The cooling effect produced by dissolving various cadmium amalgams in great excess of mercury. Kilojoules of energy absorbed per gram atom of cadmium are plotted as ordinates; atom percentage of cadmium as abscissas. Triangles indicate 1906 experiments on non-equilibrated, slowly cooled specimens (the curve is a dotted line). Crosses show aged or quickly cooled specimens of 1908 (the curve is a broken line; where these last two coincide, the curve is broken with interpolated dots). Black circles indicate fully equilibrated specimens, quenched in liquid nitrogen, 1926.

In view of these considerations, one must define the solidus point of this kind of solid solution as the beginning-of-melting *when the solid phase is equilibrated.* Practically, it must be almost impossible to measure even by a melting curve, for the formation of the first drops will at once cause inequality of distribution of cadmium on the interface, which will take weeks or months for equilibration. Much less can it be discovered by a cooling curve, as Bijl found. But by means of successive thermochemical determinations of quenched samples it can be found exactly.

Evidently in the final curve (the lowest one in Fig. 1) there is no evidence whatever of any compound of mercury and cadmium. The cusp of the curve does not correspond to a simple definite proportion; it simply means the disappearance of liquid amalgam with increasing concentration of cadmium, as has already been said. The curve does not prove that a compound may not exist in some other part of the field, but this research has no positive evidence in that direction. The heat absorbed by dissolving a cadmium amalgam in mercury is of the order of the latent heat of melting of the solid material, although somewhat larger. This and several other aspects of the question involving different experimental methods have been studied by one of us, in part in this Laboratory, continuing the present research. These results which also, so far as they go, confirm Bijl's diagram, will be made the subject of another paper in the near future.

It is a pleasure to acknowledge our indebtedness to the Carnegie Institution of Washington, and to an anonymous benefactor of the University, for most of the apparatus employed in this research.

Summary

1. This investigation was undertaken with the aim of studying the nature of cadmium amalgams by means of thermochemical methods.

2. The large amount of heat absorbed on dissolving various cadmium amalgams in mercury was determined.

3. This heat is of the order of magnitude of the latent heat of melting of cadmium and mercury, although somewhat larger.

4. It is dependent on the weight of the solid (not including entangled drops of liquid) and on the composition of the solid.

5. Its magnitude indicates clearly whether or not the amalgam is fully solid or contains included liquid mercury, and it is therefore one of the best means of locating the exact solidus point.

6. The solidus point must be defined as the point at which liquid first appears *when the solid is fully homogeneous.*

7. An amalgam exactly homogeneous at the solidus point must, after melting and slow cooling again to that point, contain drops of liquid amalgam, because of the increased concentration of cadmium in the innermost cores of the crystals. This causes a smaller thermochemical effect on solution in mercury. The investigation thus furnishes evidence of the effect of "coring" or "enveloping." Complete equilibration takes years at room temperature.

8. The results of the investigation are consistent with the researches of Bijl and of Smith between 20 and 30°.

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