The Heat of Formation of Thallium Azide[1]

By William S. McEwan and Mary Mae Williams

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The heat of formation of thallium azide has been determined by explosion in a helium atmosphere and measurement of the heat evolved. There have been no thermodynamic data published on metallic azides in recent years. In 1917, Wohler and Martin[2] prepared a number of azides and fulminates and determined their "heat of detonation." Experimental details of the determinations are not given and their value of 232 cal./gram for TlN_3 is 7 cal./gram higher than that observed by this Laboratory. The average of five determinations made by this Laboratory is 224.8 ± 0.8 cal./g.

Products of the decomposition of TlN_3 which took place in a calorimetric bomb containing 30 atmospheres of helium are metallic thallium and nitrogen. The ΔH_f of formation is in this case practically the negative of the ΔH_e of explosion. The correction, being the ΔH of expansion at constant temperature of one and a half moles of nitrogen from 30 to 1 atmosphere, was computed from the expression

$$H_{(T_1P_2)} - H_{(T_1P_1)} = (B - T\mathrm{d}B/\mathrm{d}T)(P_2 - P_1)$$

where B is the second virial coefficient for nitrogen.

		kcal.
$TlN_3 \rightarrow 3/2N_{2(30\text{ atm., }24°)} + Tl(c)$	ΔH_e	$= -55.390 \pm 0.2$
$3/2N_{2(30\text{ atm., }25°)} \rightarrow 3/2N_{2(1\text{ atm., }25°)}$	ΔH	$= 0.054$
$Tl(c) + 3/2N_{2(1\text{ atm., }25°)} = TlN_3$	ΔH_f	$= +55.34 \pm 0.2$

Details of the calorimetric equipment and procedure are given so that the character of this work may be ascertained.

Calorimetric Equipment and Procedure.—Thallium azide detonates on ignition and shatters the sample holder, therefore an expendible porcelain crucible was used in a standard Parr, 360-ml., double valve oxygen bomb.

The loaded bomb was twice filled with 25 atmospheres of grade A oil-free helium and then vented to remove any air present. It was then filled with helium to an absolute pressure of 30 atmospheres. Helium by mass spectrographic analysis showed an oxygen content of the order of 0.003 mole per cent. If it is assumed that all the oxygen present during the burning process reacts to form Tl_2O the heat evolved is 1.91 cal. This would result in the values given being too high by 0.95 cal./g.

The bomb was placed in the calorimeter, consisting of an inner and an outer metal vessel separated from each other by a 1-cm. air space. The opposing vessel surfaces are chrome-plated to reduce radiation losses. The inner jacket contains a weighed quantity of water (2000 ± 0.2 g.), a stirrer, and the charged bomb. A close-fitting lid covers the inner jacket, and a large double lid covers both the inner and outer calorimeter vessels. This outer lid is of hollow construction so that water from the bath may be drawn up into it. The calorimeter is thus completely enclosed by a 1-cm. air space which in turn is surrounded by a constant-temperature (±0.002°) bath. The ignition wires are attached, the stirrer is connected, and the calorimeter is allowed to sit until the change of temperature in the calorimeter with respect to time becomes uniform.

Temperature measurements are made with a platinum resistance thermometer using a Mueller type G-2 resistance bridge.

Heat transfer between the calorimeter and the constant temperature bath is determined by measuring the rate of temperature change before and after igniting the sample. Time intervals are recorded on a Gaertner four-channel chronograph.

The thermal-leakage coefficient and the heat of stirring are obtained by the solution of two equations of the form

$$\mathrm{d}T/\mathrm{d}t = QK + W$$

where $\mathrm{d}T/\mathrm{d}t$ is the change of temperature with respect to time in the calorimeter; Q, the thermal head, is the difference between the bath temperature and the calorimeter temperature; K is the thermal-leakage coefficient; and W is the rise in temperature produced through stirring. The total heat loss is obtained by graphic integration of the temperature–time plot.

Other corrections are made for electrical heating of the iron ignition wire and for the heat capacity of the reactants and products back to 25°.

The calorimeter was calibrated against samples of benzoic acid no. 39f supplied by the National Bureau of Standards. The experimental data are summarized in Table I.

Preparation of Material.—Thallium azide was prepared by dissolving thallium sulfate in sufficient hot water for solution, sodium azide was then added and the material permitted to cool. The precipitated thallium azide was filtered, and recrystallized from water, washed with alcohol and dried in a vacuum oven at 50°. The dried material was then pressed into 2-g. pellets in preparation for the calorimetric determination. The sample analysis gave 99.64% and 99.83% purity in two batches.

Table I

Experimental Data

Energy equivalent of calorimeter = 2280.27 cal.

Measured temp. rise, °C.	0.1977	0.1968	0.1826	0.1977	0.1957
Heat loss, °C.	+ .0011	+ .0014	+ .0018	+ .0017	− .0003
Stirring correction, °C.	− .0036	− .0018	− .0024	− .0053	− .0038
Total heat evolved, cal.	445.11	447.85	415.01	442.60	436.90
Electrical heating, cal.	3.60	1.73	1.58	1.80	1.87
C_p reactants $(25 - T_1)$, cal.	+2.53	−0.22	+0.79	+0.77	+0.66
C_p products $(T_2 - 25)$, cal.	−2.08	+0.73	−0.37	−0.29	−0.19
Weight of sample, g.	1.9673	1.9683	1.8482	1.9695	1.9419
Heat of explosion, cal./g.	224.65	226.90	223.92	224.27	224.26

Heat of explosion (av.) = 224.80 ± 0.84

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[1] Published with the permission of the Technical Director, U. S. Naval Ordnance Test Station.

[2] Wohler and Martin, *Ber.*, **50**, 595 (1917).

The Formation and Dissolution of Metal Sulfides[1]

By Herbert A. Pohl

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The precipitation of metal sulfides by the action of H_2S in solutions of the salts of the metals may be caused by the interaction of the metal ion with $S^=$ ion, with the HS^- ion or with molecular H_2S. It would appear from the work described that the

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[1] This work was done under Contract #AT(07-2)-1 with the AEC and is published with its permission.

reaction is predominantly by way of attack of the HS^- ion on the metal ion to form an intermediate reactive complex which decomposes in turn to the metal sulfide.

The precipitation may be considered in the thermodynamic sense to proceed by the reaction of the metal ion with the $S^=$ ion as is represented in the mass action equation for the solubility product: *e.g.*, $(M^{++})(S^=) = K_s$. It is difficult, however, to explain the observed rapidity of the precipitation as due solely to the direct action of the $S^=$ ion in view of the very small concentration of $S^=$ ion generally employed. This viewpoint regarding the smallness of the number of sulfide ions available was clearly stated by Smith.[2] What is essentially that argument, but using more recent and accurate values of the dissociation constants, ($K_1 = 1.02 \times 10^{-7}$, $K_2 = 1.3 \times 10^{-13}$, as redetermined by Latimer, Kury and Zielen[3]), is presented here. In this case, for example, of metal ions such as Cu^{++}, Hg^{++} Cd^{++}, etc., which are rapidly precipitated in 1 *M* acid containing 0.1 *M* H_2S, the concentration of $S^=$ ions at 25° is about 1.3×10^{-21} *M* or about 80 ions per ml. Clearly, some more rapid mechanism other than direct interaction of the metal ion with $S^=$ ion must apply. The concentrations of HS^- ion and of H_2S, on the other hand, in such an instance are much larger, being 10^{-8} and 0.1 *M*, respectively. It is accordingly more likely that the reaction is between the metal ion and either H_2S or HS^-. While it is possible to aid the understanding of the mechanism of metal sulfide precipitation with "thermodynamic" calculations of the ion concentrations and the application of intuition as to the impossibility of $S^=$ ion in such low concentration being possessed of a major role in the reaction; it must devolve upon reaction kinetics studies to decide for us whether the HS^- ion or the H_2S molecule is predominantly involved in the precipitation. A consideration of the probable actions of H_2S, HS^- and $S^=$ is given below. These may be pictured as attacks on the firmly hydrated metal ion as follows: For simplicity, the simple case of the divalent metal ion is considered.

HS^- Case

$$(M,\ xH_2O)^{++} + HS^- \xrightarrow[\text{(slow reaction)}]{} \underset{\text{(activated complex)}}{(M{\cdot}SH,\ (x-1)\,H_2O)^+} + H_2O$$

$$\xrightarrow[\text{(fast reaction)}]{} MS\downarrow + H^+ + H_2O$$

or in brief form simply as

$$M^{++} + HS^- \longrightarrow (M{\cdot}SH)^+ \longrightarrow MS\downarrow + H^+$$

The forward (precipitate-forming) rate to form the intermediate complex for the metal ion plus HS^- may be postulated as

$$r_f = k_f\,(M^{++})\,(HS^-)$$

The rate of back reaction (dissolution) is

$$r_b = k_b\,(f)$$

where (f) is some as yet unknown function. It may be evaluated by considering that at equilibrium the forward and back reaction are equal in rate, and that the ratio of the specific forward and back reaction rate constants is the equilibrium constant or, in this case, the solubility product, *i.e.*

$$r_f = r_b$$

$$k_b/k_f = K_s = (M^{++})\,(S^=)$$

hence, since for the second dissociation of H_2S

$$K_2 = (H^+)\,(S^=)/(HS^-)$$

we may substitute and get

$$(f) = (H^+)/K_2$$

We would accordingly expect to find the dissolution rate of the sulfide to be dependent on the first power of the hydrogen ion concentration, *i.e.*

$$r_b = (k_b/K_2)\,(H^+)$$

By similar reasoning, the dissolving rate may be shown to be independent of the acidity, in the case that the forward reaction is that of the attack of $S^=$ ion on the metal ion, *i.e.*

$$r'_b = \text{constant, independent of } (H^+)$$

This, for example, is the case for salts of a strong acid such as AgCl, within certain rather wide limits.

Furthermore, it may be similarly shown that the dissolving rate is to be proportional to the square of the hydrogen ion concentration in the case that the forward reaction is that of attack of molecular H_2S on the metal ion, *i.e.*

$$r''_b = k''_b\,\frac{(H^+)^2}{K_1K_2}$$

It now remains for experiment to decide which of the above mechanisms is predominant in the formation and dissolution of metal sulfides. From the following experiments, it is clear that the HS^- ion is the most prominent agent for the cases considered.

Experimental

Precipitates of FeS, ZnS and CdS were prepared by treating 5% solutions of the metal chloride or sulfate with a 7% solution of NaHS prepared by bubbling H_2S into NaOH. The precipitated sulfides were then centrifuged and washed three times with distilled water. The particle size was estimated to range principally from 1 to 10 μ. The dissolving rates were measured by noting the time it took for all but some 1% of the sulfide to dissolve, when a small quantity (*ca.* 0.05 mg.) of it was added to 5 ml. of the desired concentration of HCl and stirred slowly. In the solutions of low acid concentration, assurance of the maintenance of a large excess of acid was checked by redetermining the dissolving time in the same solution. As a check on the validity of the experiments, those on FeS and ZnS were also run using the criterion of the rate as that point at which all but some 20% had dissolved. Similar curves, parallel to those using the 1% criterion, were obtained, showing the slope to be that for a first order reaction. In the case of CdS, there appeared to be very small fraction of sulfide formed which did not dissolve in the low concentrations of acid but which would dissolve if more acid were added. This indicated the presence of either a second form of CdS or of possible impurity such, perhaps, as mercaptan from the H_2S used. This material was not studied further.

The experimental results are shown graphically in Fig. 1 for the sulfides of Fe, Zn and Cd. There appears to be little doubt that the dissolving rate is first order with acid con-

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[2] G. McP. Smith, THIS JOURNAL, **44**, 1500 (1922).

[3] J. W. Kury, A. J. Zielen and W. L. Latimer, University of California Radiation Laboratory Document No. UCRL-2108, have recently brought into harmony the results of H. Kubli (*Helv. Chim. Acta*, **29**, 1962 (1946)) and N. Konopik and O. Leberl (*Monatsh.*, **80**, 781, 788 (1949)) and others on the dissociation of H_2S. Publication of this work is understood to be scheduled for the October, 1953, *J. Electrochem.*

centration; hence it would appear preferable to consider the sulfide precipitation reaction to consist of the attack of HS^- ion on the metal ion in aqueous solution.

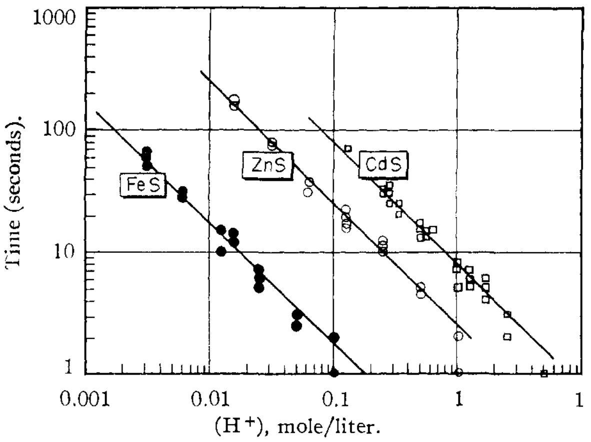

Fig. 1.—The rate of dissolution of precipitated sulfide at 25°.

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The Chelation of Praseodymium by Thenoyltrifluoroacetone[1]

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The dependence of chelation of metal ions upon *p*H has been reported by a number of workers[2a,b–6] using the β-diketone, thenoyltrifluoroacetone (referred to as TTA), as the chelating agent in a two-phase system. The over-all equilibrium involved in the distribution of praseodymium between an aqueous phase and an organic phase (TTA in benzene) may be represented by the equation

$$Pr^{+++}(aq) + 3HT(bz) \rightleftharpoons PrT_3(bz) + 3H^+(aq)$$

The equilibrium expression for this reaction is

$$K_{eq} = \frac{[PrT_3][H^+]^3}{[Pr^{+++}][HT]^3}$$

The quantity $[PrT_3]/[Pr^{+++}]$ will be defined as the distribution ratio D.R.

The distribution ratio can be evaluated by the use of Pr^{142} as a tracer and counting equal aliquots of each phase. King and Reas[7] have reported the thermodynamic activity coefficients for TTA. The activity coefficient for the metallic chelate in benzene is assumed to be equal to the known coefficient for the unchelated TTA. Kielland[8] lists the activity coefficient for praseodymium. Hydrogen ion activity was determined directly as *p*H using a Model G Beckman *p*H meter. The equilibrium concentration of the unchelated TTA was assumed to be the same as the concentration before equilibration since a large excess was always present.

Experimental

The aqueous phase was initially 0.0071 *f* Pr(III) with ammonium chloride added to give an ionic strength of 0.1. The benzene phase was either 0.2 *f* or 0.5 *f* in TTA. Praseodymium trichloride (Fairmount Chemical Co.) was used to make up the aqueous stock solutions. The authors are indebted to R. P. Hammond (Los Alamos Scientific Laboratory) for a sample of very pure (99.9%) praseodymium oxide. This compound was converted to the chloride and irradiated with neutrons, for use as a tracer. The TTA was obtained from the Dow Chemical Company.

The reaction vessel was made from 45-mm. glass tubing. A section about 20 cm. long was sealed at one end and the open end sealed to a 24/40 ₸ joint. A stirrer, fitted with a 24/40 ₸ bearing, provided constant agitation. The entire apparatus was immersed in a constant temperature bath held at 25.1 ± 0.1°.

Fifty ml. of the TTA–benzene solution and 10 ml. of the praseodymium trichloride solution were used in each run. Since it was desired to measure the extent of chelation as a function of *p*H, either dilute ammonium hydroxide or hydrochloric acid was added. Each mixture was stirred for one hour to ensure thermal and chemical equilibrium.

At the completion of a run, the *p*H of the aqueous phase was then determined immediately. The praseodymium in the aqueous phase was then precipitated by oxalic acid. The oxalate precipitate was filtered with a chimney and spring arrangement on a fritted disc and counted. The counting instrument used a Geiger–Mueller tube with a 3.5 mg./cm.² mica window. The praseodymium was removed from the benzene phase by extraction for one hour with saturated oxalic acid solution. The resulting oxalate precipitate was prepared for counting in the same manner as the sample taken from the aqueous phase

The two samples from one run were always counted within a few minutes of each other. No absorption corrections were made since the Pr^{142} beta has a maximum energy of 2.2 Mev.

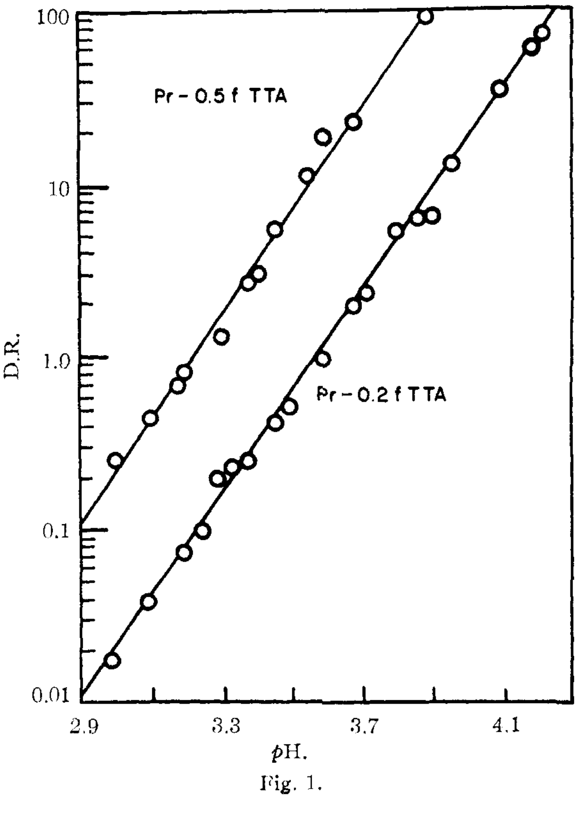

Fig. 1.

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[1] This work was performed at the University of New Mexico in coöperation with the Los Alamos Scientific Laboratory.

[2] (a) R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949); (b) A. Broido, AECD-2616.

[3] R. Bolomey and L. Wish, THIS JOURNAL, **72**, 4483, 4486 (1950).

[4] E. Huffman and L. Beaufait, *ibid.*, **71**, 3179 (1949).

[5] J. Suttle, AECD-2800.

[6] J. Suttle, AECU-741.

[7] E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1804 (1951).

[8] J. Kielland, *ibid.*, **59**, 1675 (1937).