[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Heat of Formation of Cs(Hg) and of $Cs^+(aq)$ at 25°[1]

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The following standard heats of reaction have been determined calorimetrically: Cs(c) → Cs(Hg), $\Delta H^\circ = -31.2 \pm 0.3$ kcal./mole; $Cs(c) + H^+(aq) \rightarrow Cs^+(aq) + {}^1/_2H_2(g)$, $\Delta H^\circ = -62.6 \pm 0.4$ kcal./mole. These results are compared critically with the results of earlier determinations. Combined with accepted entropy data they yield for $Cs^+(aq)$, $\Delta F^\circ_f = -70.8$ kcal./mole, and for the Cs/Cs+ couple, E°_{ox} − 3.08 volts.

In the course of an investigation of the thermodynamic properties of the alkali metal amalgams[2] it became apparent that a redetermination of the standard enthalpy of formation of aqueous cesium ion was required. In the present work this has been undertaken by calorimetric measurements of the heats of reactions (1) and (2) whose sum is reaction (3)

$$Cs(c) \longrightarrow Cs(Hg) \quad (1)$$

$$H^+(aq) + Cs(Hg) \longrightarrow Cs^+(aq) + {}^1/_2H_2(g) \quad (2)$$

$$H^+(aq) + Cs(c) \longrightarrow Cs^+(aq) + {}^1/_2H_2(g) \quad (3)$$

In this way the violent direct reaction of cesium and water is avoided and interesting data on the amalgams are also obtained.

Heat of Dilution of the Amalgams.—It is not convenient to carry out reactions (1) and (2) with the same amalgam concentration, so the effect of this concentration upon the enthalpy changes must be determined. This appears only as a small correction, however, and does not need to be determined with great relative accuracy.

From the amalgam-partition results[2] we calculate for cesium amalgams

$$\phi_L = 28m \quad (4)$$

where ϕ_L is the relative apparent molal enthalpy[3] of the solution of molality m. Now $\phi_L(m_2) - \phi_L(m_1)$ is ΔH(per mole of Cs reacting) for reaction (5).

$$(\text{Cs amalgam, } m_1 \text{ molal}) + Hg(l) \longrightarrow (\text{Cs amalgam, } m_2 \text{ molal}) \quad (5)$$

The determination of ϕ_L from the amalgam-partition data is uncertain because ϕ_L is generated as a second derivative (with respect to concentration and temperature) of the data, and because of the approximation made in calculating properties of the binary amalgams from data for the ternary amalgams. For this reason a single measurement of ΔH_5 was undertaken, with the following result

m_1	Wt. of initial amalgam, g.	Wt. of Hg, g.	m_2	Q, cal.	ΔH_5, kcal./mole
0.0204	35.6	613.4	0.0012	0.39	−0.54

The accuracy is only about 10% for the determination of such a small heat with the present apparatus. Assuming that eq. 4 expresses the correct concentration dependence, the calorimetric result is

$$\phi_L = 28m \quad (6)$$

in satisfactory agreement with the amalgam-partition result, which has an unknown, but probably larger, uncertainty.

Heat of Formation of Cs Amalgam.—In each calorimetric investigation of reaction (1) a fragile bulb of cesium metal was broken under mercury, with the results shown in Table I. The standard enthalpies are obtained from the directly measured enthalpies by correction for the enthalpy of dilution of the amalgam formed in the calorimeter. Therefore these results apply to the hypothetical one molal state of the amalgam.

TABLE I

MOLAL HEAT OF REACTION OF CESIUM METAL WITH 650 G. OF MERCURY

Cs, mmole	Heat evolved, cal.	ΔH_1, kcal./mole	ΔH_1°, kcal./mole
0.4325	13.40	−30.98	−31.00
.722	22.70	−31.43	−31.46
.985	30.605	−31.06	−31.10
			−31.2 ± 0.3

Independent thermodynamic data for reaction (1) may be derived from the measurements of Bent, Forbes and Forziatti[4] on the cell

$$Cs(c) \mid CsI \text{ in } C_2H_5NH_2 \mid Cs(Hg, 0.0141\ M)$$

combined with corrections to hyp. 1 molal std. state of the amalgam, based on the deviations from Raoult's law which were measured in the amalgam partition experiments.[2] The results for 25° are

$$\Delta F_1^\circ = -23.41 \text{ kcal./mole}$$
$$\Delta H_1^\circ = -38.9 \text{ kcal./mole}$$
$$\Delta S_1^\circ = -52.1 \text{ cal./mole deg.}$$

These results are believed to be in error. There is not only disagreement with the calorimetric ΔH_1°, but also the e.m.f. ΔS_1° is not consistent with independent data, as shown in a later section.

Heat of Reaction of Amalgam with Acid.—The experimental results for reaction (2) are presented in Table II. ΔH_2° is obtained by correcting for the heat of dilution of the amalgam (eq. 6). There is also a correction, which appears to be negligible, for the difference in ϕ_L of the initial 0.1125 molal HCl solution and of the CsCl–HCl–H_2O mixture which is formed as a product in reaction (2). Taking into account the small magnitudes of the ϕ_L's (for 0.11 molal HCl, ϕ_L = 133 cal, and for 0.11 molal CsCl, ϕ_L

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[1] (a) This research was supported by the U. S. Atomic Energy Commission; (b) presented at the meeting of the American Chemical Society in Dallas, Texas, April, 1955.

[2] H. L. Friedman and K. Schug, THIS JOURNAL, **78**, 3881 (1956).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, eq. 8-2-5.

[4] H. E. Bent, G. S. Forbes and A. F. Forziatti, THIS JOURNAL, **61**, 709 (1949).

TABLE II

THE HEAT OF REACTION OF 0.0204 MOLAL AMALGAM WITH 0.1125 MOLAL AQUEOUS HYDROCHLORIC ACID, PER MOLE OF CESIUM

Wt. of amalgam, g.	Wt. of aq. HCl, g.	Heat, cal.	ΔH_2,[a] kcal./mole	$\Delta H_2°$, kcal./mole
35.303	219.49	22.95	−32.01	−31.44
28.296	215.67	18.78	−31.97	−31.40
				−31.42 ± 0.1

[a] Includes a correction of 0.14 kcal./mole for vaporization of the solvent.

= 36 cal.)[5] and assuming that the Brönsted specific ion interaction principle applies, so that ϕ_L is a linear function of composition for mixtures of 0.11 molal HCl and 0.11 molal CsCl, then this correction is less than 5 cal./mole.

Thus $\Delta H_2°$ applies to hyp. 1 molal standard states for H^+(aq), Cs(Hg) and Cs^+(aq). The amalgam-partition[2] value, $\Delta H_2° = -30.5$ kcal./mole, is in satisfactory agreement with the more accurate calorimetric value.

The thermodynamics of reaction (2) can also be derived from the data on the potential of the cell[4]

$$\mathrm{Cs(Hg,\ 0.0141\ \mathit{m})\ |\ CsOH(aq.,\ 0.02109\ \mathit{m})\ |\ HgO(\mathit{c},\ red)\ |\ Hg(l)}$$

as a function of temperature, together with (i) correction to hyp. 1 molal amalgam, based upon the amalgam-partition results[2] for deviations from Raoult's law; (ii) correction to hyp. 1 molal aqueous solution as made by Bent, Forbes and Forziatti[4]; (iii) data for HgO, Hg, H_2O, H_2 and OH^-(aq) from the N.B.S. tables.[5] The results are presented in Table III. The "best" values were obtained by the choice of the free energy and enthalpy values shown, with entropy determined by these.

TABLE III

THERMODYNAMICS OF REACTION (2)

	BFF (ref. 4)	FS (ref. 2)	This work	Best values
$\Delta F_2°$, kcal./mole	−43.95	−43.9	....	−43.9
$\Delta H_2°$, kcal./mole	−29.59	−30.4	−31.4	−31.4
$\Delta S_2°$, cal./mole deg.	48.2	45.1	....	41.7

The Heat of Reaction of Cesium with Acid.—The data on reaction (3) are summarized in Table IV. Rengade measured the heat of reaction of Cs and water with a bomb calorimeter.[6] Bichowsky and Rossini[7] cite the result of these measurements as having an uncertainty of ± 0.10 kcal., although the three measurements reported by Rengade have a range of −0.3 kcal. and the heats of dilution required to reduce the data are poorly known. The sources of the entropy data from third law and associated measurements are given in the N.B.S. tables.[5] The value of $\Delta S_3°$ obtained in this way is probably reliable to 1 cal./mole deg. On this basis the combined results of the two e.m.f. cells investigated by Bent, Forbes and Forziatti are certainly in error, at least as far as the entropy is concerned. The present work indicates that the cell for reaction (1) was not operating properly, but gives no evidence as to what might have been wrong with the cell.

TABLE IV

THERMODYNAMICS OF REACTION (3)

	Rengade Ref. 6	Third law	BFF ref. 4	This work	Best values
$\Delta F_3°$, kcal./mole	....	..	−67.3	....	−70.8
$\Delta H_3°$, kcal./mole	−62.0	..	−68.4	−62.6	−62.6
$\Delta S_3°$, cal./mole deg.	....	27.6	− 3.9	....	27.6

The best values have been obtained by choosing the indicated entropy and enthalpy and calculating the free energy from these. The corresponding standard electrode potential of the Cs/Cs^+ couple, 3.08 volts, is larger than that of any other metal/metal ion couple.

Experimental

Materials.—Spectroscopically pure Cs_2CO_3, purchased from Johnson, Matthey and Co., London, was dissolved in water. Cs amalgam was prepared by electrolysis of this solution. Cs metal was prepared by pyrolysis of the azide which was precipitated from the Cs_2CO_3 solution. The cesium azide was contained in a nickel crucible inside of the Pyrex vacuum apparatus during pyrolysis. This process and the subsequent distillation and transfer to fragile sample bulbs were carried out in a vacuum in scrupulously clean Pyrex apparatus which was isolated from the rest of the apparatus by a freshly cleaned liquid nitrogen trap. A stick-vacuum was maintained except during the pyrolysis, when the evolved nitrogen built up to a pressure of several microns in spite of the action of the pump. A typical sample of the metal melted in the range 28.25–28.45°. Using the heat of fusion and melting point obtained by Clusius and Stern,[8] this corresponds to a minimum impurity content of 0.1 atom %. Direct analysis of a sample by flame photometry gave an upper limits for total Na, K and Rb impurities totalling less than 0.1%. All of the cesium samples prepared in this Laboratory, whether by this method or by fractional distillation of a sample of commercial C.P. cesium metal, had a definite golden color. All attempts to remove the color-producing agent by fractional distillation of the metal were unsuccessful. There is no way to tell, of course, whether this color was present only on the surface, except that the surface seemed always to be clean. The color was always more intense on the Cs-vacuum interface than on the Cs–Pyrex interface. This color has been noted before,[9] but not in the purest material.[8]

The Solution Calorimeter.—The calorimeter for reaction 2 is similar to that described by Westrum and Robinson[10] except that the thermometer and heater are contained in separate platinum tubes, each 6 mm. dia. and 10 cm. long. These are each sealed at one end to glass tubes which serve as supports, and through which the leads pass. The other ends are gold soldered to platinum closures. The thermometer is 400 ohms of No. 40 enameled iron wire and the heater is 100 ohms of No. 34 double nylon covered Manganin wire. The thermal leakage modulus is 0.0005/min., and the drift due to thermal leakage, thermometer power, and stirrer power was about 0.002 deg./min. The range of the thermometer is 24.2 to 25.8°. The auxiliary apparatus is similar to that described by Westrum and Robinson,[10] as was the conduct of the experiments, except that the acid solution was flushed with pure hydrogen to remove oxygen before each experiment, and was displaced into the hydrogen-filled calorimeter by hydrogen pressure.

The Amalgam Calorimeter.—The calorimeter vessel is a thin walled stainless steel thimble of 60-ml. capacity. It is

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(5) "Selected Values of Chemical Thermodynamic Properties," U. S. National Bureau of Standards Circular 500, F. D. Rossini, D. D. Wagman, *et al.*, Washington, D. C., 1952.

(6) E. Rengade, *Ann. Chim.*, [8] **14**, 540 (1908).

(7) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publ. Co., New York, N. Y., 1935.

(8) K. Clusius and H. Stern, *Z. angew. Physik*, **6**, 194 (1954).

(9) Gmelin, "Handbuch der Anorganische Chemie," No. 25, Verlag Chemie, Berlin, 1938.

(10) E. F. Westrum, Jr., and H. P. Robinson, in "Nat. Nuclear Energy Ser.," Div. IV, Vol. 14B, Part II, McGraw-Hill Book Co., New York, N. Y., 1949.

suspended from a plastic plug inside of a submarine which is fitted with an aluminum foil convection shield. The heater and resistance thermometer, made of the same lengths of wire as described above, were wound directly on the outer surface of the calorimeter. The stirrer and sample-breaking mechanism are the same as for the solution calorimeter. The calorimeter vessel was thoroughly flushed with hydrogen after it was filled, and a very slow stream was passed during the experiments to prevent the entry of air. The submarine was filled with Freon 114 to improve insulation, and it was cooled by injecting a stream of the liquid refrigerant when it was desired to cool the calorimeter. The thermal leakage modulus was 0.015/min., and the drift ranged from +0.015 to −0.005 deg./min. in the temperature range of this calorimeter, from 25 to 26.6°.

The cesium seemed to react completely within 10 seconds after breaking the sample bulb, but there was a lag of about 10 min., also found in the electrical calibration, before the temperature drift returned to the value characteristic of the calorimeter temperature. Neither the temperature drift nor the electrical calibrations gave any evidence of a heat effect from the reaction of the amalgam with impurities such as the oxide film which is presumably present on even the bright stainless steel surface.

Accessories.—The resistors of the heater circuit and the standard cell have been periodically compared with N.B.S. certified standards, as have the heaters themselves. Only the heaters show a measurable drift, which is small, however, compared with the accuracy required here. The limiting factor in the accuracy of the experiments described here is the reproducibility of the electrical calibrations. This can certainly be improved, although the exact source of the difficulty has not yet been established. The thermal leakage is also troublesome in the case of the amalgam calorimeter, but the large thermal leakage correction seems to be reproducible to about 0.0005 deg. per minute of "x" period.

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Thermodynamic Properties of Calcium Metaphosphate, 10 to 1400°K.

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The heat capacity of β-calcium metaphosphate crystals was measured over the range 10 to 306°K. The heat content, $H^\circ - H_0^\circ$, at 298.16°K. is 5715 cal. mole^{-1} and the entropy at 298.16°K. is 35.12 cal. deg.$^{-1}$ mole^{-1}. The heat contents of the β-crystalline and glassy forms of calcium metaphosphate were measured over the range 373 to 1370°K. and equations for the thermal properties of the materials were derived.

The thermodynamic properties of the calcium phosphates and other compounds of importance in the technology of phosphate fertilizers have for several years been the subject of a broad study.[1] As part of this study, measurements were made on calcium metaphosphate, the anhydride of monocalcium orthophosphate, in its β-crystalline and vitreous forms.

Materials and Methods.—Monocalcium phosphate monohydrate, twice recrystallized from phosphoric acid solution, was dehydrated by heating it to near constant weight at 250° and at 400°, and finally to constant weight at 750°. β-Calcium metaphosphate was the only phase detected in microscopic and X-ray examinations of the product. The chemical composition was 28.39% CaO and 71.22% P_2O_5, as compared with a theoretical composition of 28.32% CaO and 71.68% P_2O_5 for $Ca(PO_3)_2$ (formula weight, 198.03).

A method of promoting the development of crystallinity in the β-calcium metaphosphate was discovered too late for use in the present study. When the metaphosphate was heated for 1 to 2 hours at a temperature 5 to 10° below its melting point, growth of the crystals was pronounced. The resultant mass was lightly ground and digested in dilute hydrochloric acid to remove the small amount of glass phase. The product consisted of clean euhedral crystals.

Calcium metaphosphate glass was prepared by melting the crystalline metaphosphate at 1000° and allowing the melt to cool rapidly to room temperature. The melt was cooled within 30 minutes after it became molten, because phosphoric oxide is vaporized from molten calcium metaphosphate. The clear glass was crushed and the −20 + 100-mesh fraction was separated for measurements of its high temperature heat content.

The low and high temperature calorimeters have been described.[1]

One defined calorie was taken equal to 4.18331 international joules,[2] and 0° was taken to be 273.16°K.

Low Temperature Heat Capacity.—The observed heat capacities, $\Delta Q/\Delta T$, for the empty calorimeter and for the calorimeter filled with 90.9732 g. (vacuum) or 0.45939 mole of β-calcium metaphosphate were plotted, and arbitrary smooth curves were drawn through the experimental points. Values read at 5° intervals from the smooth curves were used in the calculation of curvature corrections from second differences.[3] Equations were fitted to the corrected heat capacities, a deviation plot was made, and the values calculated from the equations were corrected from the deviation plot. The observed molal heat capacities are listed in Table I. Temperatures were read to four decimal places and were so used in the calculations, since small differences were involved; the last two places were dropped in the compilation of Table I. The heat capacities at integral temperatures are shown in Table II.

The entropy at 298.16°K. is 35.12 ± 0.03 e.u., which is the sum of 0.03 e.u., obtained by Debye extrapolation ($\theta = 192$) between 0 and 10.26° K., and 35.09 e.u., obtained by graphical integration between 10.26 and 298.16°K. The graphical integration was checked by tabular integration[4] of C_p/T against T at 5° intervals. The heat content, $H^0 - H^0_0$, at 298.16°K., as derived from the integration of C_p against T, is 5715 cal. mole^{-1}. No correction was made for impurities. The derived entropy and heat content were assumed to represent the ideal state for the solid.

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(1) E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **72**, 2418 (1950); **73**, 5579, 5581 (1951); **78**, 1811 (1956).

(2) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

(3) R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1945).

(4) Works Progress Administration, Mathematical Tables Project, "Tables of Lagrangian Interpolation Coefficients," Columbia University Press, New York, N. Y., 1944.