the rate constant for the reaction of OH with P and I the radiation intensity. For low radiation doses the equation for the formation of succinic acid becomes

$$d(S)/dt = \alpha k_1(A)(OH)$$

where $\alpha \leqslant {}^1/_2$. Substituting in equation 8 and taking (P) as a constant we obtain

$$\frac{1}{G_S} = \frac{1}{\alpha k_6}\left[1 + \frac{C}{(A)}\right] \qquad (9)$$

where G_S is the experimentally observed radiation yield for succinic acid and C is a constant involving (P). A plot of $1/G_S$ against $1/(A)$ for the data in Table IA is shown in Fig. 10. A straight line is obtained which if extrapolated to $1/(A) = 0$ gives $ak_6 = 0.38$.[21] This corresponds to the case in which all of the OH radicals disappear by reaction with A through reaction 1. Then $k_6 > 0.76$ which is a minimum value for the free radical yield of reaction 6. The same relationship between G_S and (A) given in equation 9 could conceivably be obtained if P were an impurity. This situation is considered unlikely because of the relatively large amount of products formed in comparison to the possible impurity concentration and because the amount of P present would have to be consistently independent of (A).

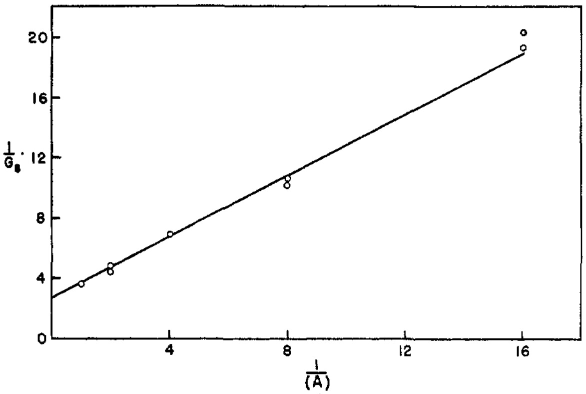

Fig. 10.—Effect of acetic acid concentration, (A), on the succinic acid yield, G_s.

At the higher radiation doses (>10^{21} ev./ml.), the kinetics become considerably more complex because of the reactions of succinic and tricarballylic acids to give malic and citric acids, respectively, and several other as yet unidentified acid products. It is apparent also from the data shown in Fig. 8 that the succinic acid and tricarballylic acid are each approaching a stationary concentration at the higher dose levels. These reactions will be discussed in a later paper.

Acknowledgments.—The authors wish to express their appreciation to Professor J. G. Hamilton, Director of Crocker Laboratory, for his interest in this work and to Professor G. K. Rollefson for advice and suggestions during the course of the investigation. We also wish to thank Mrs. Harriet Powers for most of the chromatographic separations, Miss Margaret Gee for the preparation of the figures and Mr. B. Rossi and the staff of the 60-inch cyclotron at the Crocker Laboratory for assistance in target design and for the bombardments.

BERKELEY, CALIFORNIA

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(21) We are indebted to Dr. A. O. Allen for pointing out this relationship to us.

[A CONTRIBUTION OF THE INSTITUTE FOR THE STUDY OF METALS OF THE UNIVERSITY OF CHICAGO]

A Thermodynamic Study of the Equilibrium $2Cu(s) + H_2S(g) = Cu_2S(\gamma) + H_2(g)$

BY ALFRED A. BROOKS[1]

RECEIVED DECEMBER 29, 1952

The equilibrium $2Cu(s) + H_2S(g) = Cu_2S(\gamma) + H_2(g)$ has been investigated between 342 and 1037° by a recirculating technique with particular effort to eliminate the effects of thermal diffusion.

Introduction

Several authors have investigated the equilibrium between copper, hydrogen sulfide, hydrogen and cuprous sulfide. A flow method was used by Jellinek and Zakowski,[2a] Britzke and Kapustinsky,[2b] and by Sudo[3] to investigate the solid Cu–Cu_2S system. Sano[4] and Cox[5] used a circulating method. Schuhmann and Moles[6] investigated the region of liquid copper sulfides by a flow method. The results are not in particularly good agreement and some of the data[5] show bad scattering. The flow method has the disadvantages that at low flow rates the effects of thermal diffusion are not negligible and at high flow rates equilibrium is not well established. The circulation method has the advantage that eventually equilibrium must be reached but has the disadvantage of producing relatively small samples. In addition, with some pump designs the linear flow rate may be so slow that thermal diffusion is an important error. In the present study an attempt was made to eliminate some of these disadvantages.

Experimental

Apparatus.—A schematic sketch of the apparatus is shown in Fig. 1. Variations in the entrance area and in the pumping rate were sufficient to change the linear velocity of the entrance gas from 67 to 6.7 cm./sec. and that of the exit gas from 23 to 11 cm./sec. A differential thermocouple was placed beside the Pt–PtRh measuring thermocouple and in the charge crucible. Changes in pumping rate from 10

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(1) Standard Oil Co. (Ind.), Whiting, Ind.

(2) (a) K. Jellinek and J. Zakowski, *Z. anorg. allgem. Chem.*, **142**, 1 (1925); (b) E. V. Britzke and A. F. Kapustinsky, *ibid.*, **205**, 171 (1932).

(3) K. Sudo, *Sci. Rep. R.I.T.U.*, **A2**, 513 (1950).

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(6) R. Schuhmann and O. W. Moles, *J. Metals* **3**, *Trans.*, **191**, 235 (1951).

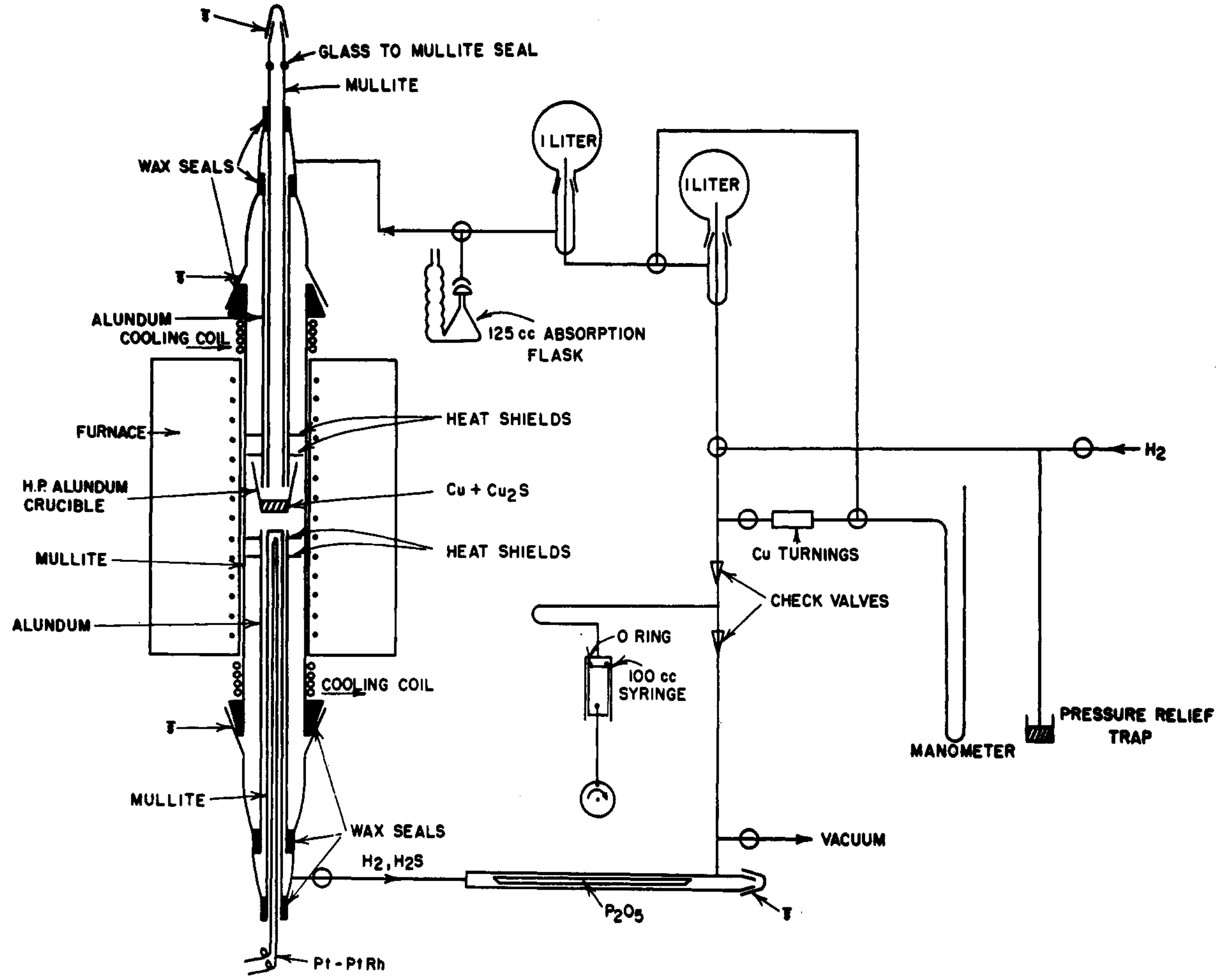

Fig. 1.—Schematic diagram of apparatus.

cc./sec. to 0 cc./sec. gave rise to temperature differences which were random and were not greater than 1° at furnace temperatures between 300 and 1000°.

Temperatures were determined by means of a thermocouple constructed of thermocouple-grade platinum and platinum–10% rhodium with a Leeds & Northrup Type K Potentiometer to measure e.m.f.'s. The thermocouple was calibrated by determining the cooling curves of pure metals (Ag, CuAg, Al, Zn). The errors in temperature measurement are estimated to be less than 1°.

Procedure.—The crucible was charged with about 30 g. of Cu_2S and 30 g. of Cu. Purified hydrogen was then admitted to the evacuated and leak-free system until the pressure was slightly over one atmosphere. The circulating pump was then started and the gas circulated from 12 to 120 hr., depending upon the temperature. The gas was kept anhydrous by passage over P_2O_5. The equilibrium conditions were approached from both high and low H_2S/H_2 ratios and when equilibrium was reached the gas sample was flushed from the calibrated sample volume (0.3–2 l.) by a stream of pure hydrogen into a KOCl solution.

Chemicals.—Cuprous sulfide was prepared by heating redistilled C.P. sulfur and C.P. copper together in an evacuated, sealed quartz tube at 700° for 20 hr. The hydrogen was purified by passing it over charcoal cooled to the hydrogen triple point. After the runs were completed, the mixture of copper and cuprous sulfide had a total analysis (Cu + S) of 99.85% and showed 0.09% metallic impurities by spectrographic analysis.

Analytical Method.—The method of Dunicz and Rosenqvist[7] was used to analyze the gaseous mixture for H_2S. The method was entirely satisfactory when precautions were taken to wash adsorbed H_2S from the walls of the absorbing flask and gave results reproducible to 0.03 ml. of 0.01 N thiosulfate solution. This represents an accuracy of +0.1% to ±1% over the entire range of H_2S concentrations.

The measurements of the sample volume, temperature and pressure allowed the calculation of the H_2S/H_2 ratio.

Results

The results are summarized in Table I, columns 1 and 2. The method of Randall[8] and the heat capacity (C_p) equations

$H_2(g)$[9]: $6.9469 - 0.1999 \times 10^{-3}\, T + 4.808 \times 10^{-7}\, T^2$

$H_2S(g)$[10]: $6.864 + 3.852 \times 10^{-3}\, T + 7.85 \times 10^{-7}\, T^2 - 6.34 \times 10^{-10}\, T^3$

$Cu(s)$[11]: $5.522 + 1.324 \times 10^{-3}\, T$

$Cu_2S(\gamma)$[12]: 20.2

give rise to the expressions

$$\Delta C_p = \alpha + \beta T + \gamma T^2 + \delta T^3$$

$$\Delta H_0^0/T + I = \epsilon R \Sigma = -R \ln K + \alpha \ln T + \beta T/2 + \gamma T^2/6 + \delta T^3/12 \quad (1)$$

where

$\alpha = 9.239$ $\qquad \delta = 6.34 \times 10^{-10}$

$\beta = -6.700 \times 10^{-3}$ $\qquad R = 1.9872$ cal./mole

$\gamma = -3.04 \times 10^{-7}$ $\qquad \epsilon = \log_e 10$

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(7) B. L. Dunicz and T. Rosenqvist, *Anal. Chem.*, **24**, 404 (1952).

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(9) H. M. Spenser and J. L. Justice, THIS JOURNAL, **56**, 2311 (1934).

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(11) J. M. Jaeger, *Proc. Acad. Sci. Amsterdam*, **35**, 772 (1934).

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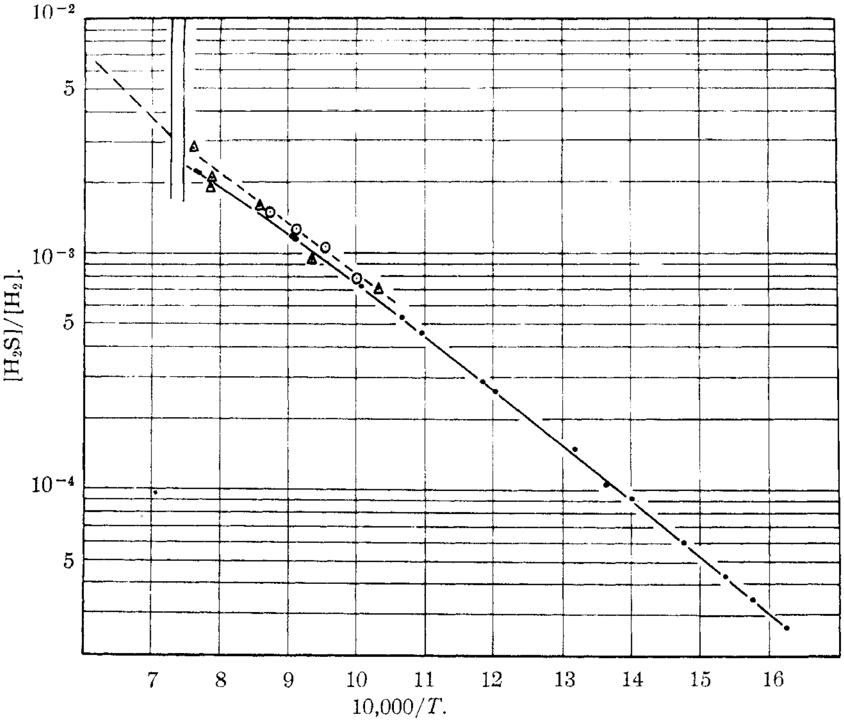

Fig. 2.—Summary of recent data (Schuhmann and Moles, - - -; Sudo, ⊙- -⊙; Cox, *et al.*, △△; present, —·—·—).

The Σ's calculated from the above are shown in Table I, column 3. All the Σ's except that at 342° (which lies below a phase transition[13]) were treated by the method of least squares and yield

$$\Delta H_0^0 = -15{,}736 \pm 35\ (0.22\%)\ \text{cal./mole}$$
$$I = 61.854 \pm 0.046\ (0.07\%)\ \text{cal./deg. mole}$$

where the errors are given as probable errors.[14] The deviations in Σ show no trend nor any correlation with the flow rate or the direction of approach to equilibrium. Table II shows the thermodynamic values derived from the above constants at 700°K., and the values corrected to 298.16°K., with the tabular data of Kelley.[13] Combining these values with data of Evans and Wagman[15] for $H_2(g) + S(r) = H_2S(g)$ results in the values given in Table II for $2Cu(s) + S(r) = Cu_2S(\alpha)$.

TABLE I

SUMMARY OF DATA

T, °C.	$[H_2S]/[H_2] \times 10^4$	Σ	T, °C.	$[H_2S]/[H_2] \times 10^4$	Σ
1037.3	22.16	10.888	572.0	2.881	9.447
1036.0	22.09	10.884	554.4	2.612	9.376
831.1	11.70	10.410	486.0	1.499	9.011
828.4	11.38	10.395	461.2	1.048	8.806
720.4	7.171	10.064	441.8	0.910	8.705
664.0	5.291	9.854	404.9	.593	8.442
660.6	5.126	9.835	378.7	.435	8.243
658.2	5.010	9.819	361.7	.349	8.108
636.8	4.609	9.755	342.0	.261	7.933

TABLE II

STANDARD THERMODYNAMIC VALUES

	$2Cu + H_2S = Cu_2S + H_2$		$2Cu + S(r) = CuS(\alpha)$ 298.16°		
	700°K.	298.16°K.	Present	Sudo[3]	N.B.S.[a]
ΔF^0, cal./mole	−13,166	−13,300	−21,198	−21,290	−20,600
ΔH^0, cal./mole	−10,907	−15,155	−19,970	−19,940	−19,000
ΔS^0, cal./mole °C.	3.23	−6.22	4.11	4.53	5.37

[a] Natl. Bur. Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

Discussion

The graph of Fig. 2 shows the more recent data for the reaction. The data of Schuhmann and Moles and those of Sudo, both taken by the flow technique, appear to be consistent, assuming no great change in slope between 1067 and 1105°. The data of Cox, *et al.*, taken by a circulation technique agree with Schuhmann and Moles above 1105° and about equally well with Sudo and the present work below 1067°. The present data lie about 10% below those of Sudo. The substitution of Sudo's data into equation 1 yields the following values: $\Delta H_0^0 = -15{,}888 \pm 477\ (3.0\%)$, $I = 62.174 \pm 0.473\ (0.76\%)$. The corresponding values for the present work lie well within the above probable errors, the difference for ΔH_0^0 being less than 1%.

The data of Sudo extrapolated along the same path as the present data give rise to a heat of formation of Cu_2S at 298.16°K. which differs from the present data by 0.76%. The value given by the Bureau of Standards disagrees with that of Sudo and the present work by about 5%, which is greater than the probable errors.

The author feels that the 10% difference in the equilibrium constants between the present work and that of Sudo is due to the failure of the flow method to give equilibrium values. Emmett and Shultz[16] found that thermal diffusion effects were negligible with hydrogen–water mixtures at flow rates of 10–18 cm./sec.; but at 0.27–0.40 cm./sec. the errors introduced were between 20–30%. The present method employs flow rates which should eliminate the thermal diffusion effects. The composition of the exit gas of a single-pass flow system will vary in a complicated manner depending upon the flow rate, the rate of thermal diffusion, the rate of reaction and the design of the reactor bed, and it seems difficult to evaluate the extrapolation of the data to zero flow rate in the absence of specific knowledge of the effects of these variables. In the case of a recirculating system, thermal diffusion is the only interfering effect and this can be simply determined.

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The present work does not support the conclusion of Hirahara[17] that a phase transition occurs in Cu_2S at 470°.

Acknowledgments.—The author wishes to acknowledge the many helpful suggestions of Drs. T. Rosenqvist and N. H. Nachtrieb.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Vapor Pressures of Inorganic Substances. XI. Titanium between 1587 and 1764°K., and Copper between 1143 and 1292°K.[1]

BY JAMES W. EDWARDS, HERRICK L. JOHNSTON AND WALTER E. DITMARS

RECEIVED SEPTEMBER 22, 1952

The vapor pressures of copper and titanium have been determined using the Langmuir method of vacuum evaporation. The heats of sublimation at the absolute zero have been calculated; and equations for the vapor pressure, as functions of temperature, have been formulated. The accommodation coefficients have been found to be unity. A value for the spectral emissivity for pure Ti has been found, and cooling curve data were taken which confirm McQuillan's conclusion that a sharp first-order transition from α to β occurs close to 882.5°.

Introduction

The vapor pressures of titanium and of copper have been determined in this Laboratory by the Langmuir method of vacuum evaporation. The techniques and apparatus used were identical with those described in a previous paper.[2] A check of the optical pyrometer calibration was made against a new wolfram filament lamp calibrated by the National Bureau of Standards. The new calibration was in agreement with the temperature scale in use in this Laboratory.

Materials

Titanium.—The titanium was obtained from Prof. M. G. Fontana of the Metallurgy Department of The Ohio State University, and was made by the iodide method.[3]

A spectrographic analysis[4] showed the following percentages of impurity.

Fe	0.01	Cu	0.02
Si	.03	Mo	.01
Al	.005	Sn	.005
Ca	< .01	Mn	.005
Mg	.02	Cr	.001
Ag	Not detcd.	Ti	By diff., 99.884

The sample was shaped in the form of a solid cylinder 2.9934 cm. high and 1.3398 cm. in diameter. A black body hole 0.099 cm. in diameter and about 1.52 cm. deep, was drilled near the edge of the sample for temperature measurements.

Copper.—The copper sample was made from OFHC material obtained from the American Brass Company of Waterbury, Conn. A spectrographic analysis of the sample showed the following percentages of impurity.

Fe	0.0001 to 0.001	Mo	Not detcd.
Si	.001 to .01	Sn	Not detcd.
Al	.001 to .01	Mn	Not detcd.
Ca	.0001 to .001	Ca	Not detcd.
Mg	.0001 to .001	Cu	By diff., 99.977
Ag	.00005 to .0005		

The sample was in the form of a hollow closed cylinder 3.1877 cm. in height, 2.3698 cm. in diameter. The wall thickness was about 0.32 cm., while a 0.32 cm. thick plug of the sample material was press-fitted into the bore hole. There were two black body holes 0.099 cm. in diameter, one bored to a depth of 1.78 cm. near the edge, and the other bored directly into the cavity of the cylinder. The opening into the cell was used for the temperature measurement. Ordinarily, as with titanium, a cavity 1.78 cm. deep by 0.099 cm. diameter would give a nearly perfect black body, but the emissivity of copper is so low that apparent temperatures of the 1.78 cm. deep hole were 5 to 7° lower than in the central "hohlraum." No temperature gradients were observed on the sample during heating.

Both samples were suspended by means of 0.052 cm. tantalum wire.

Data and Thermodynamic Treatment

Calculations.—The calculations of the vapor pressure were made according to methods previously described.[2] The free energy functions for the solid state were calculated from data given by Kelley.[5] The high temperature values for titanium were obtained by extrapolation using the value $C_p = 7.50$. The values of the free energy functions used for titanium vapor were those computed by Gilles and Wheatley.[6] In the case of copper it was found that only the ground state of the atom made a significant contribution to the value of the electronic partition function.[7]

Experimental Errors.—For a single calculation of ΔH_0^0, the standard deviations of the measurable quantities were found to be

Temp., °C.	±1.5
Weight loss, g.	±0.0001
Eff. time, sec.	±60
Sample dimension, cm.	±0.0025

Using these values, calculation of the standard deviation for an individual value of ΔH_0^0 gives 74 cal. for titanium and 73 cal. for copper. These values are in good agreement with those calculated from the mean ΔH_0^0's of the experimental results.

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

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[4] The authors are indebted to Mr. Center, Chief Analyst, Battelle Memorial Institute, for the analysis.

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