and for a gas with tetrahedral symmetry

$$S = R\,ln\,T^3M^{3/2}VI + 87.75 + \int_0^T C_v \, \mathrm{d}\,ln\,T. \qquad (14)$$

Equations 13 and 14 point out the importance of evaluating the last terms from band spectra.

The author wishes to thank Professor R. T. Birge of the Department of Physics at this institution for his help in interpreting the band spectra data, and the members of this department for many valuable suggestions.

Summary

1. The entropy constant for diatomic gases having no vibrational energy is evaluated.
2. The entropies of hydrogen, hydrogen fluoride, hydrogen chloride, hydrogen bromide, nitrogen, carbon monoxide and nitric oxide are calculated from the equation secured and comparisons made where possible with experimental entropy determinations.
3. The moments of inertia of oxygen, hydrogen iodide and chlorine are calculated from their observed entropies and attention is called to the probability that oxygen and possibly nitric oxide do not follow the equation given.
4. The entropy equation for diatomic gases having vibrational heat capacity is discussed.
5. The constant for the entropy equation of gases whose molecules have tetrahedral symmetry is secured and the dimensions of the methane molecule are calculated.

BERKELEY, CALIFORNIA

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

THE HEAT OF SOLUTION OF THALLIUM IN DILUTE THALLIUM AMALGAMS

BY THEODORE W. RICHARDS AND CHARLES P. SMYTH

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In connection with a study of the properties of solid thallium amalgams[1] an investigation of the heat of solution of thallium in mercury and in dilute thallium amalgams was commenced. The preliminary results obtained appear to possess interest by virtue of their bearing upon recently published work dealing with the thermodynamics of these amalgams.

The negative heat of solution of thallium in fairly concentrated liquid amalgams had been previously determined[2] by an isothermal method, which was applicable only to endothermic changes and could not, there-

[1] Richards and Smyth, THIS JOURNAL, **44**, 524 (1922).

[2] Richards and Daniels, *ibid.*, **41**, 1756 (1919).

fore, be employed for the determination of the positive heat developed by solution of thallium in amalgams rich in mercury. Accordingly, an adiabatic method, similar to that used in the determination of the heat of dilution of thallium amalgams,[3] was employed in the present work. Indeed, the very calorimeter then used was remodeled for the purpose. As the original apparatus has already been described in detail, only a brief supplementary account need be given here.

Apparatus and Manipulation

The calorimeter consisted of a small cylindrical can enclosed (with surrounding air space) by an outer can which was immersed in a bath. The cover of the outer can was provided with 4 emerging tubes. One of these tubes was used for the introduction of material into the calorimeter; another provided for the stirrer (an iron ring with a glass handle); a third accommodated the sensitive mercury thermometer, and a fourth admitted carbon dioxide (which had been brought to the temperature of the bath by passage through an immersed coil of brass tubing). An inert gas was needed to prevent oxidation of the amalgam under investigation. Since the amalgamation was exothermic, no heating coil was required.

The calorimetry was adiabatic; by suitable heating or cooling and vigorous stirring, the temperature of the outer bath was kept as close as possible to that of the inner calorimeter, with the help of a sensitive standardized thermometer in the outer as well as in the inner vessel. The outer bath was contained in a large, cylindrical brass can, which, for thermal insulation, was placed in a paper pail packed to the top with magnesia pipe-covering. This bath consisted of water containing a little copper sulfate; it was heated electrically by the passage of a current through the solution.[3a] The outermost can formed one electrode, and at first the jacketing middle can was used for the other. This latter electrode was soon abandoned, however, since the alternating current was found to heat the mercury (doubtless through induction-effects.) The magnitude of the error from this cause was determined with care, and the few observations in which it had occurred were duly corrected. The results thus obtained proved to be consistent with those obtained by means of the following more satisfactory arrangement. In the improved apparatus, the inner electrode consisted of a suitable cylinder of 6mm. mesh galvanized iron netting, which surrounded the calorimeter without touching it and permitted free circulation of the liquid. A direct (instead of an alternating) current furnished the heat. Thus the bath temperature was controlled satisfactorily, without developing accidental heat inside of the calorimeter. By means of rheostats, the current could be regulated so that heating would take place at a convenient rate, and, because of the small lag of the bath and the rapidity with which the current could be thrown on or off, as desired, with a knife-switch, the bath could be kept within 0.01° of the changing temperature of the material in the calorimeter.

The present series of measurements was made with 237.3 g. of mercury in the inner can of the calorimeter. The contents of the calorimeter and the bath having been brought exactly to 20.00° (the temperature of all measurements), weighed clean strips of metallic thallium (as free from oxide as possible, and also at 20°) were slipped into the calorimeter against an outward flow of carbon dioxide. The thallium immediately began to dissolve in the mercury or dilute amalgam, which was stirred at a slow, uniform rate while the temperature changed. The attainment of a final constant temperature,

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[3] Ref. 2, p. 1746.

[3a] In the manner suggested by Derby and Marden, THIS JOURNAL, **35**, 1767 (1913).

usually within 20 or 25 minutes, indicated the completion of the solution of thallium, and the difference between this final temperature and that observed just before the addition of the metal was taken as the temperature change due to the heat evolved by the reactants in the calorimeter.

The effective heat capacity of the calorimeter was taken as 15.0 mayers (or joules/° C.), computed from the value found in the earlier investigation with allowance for the slight changes in heat capacity due to the alterations which had been made in the apparatus. The heat capacities of the amalgams were obtained from the curve given by Richards and Daniels[4] for the relation between heat capacity and composition of the amalgam.

Successive portions of thallium were added to the contents of the calorimeter, the rise of temperature being observed in each case as described, until a point was reached when the heat of solution changed from positive to negative and the temperature of the calorimeter fell on the addition of the metal, instead of rising. The composition of each amalgam was calculated from the total weight of thallium that had been added to the 237.30 g. of mercury present in the calorimeter at the beginning of the measurements. Two analyses of samples of the final amalgam left at the end of the measurements gave the thallium content as 12.36% and 12.29%, giving a mean value 12.33%, while the composition calculated for this amalgam was 12.46 % of thallium. The discrepancy between the observed thallium content and the calculated was probably due to the presence of a small quantity of oxide but, in any case, the error thus introduced was too small to be of importance.

Results

In Table I, the first column gives the composition of the amalgam to which the thallium is added at the beginning of each measurement; the second gives the composition of the final amalgam resulting from the addition of this thallium; the third gives the rise of temperature produced by the resulting energy change; the fourth gives the specific heat of the final amalgam, which must be used to calculate the heat evolved; the fifth gives (in joules) the heat actually evolved; and the sixth gives the heat which would be evolved in the solution of a gram-atom of thallium under identical conditions.

TABLE I

THE HEAT OF SOLUTION OF THALLIUM IN MERCURY

Wt. of mercury in calorimeter, 237.30 g.

Tl in initial amalgam %	Tl in final amalgam %	Rise of temperature ° C.	Spec. heat of final amalgam (mayers)	Heat evolved For wt. Tl added (joules)	 For 1 gram-atom Tl (joules)
0.00	1.84	1.205	0.1410	59.15	2706
1.84	3.13	0.716	.1420	35.65	2265
3.13	4.48	0.642	.1428	32.41	1917
4.48	5.94	0.535	.1437	27.39	1590
5.94	7.83	0.558	.1448	29.17	1075
7.83	9.69	0.236	.1459	12.59	486
9.69	11.17	0.018	.1467	0.98	45
11.17	12.46	—0.082	.1474	−4.49	−234

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[4] Ref. 2, p. 1750.

The heat evolved during an experiment was actually an average value, since the thallium concentration of the amalgam was constantly increasing as the metal dissolved. With each addition, the first portion dissolved corresponded to the addition of thallium to an amalgam of the initial concentration, while the last portion corresponded to the addition of thallium to an amalgam of the final concentration. The heat evolved, therefore, corresponded approximately to the solution of thallium in an amalgam of the average concentration. For example, in the second determination, the heat evolved during the increase of concentration from 1.84% to 3.13% corresponds closely to the solution of thallium in an amalgam of the average concentration 2.49%, the assumption being made that the curve representing the variation of the heat of solution with concentration is a straight line between the two points for the concentrations in question. As the points are close together on the curve, which is nearly a straight line in the region here studied, the small error introduced by this assumption is negligible in comparison with the probable experimental error.

The previously mentioned measurements of Richards and Daniels on the heat of solution of thallium in more concentrated amalgams were carried out at 30°, but the corresponding values at 20° may be calculated from these determinations with the aid of the Kirchhoff equation, $\mathrm{d}U/\mathrm{d}T = K_1 - K_2$, in which $\mathrm{d}U/\mathrm{d}T$ is the temperature coefficient of the total energy change, and K_1 and K_2 are the respective heat capacities of the reactants and the resultants. In these calculations, K_1 may be considered as simply the atomic heat of pure, solid thallium, which is given in the literature as about 6.2 calories, if K_2 is taken as the "partial atomic heat capacity" of thallium in the average amalgam in which the heat of solution is measured. The partial atomic heat capacities have been calculated by Lewis and Randall[5] from the determinations of the heat capacities of the amalgams made by F. Daniels and one of us. The heat of solution, U_t, at temperature t, may then obviously be calculated from the heat of solution, U_t', at a temperature, t', by means of the following equation: $U_t = U_t' + (t - t')(K_1 - K_2)$.

In Table II the results of the present series of measurements are given, together with those of the earlier experimental investigation obtained at 30° and calculated to 20°.

All the values for the heat of solution at 20° are plotted in Fig. 1, in which the average concentrations are represented as abscissas and the quantities of heat evolved as ordinates. The values obtained by the adiabatic method in the experiments here described are represented by circles, while those obtained by the earlier isothermal method are represented by small crosses. The two series of results agree so well where they overlap that they may be

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[5] Lewis and Randall, THIS JOURNAL, **43**, 239 (1921). These values they designate as "partial molal heat capacities."

TABLE II

HEAT OF SOLUTION OF A GRAM-ATOM OF THALLIUM IN AMALGAMS

Adiabatic method, present results		Isothermal method—Richards and Daniels		
Tl during each addition Av. %	Heat in joules evolved in dissolving 1 gram-atom of Tl in amalgam	Tl during each addition Av. %	Heat in joules evolved in dissolving 1 gram-atom of Tl in amalgam	
	U_{20}		U_{20}	U_{30}
0.92	2706	9.81	108	−32
2.49	2265	13.05	−641	−771
3.81	1917	17.33	−1497	−1614
5.21	1590	21.53	−2214	−2321
6.89	1075	25.55	−2611	−2711
8.76	486	29.16	−2939	−3036
10.43	45	32.65	−3216	−3310
11.81	−234	36.26	−3579	−3670

represented by a single smooth curve. Indeed, their agreement is better than might have been expected in view of the preliminary character of the present series of measurements, and leads to the belief that the results are fairly accurate.

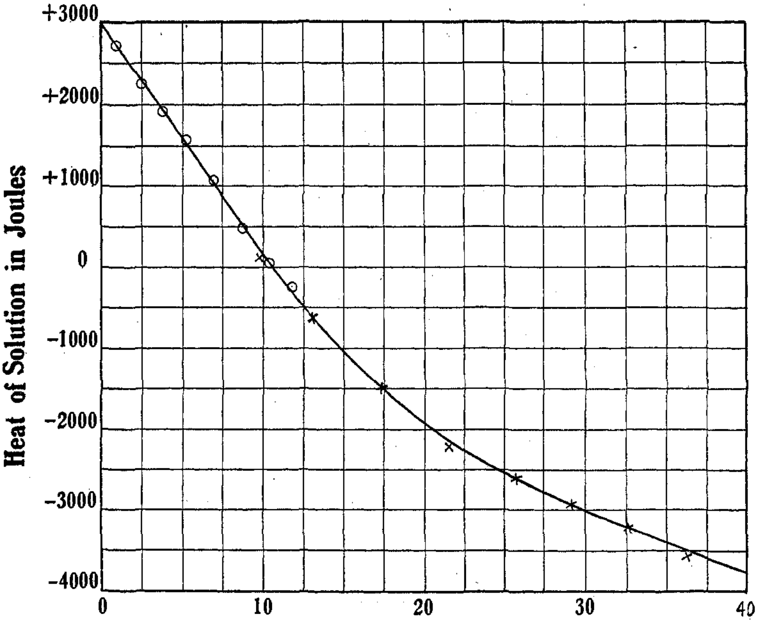

Fig. 1.

Extrapolation of the curve over a composition range of only 0.92% brings it to the heat of solution axis at a point corresponding to a heat of solution of 2970 joules, which means that the solution of 1 gram-atom of thallium in an infinite amount of mercury would be accompanied by a heat evolution of 2970 joules. From the electromotive forces and temperature coefficients of thallium amalgam concentration cells, Richards and Daniels calculated the heat effects of the cells by use of the Helmholtz equation. From these results, Lewis and Randall[5] calculated the partial molal heat contents of thallium and mercury in the amalgams and, by the use of these heat contents and the data of Richards and Daniels upon the heats of solution of thallium in the amalgams, calculated the heat evolved when 1 gram-atom of thallium dissolves in an infinite amount of mercury. The value thus obtained is 730 calories, or 3053 joules, at 30°, with a probable error of 20 calories or 83 joules. The corresponding value at 20° may be calculated by the Kirchhoff equation to be 3220 joules, which is 250 joules higher than the value obtained by extrapolation of the curve in Fig. 1. In view of the possible errors in both results, the agreement is not unsatisfactory.

Summary

The heats of solution of thallium in dilute thallium amalgams have been determined in a preliminary series of measurements. The results are consistent with those obtained by Richards and Daniels for concentrated amalgams. A short extrapolation of the curve for the variation of the heat of solution with concentration of the amalgam gives a value for the heat of solution of thallium in an infinite quantity of mercury in fair agreement with the value calculated by Lewis and Randall.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE QUANTITATIVE DETERMINATION OF PRASEODYMIUM

BY PAUL H. M.-P. BRINTON AND H. ARMIN PAGEL

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The gravimetric determination of praseodymium is attended by some uncertainty, and while the single determination of this element is not at present required in the routine of industry, it is a matter of fundamental importance in many studies of the chemistry of the rare earth elements. The precipitation as oxalate is commonly followed by ignition in air. Contrary to the action of the majority of the rare earth elements, praseodymium does not form an oxide of the R_2O_3 type on ignition in air, but gives an intermediate oxide to which the formula Pr_4O_7 is commonly assigned, and this is used as the basis of calculation in the majority of analytical directions.

In previous work[1] difficulty had been experienced in getting satisfactory results by this method, and it had been found necessary to reduce in hydrogen to the sesquioxide, Pr_2O_3, for weighing.

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[1] Brinton and James, THIS JOURNAL, **43,** 1446 (1921).