$$\Delta F = 46{,}005 + 5.05\,T \ln T - 2.67 \times 10^{-3}T^2 + 6 \times 10^3T^{-1} - 72.81T$$

From these equations for the above reaction are calculated $\Delta H_{298} = 44{,}777$ cal.; $\Delta F_{298} = 32{,}885$ cal. From these values one can calculate the standard enthalpy and free energy of formation of indium oxide at 298°K. as −216.8 and −196.4 kcal./mole, respectively. The value of −57.8 kcal./mole, given by Bichowsky and Rossini,[10] was used for the standard enthalpy of formation of H_2O(g), and −0.67 kcal./mole for the enthalpy of transition at 298°K. from In(l) to In(s), calculated from data given by Kelley.[8] The entropy of formation of indium oxide at 298°K. is then calculated to be −68.4 e.u./mole, using data given in reference 9, and the absolute entropy at 298°K. to be 30.1 e.u./mole.

The value of the enthalpy of formation of In_2O_3 given in this paper is possibly less accurate than the value of Holley and collaborators,[6] since our method is an indirect one depending in part for its accuracy on heat capacity data from the literature. The value for the free energy of formation of In_2O_3, however, is the first reported value obtained from direct experimental data, other values given in the literature being estimated. Moreover, the close agreement between calorimetric and equilibrium values for the enthalpy of formation of In_2O_3 is believed to be evidence for the direct reduction of In_2O_3 to indium with no appreciable amounts of lower oxides being formed under the conditions of reduction studied (823–1123°K.).

SOCORRO, NEW MEXICO

[10] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 20.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, METAL HYDRIDES INC., AND THE DEPARTMENT OF CHEMISTRY, TUFTS COLLEGE]

Metal–Hydrogen Systems. III. The Uranium–Hydrogen System

BY THOMAS R. P. GIBB, JR.,[1] JAMES J. MCSHARRY AND HENRY W. KRUSCHWITZ, JR.

RECEIVED MARCH 24, 1952

The dissociation pressure of hydrogen over uranium hydride has been studied as a function of temperature and composition of the solid solution in regions where the isotherms show a marked upward inflection. Observations are reported for the range 500–4900 cm. at temperatures from 357 to 650° for compositions ranging from $UH_{2.85}$ to $UH_{3.00}$. The equation for $UH_{3.00}$ is: $\log P_{\text{cm.}} = (-1730/T) + 5.78$, where T is absolute temperature. Withdrawal of hydrogen from the solid phase causes a marked decrease in the dissociation pressure. After removal of several tenths of a mole of hydrogen, the solid phase reverts to normal behavior, showing a heat of dissociation of 20.5 kcal./mole H_2, and $\Delta F_{298} = 11.8$ kcal./mole H_2.

The dissociation of uranium hydride has been studied by Newton,[2,3] Spedding, *et al.*,[4] and Flotow and Abraham,[5] whose data are in reasonable agreement. These workers employed low pressure equipment and were therefore restricted to temperatures below 450°. The single isotherm reported by Spedding was at 357° and showed a marked upward inflection as the composition of the solid phase approached $UH_{3.0}$. All three workers evidently used measurements made in the horizontal plateau regions of isotherms for preparation of $\log P$ *vs.* $1/T$ plots. The formation and properties of the compound UH_3 have been studied by Burke and Smith,[6] Driggs,[7] and Gueron and Yaffe.[8]

A tentative structure of UH_3 has been described by Rundle,[9] and the theoretical implications of this structure have been discussed by Pauling.[10]

Studies at Low Pressure.—Preliminary studies at low pressure were made in this Laboratory according to Spedding's technique, but employing the low pressure equipment described in a previous paper.[11] A 357° isotherm was observed which corresponded very well with that of Spedding except that hysteresis was slightly more pronounced. The same dip was noted in the descending arm of the hysteresis loop at composition $UH_{2.94}$. This isotherm is shown in Fig. 3, but neither the dip nor the minor deviation from Spedding's isotherm are perceptible because of the scale required for inclusion of the other isotherms. Attainment of equilibrium in this range is very slow unless an absolutely constant temperature may be maintained.

A second isotherm at 375° was attempted, and the data obtained indicated a much larger dip near the inflection at composition $UH_{2.40}$. There was sufficient drifting of the measurements, however, to cause some doubt that true equilibrium values were obtained. This drift was also noted in a 400° isotherm. Only the descending arm of the hysteresis loop was observed, and the low pressure experiments were discontinued because of the apparent difficulty of obtaining true equilibrium data. An overpressure is noted when samples of UH_3 are heated above 400°. This overpressure develops rapidly and is for the most part reversible on cooling slightly below 400°, but the latter stages of reabsorption are extremely slow. A possible explanation is that a small temperature increase may cause the plateau pressure of the sample to change to the much higher pressure of the ascending portion of the isotherm at the increased temperature. In any

[1] Department of Chemistry, Tufts College, Medford 55, Mass.

[2] A. S. Newton, *et al.*, MDDC 1585 12 pp. decl. Dec. 16, 1947.

[3] A. S. Newton, U. S. Patent 2,446,780 (August 10, 1948).

[4] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. M. Nottorf, I. S. Johns and A. H. Doane, *Nucleonics*, **4**, 4 (1949).

[5] H. E. Flotow and B. Abraham, AECD 3074; *cf. Nuclear Science Abstracts*, 5,445 (1951).

[6] J. E. Burke and C. S. Smith, THIS JOURNAL, **69**, 2500 (1947).

[7] F. H. Driggs, U. S. Patents 1,816,830 (August 4, 1930); 1,834,024 (Dec. 8, 1930).

[8] J. Gueron and L. Yaffe, *Nature*, **160**, 575 (1947).

[9] R. E. Rundle, THIS JOURNAL, **69**, 1719 (1947).

[10] L. Pauling, *ibid.*, **70**, 1660 (1948).

[11] T. R. P. Gibb, Jr., and H. W. Kruschwitz, Jr., *ibid.*, **72**, 6365 (1950).

case. it is evident that difficulties are encountered in the study of the region around 400°.

Studies at Higher Pressures and Temperatures.—The technique employed previously in the case of the titanium–hydrogen system was used.[12] Stainless steel bombs containing the uranium hydride in argon were evacuated, filled with purified hydrogen to the desired pressure and slowly heated as the pressure was recorded. A series of typical records is shown in Fig. 1. The intersection of the linear portion, due to thermal expansion, with the rapidly ascending right-hand portion, due to dissociation, is taken as the point at which $UH_{3.00}$ commences to dissociate. The scatter of the data is best seen in Fig. 3. Smoothed values are given in Table I. From the observed pressure increase beyond the point of first dissociation the composition of the solid phase may be calculated, since the hot and cold volumes of the bomb-line are known with some accuracy. From the pressure and temperature, the amount of hydrogen in the gas phase is calculated, the original amount of gaseous hydrogen is subtracted and the difference represents the amount lost by the solid phase, whose composition is thus established. If equilibrium prevails in the system, as the constancy of pressure measurements implies, then any solid phase of calculated composition must be in equilibrium with the prevailing pressure. Values for compositions ranging from 99.9 to 92 mole per cent. UH_3 or from $UH_{2.997}$ to $UH_{2.76}$ are shown in Figs. 2 and 3 as solid lines. The broken lines of Figs. 2 and 3 are values calculated from the data of Spedding, *et al.*[4]

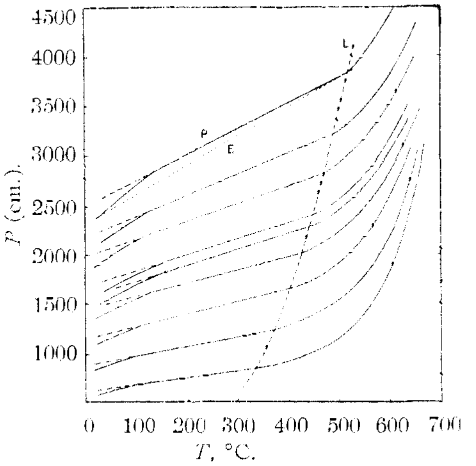

Fig. 1.—Replot of recording pressure gage record: P, observed thermal expansion; E, calculated thermal expansion; L, locus of intersections of expansion and dissociation curves. (Bomb contained 158 g. of $UH_{2.95}$, analyzed prior to filling; system volume 162 cc.; net volume 98.3 cc.).

Table I

Dissociation Pressures of $UH_{3.0}$

T, °C.	$P_{cm.}$	T, °C.	$P_{cm.}$
350	1000	450	2460
400	1620	475	2950
410	1780	500	3470
425	2000	525	4080

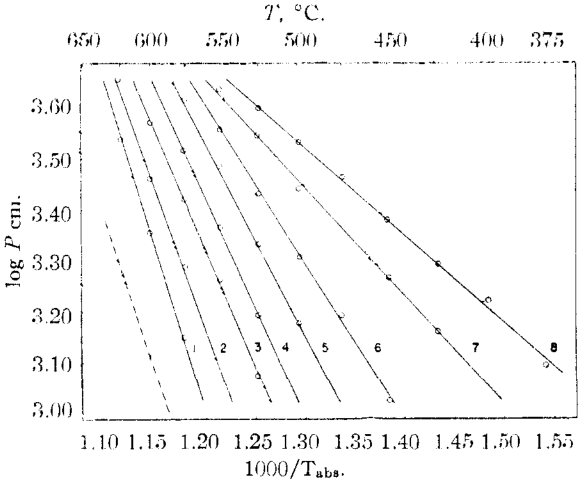

Fig. 2.—$Log_{10}P$ cm. *vs.* 1000/T°K. Numbers refer to "mole per cent. UH_3," or per cent. maximum H-content (UH_3 = 100%) in the sequence: 1, 96%; 2, 97%; 3, 98%; 4, 98.5%; 5, 99%; 6, 99.5%; 7, 99.9%; 8, 100%. The broken line represents values extrapolated from (4).

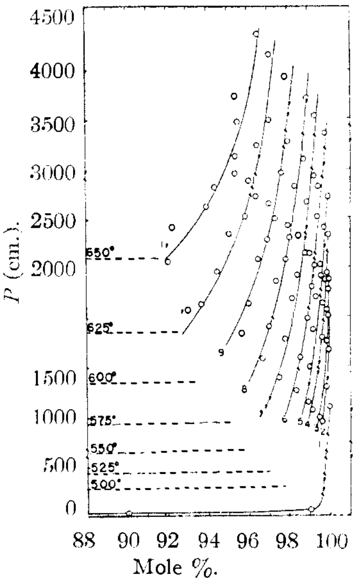

Fig. 3.—Isotherms of the U–H system. The 357° curve (number 1) was obtained with low pressure equipment. The broken lines are assumed plateaus extrapolated from the data of (4). Isotherms are numbered as follows: 1, 357°; 2, 425°; 3, 450°; 4, 475°; 5, 500°; 6, 525°; 7, 550°; 8, 575°; 9, 600°; 10, 625°; 11, 650°.

Experimental

Apparatus.—The equipment and techniques employed have been described in a previous paper.[11,12] The low pressure equipment was modified so that the pure hydrogen used was obtained from the decomposition of uranium hydride rather than titanium hydride, and a minor improvement was made in the thermostat. For the studies at 357° a boiling mercury-bath was used to maintain constant temperature. Previously cited precautions were taken to avoid contact between the uranium or hydride and quartz, or mercury vapor from the gas buret and manometers.

Materials.—Uranium metal of highest purity was employed. It contained no impurities detectable by ordinary analytical procedures and assayed 100% within the limits of

---

(12) T. R. P. Gibb, Jr., J. J. McSharry and R. W. Bragdon, *This Journal*, **73**, 751 (1951).

analytical error. Selected portions of rectangular rods were taken, abraded until smooth, etched with nitric acid, and washed with special distilled water and then with alcohol and ether. The final rinse was removed in the vacuum lock of a dry-box and the metal was not subsequently handled in air. The dry-box contained sodium hydride as a desiccant. The hydride used in the low-pressure studies was made in the equipment for dissociation measurement and the amount of hydrogen absorbed could be determined accurately. Prior to hydriding the metal was degassed for 16 hr. at room temperature below 0.02 micron and briefly at 273° and was then cooled slowly. Absorption took place readily and quantitatively.

The hydride used in the high pressure studies was made in a Pyrex bulb at 225–250°. It was handled exclusively in the dry-box and was loaded into the bombs under dry argon. A sample was removed from the dry-box and analyzed. It corresponded to the composition $UH_{2.95}$, but it is possible that small losses of hydrogen occurred during analysis. Since the material was rehydrided subsequently, little significance attaches to the analysis. The bombs were attached to the pressure manifold and evacuated overnight to remove the argon. They were then flushed with hydrogen purified by passage over incandescent zirconium hydride under pressure.

The hydride analyzing $UH_{2.95}$ was immersed in Nujol and examined microscopically. It was gray-black in color and consisted of irregular particles ranging from 0.1 mm. to below the limit of the optical microscope. The mode particle size was approximately 0.015 mm. Most of the particles resembled lumps of coke in that they were noticeably porous and possessed some luster. A very few were smooth and metallic in appearance. Some of the coke-like lumps had needle-like spicules protruding from them as observed by Spedding.[4]

Discussion

Two assumptions are basic to the technique employed. First that $UH_{3.00}$ is a limiting composition which may not be exceeded by use of moderate pressures of hydrogen. This appears to have been established by all previous workers and is confirmed by us, and by the consistency of the data obtained as evidenced in Fig. 2. The second assumption is that data obtained by the two techniques employed are truly equilibrium data. There is little question but what this is true of the results obtained with the 357° isotherm, where the samples could be held at constant temperature for periods of a week or more without changing the observed pressure. At the higher temperatures used for studies in metal equipment equilibrium should be attained far more rapidly, and indeed the points obtained represent definite, reproducible pressure measurements constant over periods of time sufficient for the detection of even a slight downward or upward trend. However, because diffusion losses would become significant in a period of days, no attempt was made to observe trends over such long periods of time. If the recorded values do not represent true equilibria, then they certainly represent apparent equilibria of sufficient stability to be physically significant.

In extending their dissociation measurements to other temperatures, previous workers have evidently used only pressure values from the horizontal or plateau portions of isotherms rather than from the intercept corresponding to $UH_{3.0}$. The equation relating pressure to temperature for such plateau regions is given by Spedding as: $\log P_{\text{cm.}} = -(4500/T) + 8.28$. This equation corresponds closely with that of Flotow.[5] The work reported herein, however, is primarily concerned with the rapidly ascending portions of the isotherms where the above equation is not applicable and where the composition of the solid phase actually approaches that of uranium hydride, UH_3.

Before discussing the results of this work attention should be drawn to a peculiarity observed in connection with the technique employed. The shape of the curves in Fig. 1 reveals a trend at the lower temperatures toward slightly higher pressures than can be accounted for on the basis of thermal expansion. The observed expansion curve P represented by the solid line shows an overpressure of 130 cm. at 150°. The dotted line E shows the expected thermal expansion calculated from the known volume of the hot zone. Fortunately the two curves intersect just at the point where dissociation commences. A simple calculation shows that a maximum of only about 200 cc. of gas at S.T.P. need be evolved to give the observed increase in pressure. This is less than 1% of the total hydrogen contained. Proportionately smaller volumes are required to account for the differences observed at lower pressures. Evidently heating rapidly to 100° causes a desorption or rearrangement of some kind, possibly due to local overheating near the wall of the container. In any case, there appears no reason to question the validity of the dissociation data because of this effect.

The pressure and temperature of dissociation obtained from a large plot of Fig. 1 are replotted in the conventional manner in Fig. 2, where the uppermost line is considered to represent the compound UH_3 and the lower lines alloy-like systems of lower hydrogen content. The latter is expressed as per cent. theoretical maximum hydrogen content or loosely as mole per cent. UH_3. The striking drop in dissociation pressure accompanying withdrawal of as little as 0.1% combined hydrogen is remarkable although shown to a smaller extent by other metal–hydrogen systems.[12–14] The equation representing the dissociation of $UH_{3.0}$ is given as: $\log P_{\text{cm.}} = -(1730/T) + 5.78$.

The data used in Fig. 2 are replotted as isotherms in Fig. 3 to better illustrate the scatter of points and the very steep slope of the right hand portions. The broken line curves of Figs. 2 and 3 represent extrapolations of Spedding's equation. In view of the fact that a considerable extrapolation is required to bring this equation into the region covered by Fig. 2, the lack of agreement is not surprising. The horizontal displacement is not much more than could be accounted for by a 2 mole per cent. difference in composition or by very small differences in impurity content. The slope of the broken line is practically identical with that of the 97 mole per cent. curve. It is interesting that extrapolation of the 100% curve of Fig. 2 to 30° gives a dissociation pressure of approximately 1 cm. If this is a fair approximation, it may explain some of the difficulty experienced in this Laboratory and by others in obtaining a correct analysis for stoichiometric hydride. Much greater stability would be predicted for the 99.5 mole per cent. material.

The broken lines of Fig. 3 are drawn horizontally

(13) W. C. Johnson, *et al.*, THIS JOURNAL, **61**, 318 (1939).

(14) M. N. A. Hall, S. L. H. Martin and A. L. C. Rees, *Trans. Faraday Soc.*, **41**, 306 (1945).

on the assumption that they represent plateau values. They are included in the figure merely to indicate a possible lower limit at each temperature. Flotow's values[5] are slightly lower at the higher temperatures but no choice may be made on the basis of the experimental points. Extension of the latter into regions of lower composition is not considered wise because of the limitations of the technique employed. There is also reason to expect that marked hysteresis and slowness to attain equilibrium will be encountered in the regions where the plateaus turn sharply upward. Indications of this were obtained in the low-pressure studies of the 375 and 400° isotherms.

The existence of two phases in the plateau regions, as predicted by the phase rule, is well established by X-ray observations.[4] The rapidly ascending portions of the isotherms however may be presumed to represent a single solid solution phase whose composition must approach UH_3,[9] and which would not necessarily be altered by removal of small amounts of hydrogen.

The shape of the isotherms of Fig. 3 is consistent with the following interpretation: when uranium hydride is heated under conditions which prevent loss of hydrogen, a very high dissociation pressure develops whose magnitude is given by the above equation. As hydrogen is withdrawn from the solid phase the dissociation pressure decreases markedly and a dilute solid solution of U in UH_3 or a reasonable equivalent thereto is formed. As more hydrogen is withdrawn the solid solution is resolved into two phases, the new phase probably being uranium. The point at which this occurs depends on the history of the sample, rate of heating or cooling, etc., and marked hysteresis is expected in this region.. Once the two-phase system is stabilized, the dissociation pressure is considerably smaller and nearly independent of hydrogen content until the hydride phase is depleted. The dissociation pressure in this plateau region is given by the equation of Spedding. The first appearance of the two-phase system depends on the temperature; for low temperatures it appears as soon as small amounts of hydrogen have been withdrawn, whereas at 650° the uranium phase does not appear until approximately 8% of the original hydrogen content has been removed.

Thermodynamic Properties.—The (composition-dependent) heat of dissociation of UH_3 may be calculated from the slope of the dotted line in Fig. 2 by means of the van't Hoff isochore, on the assumption that the products of dissociation are uranium and hydrogen.

The thermodynamic properties of the uranium–hydrogen system thus derived by classical means are shown in Table II.

TABLE II

CALCULATED THERMODYNAMIC PROPERTIES OF THE URANIUM–HYDROGEN SYSTEM

Ht. of dissoc. $\Delta H = \Delta H_0$, kcal./mole H_2	20.5
ΔF_{298}, kcal./mole H_2	11.8
ΔS_{298}, e.u.	29.2
ΔH (Nernst approx.), kcal./mole H_2	20.4
ΔS (tabular), e.u.	27.0

The evaluation of ΔH is accomplished by means of the equation

$$2.3R \, \mathrm{d} \, (\log P^n{}_{\mathrm{atm}})/\mathrm{d}(1/T) = -\Delta H = -4.57nA$$

where n is the number of moles of hydrogen produced by the dissociation of one mole of hydride and

$$\log P_{\mathrm{atm}} = (-A/T) + b = (-4500/T) + 6.40 \quad \text{(two-phase region)}$$

$$\log P_{\mathrm{atm}} = (-1730/T) + 3.90 \text{ (for } UH_{3.0})$$

The method of Lewis and Randall[15] is employed for the evaluation of ΔH_0 and ΔF, and that value of ΔC_p is chosen which will give a constant value of I in the equation

$$\Delta F = \Delta H_0 - 2.3 \, \Delta \, C_pT \log T + IT$$

This is accomplished by substituting for ΔF its equivalent $-2.3\,RT \log P^n{}_{\mathrm{atm}}$ and for ΔH_0 its equivalent $\Delta H - \Delta C_pT$, and solving for ΔC_p at several temperatures within the range of measurements.

Both ΔH and ΔS may be calculated independently by empirical methods to provide a check on the above values. The Nernst approximation is used to calculate ΔH, and ΔS is estimated by the method of Latimer.[16] The atomic entropy of combined H is estimated as follows: If H is assigned a mean entropy of about 1.3 when combined with univalent metals and 0.6 when combined with divalent metals,[17] then it should have an entropy of about 0.4 when combined with a tervalent metal. The tabular entropy of $U^{III} = 16$ and $U^0 = 12$, hence since the value for $^1/_2\,H_2$ is 15.6 the entropy change per mole H_2 produced is 27.0 e.u. This value is independent of the stoichiometry of dissociation. The experimental value of ΔS is given by the equation $\Delta S = 4.57nb$.

As shown in Table II, rather good agreement between the experimental and empirical values of ΔH and ΔS is obtained for normal dissociation where the dissociation pressure is not changing rapidly with hydrogen content. The data of Spedding[4] may be used interchangeably with values from the 98% curve of Fig. 2 (which indicates that the 96, 97 and 98% curves should lie closer together). Spedding showed that in the regions he investigated, uranium and the hydride were coexistent and the leveling off of the isotherms in these regions follows from the phase rule. Whether or not the solid phase actually consists of a mixture of uranium and a hydride phase is difficult to ascertain even though uranium lines are visible in the X-ray diffraction pattern. The mobility of hydrogen is such that it is unlikely that there are distinct phase boundaries in the ordinary sense.

Application of the above calculations to the 99 or 100% curves of Fig. 2 shows that the dissociation of compositions higher in hydrogen content than the plateau compositions is abnormal in the sense that results are not concordant. The following are obtained: *e.g.*, $\Delta H = 7.9$, $\Delta F_{298} = 2.6$, $\Delta S_{298} = 18$. The fact that the experimental values of ΔH and ΔS are so much smaller than the empirical values rules out the possibility that some different chemi-

---

[15] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 472.

[16] W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951).

[17] W. M. Latimer, private communication.

cal mechanism of dissociation is involved. Rupture of just one of the U–H bonds would be expected to give a slightly higher value of the entropy change per mole H_2 than rupture of all three bonds. Neither assumption of partial dissociation in this sense, nor assumption of a larger molecular aggregate for UH_3 leads to improved consistency. From the small magnitude of ΔH it may be inferred that release of hydrogen from the solid phase requires relatively little energy. The rapid decrease of this energy with increasing amounts of hydrogen in the solid phase is shown in Table III.

TABLE III

PRESSURE EQUATIONS AND VALUES OF ΔH FOR $UH_{2.94}$ TO $UH_{3.0}$

Values of A and b in equation $\log P_{\text{atm}} = (-A/T) + b$; ΔH in kcal./mole H_2

x in UH_x	A	b	ΔH (apparent)
2.940	4540	6.88	20.8
2.955	4230	6.63	19.4
2.970	3820	6.24	17.5
2.985	3125	5.47	14.3
2.997	2130	4.33	9.7
3.000	1730	3.90	7.9

The apparent variation of ΔH with composition for compositions in the vicinity of UH_3 suggests a solution process in which the hydride and metal are in solid solution. Such a system would be expected to behave in the manner shown. This possibility is being explored by the senior author and C. E. Messer and preliminary results with the Pd–H system[18] seem to indicate that such solid systems as this may be treated by a classical method based on Margules' equation. According to this interpretation the logarithm of the equilibrium pressure along the ascending portions of the isotherms should be proportional to $\log (a_{UH_3}/a_U)$, where a refers to activity.[19] This permits not only a quantitative interpretation of the observed behavior of the U–H system in the regions where the isotherms are ascending but also leads to a fundamental relationship between composition, temperature and pressure which expresses the behavior of the system as a whole, plateau regions as well as ascending regions.

Acknowledgment.—The experimental data reported here were obtained under a contract with the Fairchild Engine and Airplane Corporation on the Air Force sponsored N.E.P.A. Project.

[18] L. J. Gillespie, *et al.*, THIS JOURNAL, **48**, 1207 (1926); **58**, 2565 (1936); (also *cf.* J. R. Lacher, *Proc. Roy. Soc.* (*London*), **525**, 161 (1937)).

[19] An approximate interpretation along this line has been suggested by one of the referees, R. E. Powell, who has pointed out that the isotherms at 600, 625 and 650° when plotted with log P as abscissa and log (mole fraction UH_3/mole fraction U) as ordinate, are straight lines having a slope of 3/2 in keeping with the equation UH_3 (solid solution) $\rightleftarrows$ U (solid solution) + 3/2 H_2. This permits calculation of the value of $\Delta H \cong 20$ for the dissociation of UH_3 which is in good agreement with the plateau value of 20.5 kcal./mole H_2. The interpretation assumes however that the mole fraction ratio is equivalent to the activity ratio and is applicable only to the ascending portions of an isotherm, whereas the rigorous treatment is applicable over the entire isotherm without commitment as to the nature of the phases present.

MEDFORD, MASS.

[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES, REGION VIII]

Hexagonal Iron Carbide as an Intermediate in the Carbiding of Iron Fischer–Tropsch Catalysts[1,2]

BY MILTON MANES, ARTHUR D. DAMICK, MORRIS MENTSER, ERNST M. COHN AND L. J. E. HOFER

RECEIVED JUNE 27, 1952

In the course of a study of the composition of Fischer–Tropsch catalysts and of the relationships between iron carbides in catalysts and in steels, a method has been developed for the thermomagnetic analysis of mixtures containing α-iron, Hägg iron carbide (χ), and hexagonal close-packed iron carbide (ϵ). Iron catalysts have been carbided to about 25% carbide at temperatures ranging from 190 to 350°. Analyses of these catalysts by the new method demonstrate that the hexagonal close-packed carbide may be the only carbide component up to 250° and is formed at temperatures as high as 325°. The results are evidence that hexagonal close-packed carbide is the precursor of Hägg carbide. Furthermore, it appears likely that both higher carbides are precursors of cementite. The data explain why hexagonal close-packed iron carbide is rarely found in fully carburized catalysts even though it is the first-formed carbide over a relatively wide range of temperatures.

The present work was undertaken as part of a program for investigating the composition of Fischer–Tropsch catalysts and the relationships between iron carbides in catalysts and in steels.

Two distinct iron carbides of approximate composition Fe_2C, namely, hexagonal carbide (ϵ) and Hägg carbide (χ), have been identified as products of the reaction of carbon monoxide with reduced iron Fischer–Tropsch catalysts. ϵ-Carbide tends to predominate at low reaction temperatures and in copper-containing catalysts, χ-carbide at higher temperatures. For example, Hofer, Cohn and Peebles[3] found χ- but not ϵ-carbide when a fused, synthetic ammonia-type catalyst was fully carbided at 240°. They found ϵ-carbide as the principal product when a precipitated, copper-promoted catalyst was fully carbided at 190°. More recently, however, Podgurski, Kummer, DeWitt and Emmett[4] found only ϵ-carbide in a copper-free fused catalyst partly carbided at 215°. Moreover, (unpublished) experiments in this Laboratory on the carbiding with carbon monoxide of copper-free sintered and fused catalysts to about 50% carbide at 220° have yielded mixtures of ϵ- and χ-carbides.

These observations are consistent with the hypothesis that ϵ- is a precursor of χ-carbide. Since ϵ-carbide is metastable and is converted to χ-carbide by heating,[3] the presence of ϵ-carbide in partly car-

---

[1] This work was supported in part by the U. S. Air Force under project number 52-670A-270.

[2] Article not copyrighted.

[3] L. J. E. Hofer, E. M. Cohn and W. C. Peebles, THIS JOURNAL, **71**, 189 (1949).

[4] H. H. Podgurski, J. T. Kummer, T. W. DeWitt and P. H. Emmett, *ibid.*, **72**, 5382 (1950).