drolysis of samarium nitride three additional DTATGA runs were made. In the first, $Sm(OH)_3$ was precipitated, washed, and vacuum dried at room temperature; the weight and DTA curves were largely without character. In a second run the $Sm(OH)_3$ was precipitated, washed and dried at 110° for six hours. An X-ray powder diagram of the dried material showed a complex lattice of large cell dimension quite different from the hexagonal structure of the $Sm(OH)_3$ produced by hydrolysis of SmN. A DTATGA run on this material was in general aspect similar to the vacuum dried material and both had a large amount of water, $Sm(OH)_3 \cdot 2.3H_2O$ and $Sm(OH)_3 \cdot 2.8H_2O$, respectively. A third preparation similar to the second but from which almost all the water ($Sm(OH)_3 \cdot 0.12\ H_2O$) had been removed showed the same hexagonal structure reported above and gave DTATGA curves very similar to the ones observed from the hydrolyzed SmN. That is, a sharp break in the weight curve at 375° with DTA peaks corresponding to the initial endothermic decomposition of $Sm(OH)_3$ and of a composition around SmO(OH).

The $Sm(OH)_3 \cdot 2.8H_2O$ and other highly hydrated materials apparently have water incorporated within the crystal lattices. This water is completely lost only at temperatures far above the decomposition temperature of $Sm(OH)_3$, hence, the latter decomposes rapidly without indicating the low molecular weight hydrated material.

All the samples of EuN contained a trace contaminant exhibiting a complex powder diagram which was believed to be an oxide. Because of this impurity and the scarcity of europium, no additional work was done on EuN.

Samples of YbN prepared by direct combination of the metal with nitrogen always contained some unreacted metal. Even at 1000°, 200° above the melting point of ytterbium, the reaction did not go to completion. When these samples containing metal and YbN were distilled in a high vacuum (10^{-5} mm.), both ytterbium metal and YbN were found in the distillate. A complete distillation occurred if sufficient time was allowed at 1400°. This may imply a high vapor pressure for YbN. SmN heated to 1600° did not exhibit any tendency to distil. This suggests a considerable thermal stability and low vapor pressure. Samples of YbN prepared by the reaction of YbH_2 and N_2 at 1000° were monophasic. At lower temperatures conversion was not quantitative.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Heat of Precipitation and Formation of Silver Molybdate

BY C. N. MULDROW, JR., AND L. G. HEPLER

RECEIVED JULY 23, 1956

The heat of precipitation of silver molybdate has been determined from two series of calorimetric experiments. From these data and the results of earlier investigators, we calculate the heat of formation of Ag_2MoO_4 to be −200.4 kcal./mole and the free energy and entropy of solution of Ag_2MoO_4 to be +15.6 kcal./mole and −9.4 cal./deg. mole, respectively.

As part of a systematic investigation of the thermochemistry of molybdenum, it was desired to have reliable values for the heats of formation and precipitation or solution of one or more slightly soluble molybdates. Therefore, the heat of precipitation of Ag_2MoO_4 has been carefully determined, and from this quantity several thermodynamic calculations have been made.

Experimental

The high-precision solution calorimeter used in this investigation has been previously described in some detail.[1] The silver nitrate was Mallinckrodt Analytical Reagent crystals. Fisher Certified Reagent sodium molybdate (Na_2MoO_4) was dried for 24 hours at 110° and found by analysis to be 46.7% Mo as compared with the calculated value of 46.6%. The analysis was done by the permanganate method.[2]

The calorimeter used in this investigation has been checked periodically by determining the heat of solution of potassium chloride.[1] Agreement with reported values is excellent.[3,4] All heats of reaction have been carried out at 25.0 ± 0.5°.

Results

The heat of reaction of crystalline Na_2MoO_4 with dilute solutions of $AgNO_3$ was measured to determine the heat of precipitation of Ag_2MoO_4. The calorimetric reaction may be written as eq. 1

$$Na_2MoO_4(c) + AgNO_3\text{ (excess dil. soln.)} = Ag_2MoO_4(c) + AgNO_3\text{ (dil. soln.)} + NaNO_3\text{ (dil. soln.)} \quad \Delta H_1 \qquad (1)$$

The results of these experiments are given in Table I. The heats were actually determined to the nearest 0.02 kcal./mole, but because of the spread of values they are reported only to the nearest 0.1 kcal./mole. All determinations were made using 950 cc. of solution.

To calculate the standard heat of formation of Ag_2MoO_4 from the experimental values of ΔH_1, it is necessary to know the heats of formation of $Na_2MoO_4(c)$,[1] $NaNO_3(aq)$[3] and $AgNO_3(aq)$.[3] We

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[1] R. L. Graham and L. G. Hepler, THIS JOURNAL, **78**, 4846 (1956).

[2] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 307.

[3] "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

[4] F. H. Spedding and C. F. Miller, THIS JOURNAL, **74**, 3158 (1952).

TABLE I

HEATS OF REACTION OF Na_2MoO_4(c) WITH $AgNO_3$(aq)

$AgNO_3$, moles	Na_2MoO_4, moles	$-\Delta H_1$ (kcal./mole)
0.0702	0.0290	14.2
.0589	.0204	15.1
.0589	.0230	15.6
.0294	.0107	14.1
.0590	.0114	14.1
.0956	.0184	14.5
.0478	.0106	14.9
.0503	.0123	14.3

Av. ΔH_1 = −14.6 kcal./mole. Average deviation 0.5 kcal./mole.

have ignored the heats of dilution of $NaNO_3$ and $AgNO_3$ because in these dilute solutions these heats are small and tend to cancel each other. Using the average value for ΔH_1 of −14.6 kcal./mole, we calculate the heat of formation of Ag_2MoO_4(c) to be −199.8 kcal./mole.

Another series of experiments determined the heat of reaction of excess $AgNO_3$(c) with dilute solutions of Na_2MoO_4. Equation 2 gives the calorimetric reaction

$$AgNO_3\text{ (c, excess)} + Na_2MoO_4\text{ (dil. soln.)} = Ag_2MoO_4\text{(c)} + AgNO_3\text{ (dil. soln.)} + NaNO_3\text{ (dil. soln.)} \quad \Delta H_2 \qquad (2)$$

The results are given in Table II. Again 950 cc of solution were used in each run.

TABLE II

HEATS OF REACTION OF $AgNO_3$(c) WITH Na_2MoO_4(aq)

$AgNO_3$, moles	Na_2MoO_4, moles	Heat absorbed (cal.)	Heat absorbed minus heat of soln. $AgNO_3$
0.04204	0.008577	116.8	−109.0
.06257	.008604	217.0	−119.0
.06955	.006006	300.3	− 73.2
.08364	.010767	300.1	−149.0

Values obtained in this Laboratory for the heat of solution of $AgNO_3$ agree well with the heat calculated from the Bureau of Standards data.[3] As with the first series of determinations, heats of dilution were ignored in making calculations. Because dilute solutions were used, the heats of dilution are again small and also tend to cancel each other. In view of the final uncertainty of several tenths of a kilocalorie and the lack of pertinent heats of dilution, ignoring these small heats is acceptable. The heat absorbed in dissolving the excess solid $AgNO_3$ is calculated from Bureau of Standards data.[3] This heat is subtracted from the total measured heat to give the heat of the precipitation reaction. From the experimental heats of reaction 2 and the previously mentioned heats of formation, the heat of formation of Ag_2MoO_4(c) has been calculated to be −200.7 kcal./mole with an average deviation of 0.6 kcal./mole.

Discussion of Results

Britton and German[5] have shown that normal alkali molybdates react with silver nitrate to give normal silver molybdate. Every precipitation in the present investigation was carried out with excess silver nitrate to prevent formation of polymolybdates. However, some slight formation of polymolybdate may be responsible for the fact that deviations from the average are considerably larger than the uncertainty in any one run.

Several earlier investigations of Ag_2MoO_4 are related to ours. Ricci and Linke[7] have determined the solubility of Ag_2MoO_4 over a range of temperatures. Neglecting small hydrolysis effects, we have calculated from their data thermodynamic solubility products at several temperatures. With the van't Hoff equation and these equilibrium constants we calculate the heat of solution of Ag_2MoO_4 to be +12.6 kcal./mole. This heat and the heats of formation of Ag^+(aq)[3] and $MoO_4^=$(aq)[1] give −200.2 ± 0.6 kcal./mole as the heat of formation of Ag_2MoO_4.

Pan[7] has investigated Ag_2MoO_4 with a silver–silver molybdate electrode and has reported values for the standard free energy and heat of solution of Ag_2MoO_4. From his results and our recently determined heat of formation of aqueous molybdate ion,[1] we calculate that the heat of formation of Ag_2MoO_4(c) is −200.5 kcal./mole. It is difficult to estimate the uncertainty of this value, but it is certainly fairly small.

From our two series of determinations of the heat of precipitation of Ag_2MoO_4 and from our calculations based on Ricci and Linke's solubility work[6] and on Pan's e.m.f. work,[7] we take −200.4 ± 0.2 kcal./mole as the best value for the heat of formation of Ag_2MoO_4(c).

Pan's[7] free energy of solution of Ag_2MoO_4 and that calculated from Ricci and Linke's[6] solubility work at 25° agree fairly well. Ricci and Linke also discuss earlier determinations of the solubility. We take the best value of the free energy of solution and the solubility product at 25° to be +15.6 kcal./mole and 2.8×10^{-12}, respectively. From this free energy of solution and the heats of formation of Ag_2MoO_4(c), Ag^+(aq)[3] and $MoO_4^=$(aq),[1] we calculate the entropy of solution of Ag_2MoO_4 to be −9.4 cal./deg. mole. Determination of the entropy of Ag_2MoO_4(c) from heat capacity measurements and the Third Law would thus make it possible to calculate the entropy of $MoO_4^=$(aq). The above entropy of solution and that calculated from estimated entropies[8] of $MoO_4^=$(aq) and Ag_2MoO_4(c) and the known entropy of Ag^+(aq)[3] are about the same.

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The Heterogeneous Exchange Reaction between Hydrogen Chloride and Chlorine on Glass and Fluorocarbon[1a,b]

BY J. R. WALTON[2] AND W. H. JOHNSTON

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The heterogeneous exchange reaction between hydrogen chloride and chlorine was studied on Pyrex and Vycor glasses and on fluorocarbon using chlorine-36. Evidence was obtained that this reaction proceeds through catalysis by adsorbed water which was removed both by evacuations at elevated temperatures and by treatment with diborane at room temperature. By varying the amount of adsorbed water, half-times of exchange were obtained from one minute to six days. The rate law of the reaction producing exchange was determined on Vycor and found to be consistent with equilibria adsorptions and a rate-controlling surface reaction. The rate in moles liter^{-1} sec.$^{-1}$ was $5.0 \times 10^{-6}(HCl)^{0.37}(Cl_2)^{0.37}$ for concentrations in moles liter^{-1}.

Introduction

In 1951 Johnston and Libby reported a rapid heterogeneous exchange reaction between hydrogen chloride and chlorine in the gaseous state.[3] The present paper describes further experiments on several glasses and fluorocarbon and reports the discovery that adsorbed water is responsible for the catalytic activity of these surfaces. Originally, the adsorbed water was removed by evacuation at elevated temperatures. In order to avoid possible structural changes accompanying these evacuations, additional experiments were done in which the water was removed by chemical treatment with diborane at room temperature. A rate law is reported and related to a proposed mechanism for exchange. No evidence was found for an homogeneous dark reaction.

Experimental

The radioactive chlorine-36 was obtained from the Isotopes Division, Oak Ridge National Laboratory, U.S.A.E.C. as high specific activity dilute hydrochloric acid. A small amount of this solution was mixed with excess concentrated ammonium hydroxide and evacuated to dryness in a glass bulb. Following extensive evacuation, a large excess of anhydrous hydrogen chloride was added to the vessel. The radioactive ammonium chloride was sublimed carefully to the upper half of the bulb. By this procedure the chlorine-36 was efficiently introduced into the anhydrous hydrogen chloride.

The procedure for measuring exchange was essentially the same as that described previously.[3] In each experiment the gases were mixed in the dark and separated by passage through two traps in series under vacuum. The first trap for chlorine was maintained at −125 to −130° by an ethanol bath; the trap for hydrogen chloride was immersed in liquid nitrogen. In each experiment the initial and final specific activities were determined by measuring the activities in an annular Geiger counter as a function of pressure. The over-all recoveries of pressure and activity were determined in each experiment and found to be 90 to 100%.

Preparation of Surfaces.—In the thermal preparation of the Pyrex surface, a 500-ml. virgin Pyrex flask was successively evacuated by heating for two days at 150–170° and by a series of heatings for $^1/_2$-hour each at 250–400° with a glass-working torch. Each evacuation was at a pressure of less than 10^{-3} mm. The Vycor surface was a 800-ml. Kjeldahl flask which was initially cleaned with chromic acid cleaning solution and carefully steamed. It was successively evacuated at less than 10^{-3} mm. by a series of heatings for $^1/_2$ hour each at 250–400° and by heating under vacuum at 700° for one week.

The fluorocarbon surface was a mixture of saturated long-chain fluorocarbons, du Pont perfluorolube oil FCX-335. The reaction vessel was a 500-cc. Pyrex flask which was coated with the fluorocarbon by melting it at 60–90°. This vessel was evacuated at less than 10^{-3} mm. for one week at room temperature.

In several experiments adsorbed water was added to the Pyrex and fluorocarbon surfaces by introducing 2 mm. of water vapor and evacuating at 10^{-3} mm. for 3 hours.

In an effort to chemically remove adsorbed water, a 270-cc. Pyrex flask was given a series of pre-treatments with diborane at room temperature. The diborane was prepared by the reaction between boron trifluoride etherate and lithium aluminum hydride and purified by distillation.[4]

Results and Discussion

Catalysis by Adsorbed Water.—The half-times for isotopic exchange between hydrogen chloride and chlorine on fluorocarbon, Pyrex and Vycor following various thermal pre-treatments under vacuum are shown in Table I. It is interesting to note the wide range of speeds of this heterogeneous reaction; the half-time of exchange ranged from a few minutes to almost a week.

TABLE I

HETEROGENEOUS EXCHANGE BETWEEN HYDROGEN CHLORIDE AND CHLORINE ON FLUOROCARBON, PYREX AND VYCOR AT 20°

Surface		Treatment[a]	Half-time[b]
Fluorocarbon	1.	25° for 1 week	38.0
	2.	25° for 10 min.	39.0
	3.	Plus 2 mm. of H_2O	0.8
	4.	25° for 3 hours[c]	16.0
Pyrex	1.	170–200° for 2 days	1.2
	2.	250–400° for $^1/_2$ hr.	3.3
	3.	250–400° for $^1/_2$ hr.	5.6
	4.	250–400° for $^1/_2$ hr.	7.3
	5.	Plus add. H_2O[d]	0.2
Vycor	1.	250–400° for $^1/_2$ hr.	1.5
	2.	250–400° for $^1/_2$ hr.	3.7
	3.	250–400° for $^1/_2$ hr.	5.1
	4.	No additional treat.	5.1
	5.	700° for 1 week	134.0
	6.	No additional treat.	134.0

[a] Sequence of evacuations (at 10^{-3} mm.) or additions. [b] Isotopic exchange half-time in hours. [c] Adsorbed water remaining from run 3. [d] Added as in run 4-fluorocarbon.

With each successive evacuation at an elevated temperature, the rate of exchange was slower. This observation suggested an adsorbed catalyst which was progressively removed by the evacuations. Prior to runs fluorocarbon-4 and Pyrex-5

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(1) (a) This work was supported in part by the A.E.C. under Contract At(11-1)-166 with Purdue University; (b) parts of this paper were presented at the XIIth International Congress of Pure and Applied Chemistry on September 10, 1951, in New York.

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