[CONTRIBUTION FROM HOKKAIDO UNIVERSITY, SAPPORO, JAPAN]

Equilibrium in the System GeO_2–H_2–Ge–H_2O[1]

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A measurement has been carried out as to equilibrium in the system GeO_2-H_2-Ge-H_2O by a circulation method over the temperature range of 500–650°. An equation is obtained for the free energy of formation of germanic oxide: $\Delta F^0 = -131{,}700 + 41.4T$, and -132.3 kcal./mole is derived for the standard heat of formation.

The free energy of formation of germanic oxide has not yet been measured experimentally in spite of its great practical importance. Becker and Roth[3] and Hahn and Juza,[4] respectively, found the heat of oxidation of germanium to be -128.1 and 128.6 kcal./mole at 298°K. Jolly and Latimer[5] measured the heats of solution of germanium and of its oxide in an alkaline solution of hypochlorite. From those values they determined the heat of formation of the oxide to be -129.2 kcal./mole. By using these data and other thermodynamic quantities, Coughlin[6] calculated the free energy of formation of germanic oxide.

In the present paper a measurement of the reduction and oxidation equilibrium in the system GeO_2–H_2–Ge–H_2O is reported and some thermodynamic values computed from those results are compared with the data shown in the table of Coughlin.

Experimental

Experiments were performed for measuring the equilibrium

$$Ge(s) + 2H_2O(g) = GeO_2(s) + 2H_2(g) \qquad (1a)$$

from both the reduction and oxidation sides. A circulation method was selected in preference to a simple static method, because in the latter, (1) a much longer time (50–60 hr. in this case) is necessary to reach equilibrium; (2) the effect of thermal diffusion must be taken into consideration; and (3) side reactions involving gaseous germanous oxide make the measurement erroneous by the following reason. In this germanium-germanic oxide coexisting system, germanous oxide vaporizes by the reaction

$$Ge(s) + GeO_2(s) = 2GeO(g)$$

Thus the vapor pressure of germanous oxide is of the order of 10^{-6} atm. at 800°K.[5] This vapor diffuses from the part surrounding the sample toward the colder part of the reaction tube, being accompanied by the reactions

$$GeO(g) + H_2(g) = Ge(s) + H_2O(g)$$

or

$$GeO(g) + H_2O(g) = GeO_2(s) + H_2(g)$$

Then, the partial pressure ratio of hydrogen to water vapor tend to vary with the temperature along the tube as far as the both ends of the furnace, where the vapor of germanous oxide condenses on the wall.

The effects (2) and (3) overlapping each other, it is quite difficult to estimate the final deviation. These difficulties seem to be diminished considerably when the circulation method is employed, since the gas mixture, after having reacted with the sample, flows away through a narrow tube (B in Fig. 1) at a sufficient speed not to be influenced by the reaction with the germanous oxide produced as above mentioned. For the sake of comparison an ordinary static method also was used at two temperatures.

Apparatus.—The apparatus is shown in Fig. 1. The furnace was made of a porcelain tube, 25 cm. long and 3 cm. in diameter, wound with nichrome wire. The reaction tube A of porcelain was fitted to glass tubes by ground joint with picein at both ends; through one of these tubes a narrow quartz tube B, 4 mm. int. diam., was fixed. Temperature was measured at the outer wall of the reaction tube by a platinum-platinum-rhodium thermocouple; it was ascertained that there was no difference between the temperature of the flowing gas and that of the outer wall under the experimental conditions. Temperature of the furnace was automatically regulated within ±2°. The water vapor was supplied from a Pyrex flask C containing redistilled water, kept in a thermostat regulated within ±0.01°. Total pressures were read to 0.01 mm. by a cathetometer.

Material.—Germanic oxide (Eagle Picher product) was powdery and of hexagonal modification, having a purity of 99.999%.

Procedure.—A high alumina boat filled with about 1 g. of sample was set in the reaction tube, which was then evacuated to the pressure of 10^{-5} mm.; hydrogen, generated by electrolysis of a potassium hydroxide solution, was introduced up to the desired pressure. The rate of gas flow was 100–200 cc./min. The measurements were thus carried out over the temperature range of 500–650°.

Results

The results are shown in Table I. The 2nd column gives the equilibrium total pressures and the next denotes the water vapor pressures at the temperature of thermostat. The values in the 2nd and 3rd lines of Table I are obtained by using the static method; in these cases each P_{H_2O} value is corrected as to the effect of thermal diffusion. The equilibrium constants K shown in the 4th column have been calculated by the equation

$$\Delta F^\circ_{(1)} = -RT \ln K;\ K = \left(\frac{P_{H_2}}{P_{H_2O}}\right)^2 \qquad (1b)$$

The values of K, thus obtained, are plotted against reciprocal temperature in Fig. 2. The deviation of the data gained by the static method is attributed both to the effect of germanous oxide slightly produced and to the frequent changes of room temperature, which disturb the reaction steadily proceeding to the equilibrium.

TABLE I

Temp., °C.	Pressure, mm. Total	Pressure, mm. Water vapor	log K	ΔF^0, cal.	Reaction side
500	36.4	13.42	0.4670	-1651	Oxidn.
500[a]	32.0	13.60	.2626	$-$ 929	Oxidn.
530[a]	30.5	11.53	.4322	-1587	Oxidn.
550	31.7	13.42	.2682	-1010	Oxidn.
575	29.2	13.42	.1410	$-$ 549	Reductn.
600	27.1	13.42	.0160	$-$ 64	Oxidn.
600	27.3	13.42	.0290	$-$ 114	Reductn.
625	25.7	13.42	$-$ .0772	316	Reductn.
650	24.8	13.42	$-$ .1432	604	Reductn.

[a] Data from static method; each p_{H_2O} is corrected as to thermal diffusion.

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(1) Presented before the annual meeting of Chemical Society of Japan held on April 3, 1956.

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(3) G. Becker and W. A. Roth, *Z. physik. Chem.*, **A161**, 69 (1932).

(4) H. Hahn and R. Juza, *Z. anorg. allgem. Chem.*, **224**, 120 (1940).

(5) W. L. Jolly and W. M. Latimer, THIS JOURNAL, **74**, 5757 (1952).

(6) J. P. Coughlin, Bureau of Mines Bull., No. 542, 22 (1954).

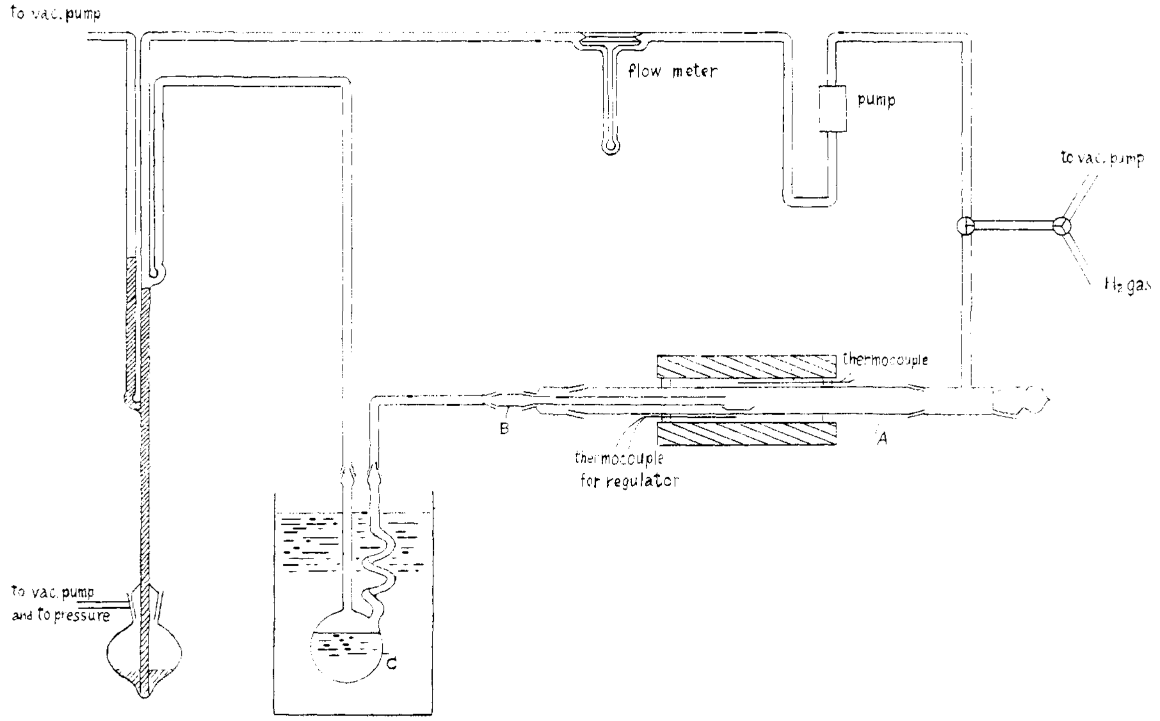

Fig. 1.—Apparatus for circulation method.

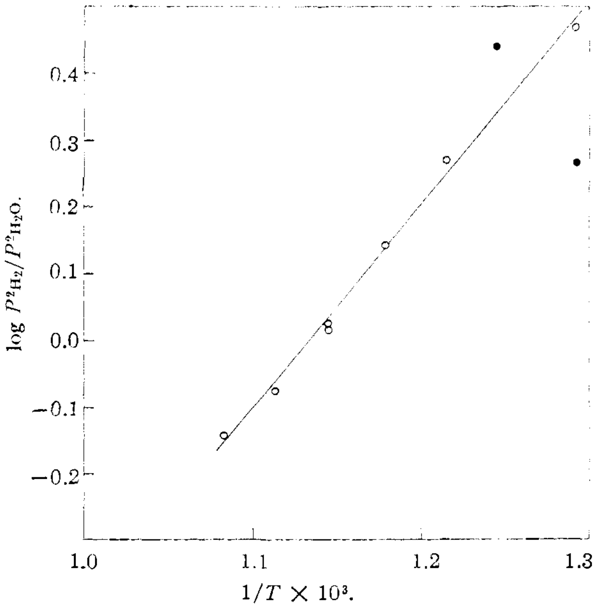

Fig. 2.—Relation between log K and $1/T$: ●, static method; ○, circulation method.

Thermodynamic Calculation and Discussion

By the method of least squares, the temperature dependence of ΔF^0 is obtained

$$\Delta F^0_{(1)} = -13{,}750 + 15.60T\ (\pm 100\ \text{cal./mole})$$

giving the heat of reaction −13,750 cal./mole with an estimated standard deviation of 560 cal./mole. Here the data obtained by the static method are excluded in the calculation.

The heat and free energy of formation of water vapor are $\Delta H^0_{850} = -58970$ cal./mole and $\Delta F^0_{850} = -47995$ cal./mole, according to Rossini, *et al.*[7] Then with regard to the formation of germanic oxide the following results are obtained

$$\text{Ge} + \text{O}_2 = \text{GeO}_2 \qquad (2a)$$

$$\Delta F^0_{850} = -96{,}480 \pm 200\ \text{cal./mole}$$

$$\Delta H_{850} = -131{,}700 \pm 1000\ \text{cal./mole}$$

$$\Delta F^0_{(2)} = -131{,}700 + 41.4T\ (\pm 200\ \text{cal./mole}) \qquad (2b)$$

A corresponding formula is derived from the values calculated by Coughlin, that is

$$\Delta F^0_{(2)} = -127{,}600 + 40.6T$$

$$(\pm 1500\ \text{cal./mole at } 700\text{–}1000\,^\circ\text{K.})$$

Using the heat capacities of germanium and its oxide,[8] the standard heat and free energy of formation of germanic oxide can be calculated.

The results are

$$\Delta H_{298} = -132{,}300 \pm 1000\ \text{cal./mole}$$

$$\Delta F^0_{298} = -119{,}700 \pm 1500\ \text{cal./mole}$$

On the other hand, the values in Coughlin's table are

$$\Delta H_{298} = -128{,}300 \pm 1000\ \text{cal./mole}$$

$$\Delta F^0_{298} = -115{,}900 \pm 1500\ \text{cal./mole}$$

ΔH in the present work is more negative than that of Coughlin by 4 kcal/mole at 850°K. ΔS shows a similar deviation, though within uncertainty. These discrepancies seem to be due mainly to the difference of the structure of germanic oxide employed which is hexagonal in the present work but was amorphous in the case of Coughlin. The above result, however, cannot be discussed only from the viewpoint of the modifications of the oxide sample, since ΔH in the present work has uncertainty of 1

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(7) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Series III, Nat. Bur. of Standard.

(8) K. K. Kelley, Bureau of Mines, Bull., No. 476, 208 (1949).

kcal. and Coughlin's free energy values show a probable error due to using an estimated entropy of germanic oxide. Table II shows the heat and entropy of formation of germanic oxide, both amorphous and hexagonal, together with the corresponding values of silica.[9] For germanium the comparison was made at 850°K. in order that the error due to the use of the estimated heat capacity may be avoided in the data for the hexagonal modification.

TABLE II

	State	H, kcal.	S, e.u.
GeO_2 (at 850°K.)	Amorphous	−127.6	−40.6 (calcd.)
	Hexagonal	−131.7	−41.4
SiO_2 (at 298°K.)	Amorphous	−202.5	−42.27
	Tridymite	−204.8	−43.11

Solubility of Oxygen.—In the above discussion it was assumed that germanium metal does not dissolve oxygen. However, if there is any solubility in this case, it would decrease the activity of germanium. Contrary to this apprehension, Candidus and Tuomi[10] have reported that the solubility is negligible, and Trumbore and his coworkers[11,12] have shown error in the work of Hoch and Johnston[13] who observed a large solubility of oxygen. It may be concluded, therefore, that germanium does not dissolve oxygen appreciably.

Supplement.—After the present experiment had finished, the authors found that Ono and coworkers[14] had investigated the same equilibrium by a flow method. They obtained −141.8 kcal./mole as the standard heat of formation of germanic oxide. They measured only from the reduction side, while the present measurement were carried out from both the reduction and oxidation sides with sufficient agreement. Besides, the present results seem to show that a circulation method is more suitable than a flow method, since hydrogen pressure is comparable to water vapor pressure in equilibrium. Then, the present results may be more accurate.

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[9] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Series I, Nat. Bur of Standards, Washington, 1952.

[10] E. S. Candidus and D. Tuomi, *J. Chem. Phys.*, **23**, 588 (1955).

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[12] F. A. Trumbore, C. D. Thurmond and M. Kowalchik, *J. Chem. Phys.*, **24**, 1112 (1956).

[13] M. Hoch and H. L. Johnston, *ibid.*, **22**, 1376 (1954).

[14] K. Ono, Y. Inada and I. Konno, *Bull. Research Inst. of Min. Dressing and Metall.*, **11**, 159 (1955).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Halogen Atom Reactions Initiated by Nuclear Processes in Hydrocarbon Solutions

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The organic yields of I^{128} and Br^{80} activated as a result of the $I^{127}(n,\gamma)I^{128}$, $Br^{79}(n,\gamma)Br^{80}$ and $Br^{80m} \xrightarrow{\text{I.T.}} Br^{80}$ processes are higher in dilute hydrocarbon solutions than in pure organic halides. They increase with increasing chain length of the hydrocarbon. For the (n,γ) activations in hydrocarbon solutions they decrease by about one-fifth in going from 0 to 100°. These variations in yield are all rather insensitive to the addition of free halogen as scavenger and therefore involve "hot" processes. The results, correlated with those of other investigations, suggest that a number of previously unexplained facts about reactions of hydrogenous material with I^{128}, Br^{80} and Cl^{38} activated by the (n,γ) process may be explained by ionic reactions. The organic yields from the Br^{80m} isomeric transition in liquid hydrocarbons depend on the source molecule containing the Br^{80m} to an extent which is consistent with earlier observations of failure of the transition to rupture C–Br bonds in liquid bromine as the solvent.

Introduction

There are several reasons for studying the chemical consequences of activation of halogen atoms by nuclear processes[2] in each of a series of hydrocarbons: (1) the sizes and weights of the molecules with which the energetic halogen atom is surrounded while losing its energy can be varied without varying the types of bonds to be broken (*i.e.*, only C–C and C–H); (2) conservation of momentum requirements make it impossible for a halogen atom to enter organic combination in such a medium by a "billiard ball collision" mechanism; (3) preliminary observations[3] on such systems have shown changes in organic yields[4] dependent on the size of the hydrocarbon molecules; (4) such studies should contribute to a better understanding of the mechanisms of the various hydrogen replacement reactions cited in the next paragraph; (5) the mechanism of replacement of H^1 by H^3 in tritium recoil reactions[5a] (and possibly also in systems activated by the decay of tritium[5b] may be similar to

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[1] Fulbright-Smith-Mundt Scholar 1953–1954, Project Assoc. (1954–1955), Univ. of Wisconsin; Ravenshaw College, Cuttack, India.

[2] For a discussion of the physical processes involved and a review of earlier work on their chemical consequences see: J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

[3] (a) S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951); (b) S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

[4] The organic yield is the percentage of the atoms produced by nuclear transformation which become stabilized in organic rather than inorganic combination.

[5] (a) See, for example, and references: R. Wolfgang, J. Eigner and F. S. Rowland, *J. Chem. Phys.*, **60**, 1137 (1956); (b) K. E. Wilzbach, THIS JOURNAL, **79**, 1013 (1957).