scribed column of about fifteen theoretical plates. Analysis by distillation indicated that, in addition to the compounds reported above, appreciable amounts of silicon tetrabromide were present in the crude products. The following table lists the results of five successive runs (the values of n refer to the formula $(CH_3)_nSiBr_{4-n}$).

CH₃Br. g.	Time. hr.	Product. g.	ml.	Composition (vol. %) $n = 3$	$n = 2$	$n = 1$
1180	118	847	492	18	60	20
1390	119	1021	530	7	35	32
1250	118	962	493	7	38	35
1170	96	586	249	3	11	33
1710	114	976	488	4	37	33

Summary

Methyltribromosilane, dimethyldibromosilane and trimethylbromosilane, isolated as products of the reaction of methyl bromide with sintered copper-silicon powder at 300°, have been purified and characterized.
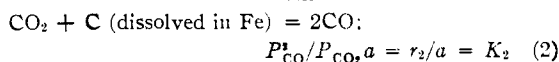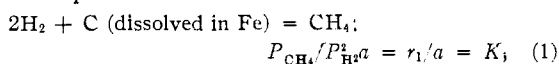

[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

Equilibrium of Iron–Carbon Alloys with Mixtures of CO–CO₂ and CH₄–H₂
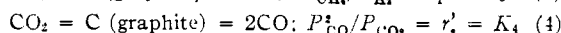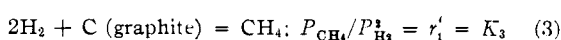
BY RODNEY P. SMITH

As the consistency and range of the available data on the equilibrium between carbon dissolved in iron and definite mixtures of either carbon monoxide with carbon dioxide, or methane with hydrogen, leaves something to be desired, and as accurate information on this matter has considerable practical significance, it was decided to reinvestigate these systems. Accordingly measurements were made of the concentration of carbon, induced in iron at a number of temperatures ranging from 750 to 1200°, by contact with each of a series of ratios of one or other of these pairs of gases.

The equilibria involved may be represented by the equations

$2H_2 + C$ (dissolved in Fe) $= CH_4$:

$$P_{CH_4}/P_{H_2}^2 a = r_1/a = K_1 \quad (1)$$

$CO_2 + C$ (dissolved in Fe) $= 2CO$:

$$P_{CO}^2/P_{CO_2} a = r_2/a = K_2 \quad (2)$$

where P is measured in atmospheres and a is the activity of dissolved carbon. For either system in equilibrium at constant temperature and pressure, a given value of the partial pressure ratio r determines the composition of the solid phase, or *vice versa*, so long as only one solid phase is present. In the temperature range considered the solid phase may be ferrite, a solid solution of carbon in α-iron (body-centered cubic), or austenite, a solid solution of carbon in γ-iron (face-centered cubic), the transition temperature depending upon the carbon content; accordingly interpretation of the results to be presented is facilitated by reference to the pertinent portion of the iron–carbon equilibrium diagram represented in Fig. 1, in which, for clarity, the scale of abscissa for the line GP is ten times as large as for the other lines. If we consider the isothermal line A, B, C, D it is evident that for a gas mixture of low carburizing power the solid phase is ferrite, and as carburizing power increases each gas ratio produces a solid phase of definite composition in the range A to

B.[1] The gas mixture in equilibrium with ferrite of composition B is also in equilibrium with austenite of composition C, and the gross composition of the solid phase may have any value from B to C depending on the relative amount of the two solid phases. A further increase in carburizing power of the gas causes the ferrite phase to transform completely to austenite, and the gas ratio fixes its composition in the range C to D. The line $S'E'$ represents the equilibrium of austenite with graphite; thus the gas ratio, r, in equilibrium with austenite of composition D is also in equilibrium with graphite, and its value (r') at this point gives the equilibrium constant K_3 or K_4 for the reactions

$2H_2 + C$ (graphite) $= CH_4$: $P_{CH_4}/P_{H_2}^2 = r_1' = K_3 \quad (3)$

$CO_2 = C$ (graphite) $= 2CO$: $P_{CO}^2/P_{CO_2} = r_2' = K_4 \quad (4)$

The case is similar for all temperatures between 738 and 910° except that, as temperature increases, the range of stability of ferrite decreases and that of austenite increases. For the temperatures 1000 and 1200° and the carbon range 0 to 1.5%, the only solid phases encountered are austenite and graphite.[1]

If graphite is chosen as the standard state for carbon, the constants K_1, K_2 of equations (1) and (2) become identical with the constants K_3, K_4 of equations (3) and (4). Equation (1) and (2) may then be written

$$a_c = P_{CH_4}/P_{H_2}^2 K_3 = r_1/K_3 \quad (1a)$$

$$a_c = P_{CO}^2/P_{CO_2} K_4 = r_2/K_4 \quad (2a)$$

where a_c is the activity of carbon in iron relative to graphite, and r_1 or r_2 is the ratio at equilibrium with carbon dissolved in iron at a concentration corresponding to the activity a_c. Thus measurements of these ratios and the corresponding carbon

(1) In the case of CO-CO₂ mixtures low in carbon monoxide, the system is complicated by the presence of an iron oxide phase. The above statements apply only to gas mixtures which will not oxidize iron at these temperatures.
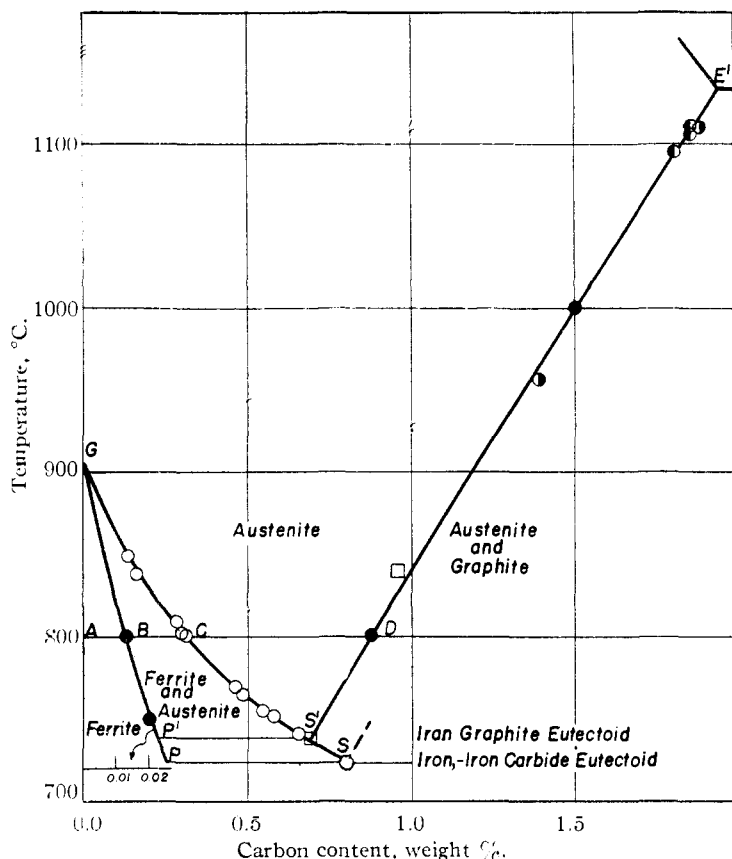
Fig. 1.—A portion of the iron carbon equilibrium diagram: ● Smith, those for graphite solubility; O Mehl and Wells; ☐ Wells; ◖ Gurry, equilibrium with graphite; ◑ Gurry, equilibrium with carbon from toluene The abscissa for the line GP is ten times that for the other lines.

content permit calculation of the activity of carbon and of various other thermodynamic quantities pertaining to these systems. Equations (1a) and (2a) also give a convenient means of comparing the results obtained with the two sets of gases, provided consistent values of K_3 and K_4 are available.

The range of composition covered was from 0.0008 to 1.5% carbon in the iron phase, 0 to 5% methane in mixture with hydrogen, and 0.3 to 27% carbon dioxide mixed with carbon monoxide: the temperatures were mainly 800 to 1000° but a few measurements at 750 and 1200° are included.

Experimental

The iron sample was suspended from a platinum wire in a vertical porcelain tube, held at constant temperature, through which passed upward a stream of the fixed gas mixture, and kept there until equilibrium had been attained. In some cases equilibrium was approached by carburization, in others by partial decarburization of a previously carburized sample. When equilibrium was attained with the particular gas mixture, the sample was quenched by raising it into the upper glass extension of the porcelain furnace tube; its carbon content was then determined.

Iron Samples.—Most were of electrolytic iron[2]; the others of carbonyl iron.[2] They were in the form of strips about 0.2 mm. thick, 1 cm. wide and 6–15 cm. long, wound into a loose coil. Each was provided with an integral hook for convenience of suspension; this hook was removed before the sample was analyzed. This form of sample has the advantages of compactness with large surface, and that it is easily prepared for analysis without danger of contamination by carbonaceous material.

Preparation of Constant Gas Mixtures.— The methods of preparation, purification and utilization of flowmeters to produce CO-CO₂ mixtures of controlled composition were exactly as described by Darken and Gurry,[3] except that the mixture was further dried by passing it through a tube surrounded by a Dry Ice–acetone mixture. The ⁻CO⁻²/CO₂ ratio (r_2) as determined by analysis of a number of representative samples checked that calculated from the calibration of the flowmeters within a few parts in a thousand.

The CH₄–H₂ mixtures were made from commercial hydrogen and either methane from Buttonwillow field, California or commercial methane[4]; the total impurities in either were less than 1% and the purified mixtures from either source gave the same result. Pure methane is not stable at temperatures required in the purification train; therefore primary mixtures containing about 10, 20 and 60% methane were made in hydrogen cylinders which were allowed to stand by a radiator for some months to ensure thorough mixing. These mixtures were analyzed by combustion over copper oxide with a reproducibility of about ±0.5% of the methane present. Subsequent analysis indicated that these mixtures were uniform. These primary mixtures were purified by passing successively through ascarite, activated alumina, copper gauze at 450°, ascarite, activated alumina, and finally phosphorus pentoxide; hydrogen was purified by a similar train. The final mixtures were made from these gases by a flowmeter system similar to that used for the CO-CO₂ mixtures. From the flowmeter system the gas passed through a mixing chamber, entered the furnace tube at its lower end through a mercury seal and left at atmospheric pressure through its upper extension beyond the furnace.

The flowmeters for the CH₄–H₂ mixtures were calibrated by measuring the time to deliver a fixed volume: the small temperature corrections were calculated from the known viscosity[5] of the two gases. At constant temperature the flowmeter constant K' is given by the equation

$$K' = t\Delta P\left(1 + \frac{\Delta P/2 + \Delta P'}{P}\right)$$

where t is the time to deliver a fixed volume of gas, ΔP the pressure drop through the capillary, $\Delta P'$ the back pressure between collecting flask and capillary, and P is one atmosphere, all pressures being expressed in centimeters

(2) Analysis—electrolytic iron: Si, 0.007; Cu, 0.05; Ni, 0.02; Pb, 0.04; C, 0.012; O, 0.02, P, 0.004, S, 0.003, Al, B, Mn, Ti, Cb, Mo, Cr, Ge < 0.001. Carbonyl iron: Si, 0.008; Ni, 0.017; O 0.012; Mn, Ti, Co, Mo, Cr, Ge < 0.001; Cu, Al, Pb, B, none. We are indebted to the analytical department of Gary Works, Carnegie-Illinois Steel Corporation, for the spectroscopic analysis of these metals.

(3) L. S. Darken and R. W. Gurry, THIS JOURNAL, 67, 1398 (1945).

(4) From The Matheson Co., East Rutherford, N. J.

(5) "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y.

of butyl phthalate. In each case the reproducibility of the flowmeter constant was better than ± 0.5%; the accepted value was the average of twenty determinations which covered a large portion of the possible range of ΔP. The ratio of the constant for the hydrogen flowmeter to that for the mixture flowmeter was about 20; the effect of change of room temperature on this ratio is negligible so long as both capillaries are at the same temperature. The total rate of gas flow to the furnace was sufficient to prevent changes in composition due to thermal diffusion.[4]

Analysis of the final mixtures by combustion over copper oxide was cumbersome owing to the large amount of water produced compared to carbon dioxide. Two mixtures made from the 10% primary mixture were analyzed; the result on one was 1.36, on the other 1.46% methane as determined by the flowmeter calibration combined with the composition of the primary mixture, compared with 1.34 and 1.43% methane, respectively, as determined by combustion. Analysis by combustion indicates a slightly lower proportion of methane in each case; we believe the result derived from the gage calibration to be more accurate, because of the difficulty inherent in the combustion method for such a mixture. A further check on the relative accuracy of the 10 and 60% primary mixtures is given by the fact that sample b, Table II (0.484% C at 800°), for which the primary mixture was 10% methane, is in accord with other samples of this series for which the primary mixture was 60% methane.

Carbon Content of Equilibrated Samples.—Samples containing from 0.05 up to 1.5% carbon were analyzed by the usual combustion method; those with less than 0.05% carbon by the low pressure combustion method, as described by Gurry and Trigg,[6] for which the accuracy is claimed to be 0.0007% and the reproducibility ±0.0003% carbon. The mean value found for Bureau of Standards samples 16c and 11d was 1.008 ± 0.003 (10 determinations) and 0.202 ± 0.001 (4 determinations), respectively, as compared with the recommended values 1.01 and 0.202%. The samples, before exposure to the CO–CO₂ mixtures at 1000°, were treated with hydrogen to remove carbon and oxygen, and the carbon content at equilibrium was determined both by gain in weight of the sample and by combustion. The maximum difference between these two methods was 0.004% carbon; the average for 12 samples was 0.001% greater as measured by gain in weight than by combustion. This is the type of difference to be expected if oxygen from the gas entered the samples; but the number of determinations is insufficient to render this result significant.

Temperature Measurement and Control.—The furnaces and method of temperature control were the same as described by Darken and Gurry.[3] Temperature at the position of the sample was read after each equilibration period by a platinum-platinum-rhodium couple and suitable potentiometer; this couple was compared at frequent intervals with a similar couple certified by the Bureau of Standards. To prevent contamination of the couple, the furnace tube was flushed with air, in the case of the CO–CO₂ mixtures, and with nitrogen, for the CH₄–H₂ mixtures, prior to the measurement.

Over short periods the variation of the furnace temperature was less than ±0.1°; however, since the action of the controller was not entirely independent of room temperature it occasionally varied by as much as ±1.0° in twenty-four hours. Since the latter variation was always very gradual, it is justifiable to consider that the equilibrium measured corresponds to the temperature measured at the end of the period of exposure of the iron specimen. When the measured temperature differed from that specified (this difference never being more than 1°), r was corrected correspondingly.

Equilibration Period.—The time required for the sample to come to equilibrium with the gas depends upon the rate at which the gas supplies available carbon to the furnace atmosphere, the rate of transfer of carbon from the

gas through the iron surface, the rate of diffusion of carbon through iron, and the dimensions of the sample. For one 0.2 mm. thick, the time required for diffusion is of the order of a few minutes to about four hours for the temperature range covered.[7] If this time is relatively short and if the surface of the sample is always in equilibrium with the gas, the period required for the carbon to reach 99.5% of its equilibrium concentration in the iron at the highest carbon content and for a gas flow of 40 cc. per minute, is about seventeen hours for the CH₄–H₂ mixture but less than half an hour for CO–CO₂. The rate of carbon transfer through the surface is not known; but extensive tests showed that a period of forty-eight hours is ample for equilibrium under the conditions of this investigation.

The time required for diffusion of oxygen through austenite is of the order of a thousand times that for carbon[8]; therefore the final oxygen content of samples equilibrated with a CH₄–H₂ mixture will depend upon temperature and length of exposure. Since each CO–CO₂ mixture exerts a definite, though small, oxygen pressure, the final oxygen content of these samples will be greater than for those equilibrated with CH₄–H₂ mixtures.

Experimental Results

Equilibrium with Ferrite.—Table I gives the experimental results for the equilibrium of CH₄–H₂ mixture with electrolytic iron at 750 and 800° and with carbonyl iron at 800°. A plot of

TABLE I

EXPERIMENTAL MEASUREMENTS OF EQUILIBRIUM OF CH₄–H₂ MIXTURES WITH FERRITE: $r_1 = P_{CH_4}/P_{H_2}^2$, WHERE P IS IN ATMOSPHERES

Electrolytic 750°		Electrolytic 800°		Carbonyl 800°	
r_1	Final carbon content % by weight	r_1	Final carbon content % by weight	r_1	Final carbon content % by weight
0.00	0.0040ᵃ	0.00	0.0040ᵃ	0.00	0.0008ᵃ
.0144	.0090	.00045	.0045ᵃ	.0025	.0027
.0226	.0122	.00092	.0046	.0051	.0052ᵃ
.0295	.0146	.0014	.0051ᵃ	.0065	.0063
.0363	.0168	.0025	.0064ᵃ	.0114	.0104ᵃ
.0387	.0182	.0033	.0074	.0111	.0103
.0436	.0196	.0050	.0088ᵃ	.0127	.0121
.0529	.0244	.0065	.0100ᵃ		
.0540	> .04	.0066	.0104ᵃ		
		.0090	.0130		
		.0091	.0125		
		.0108	.0146		
		.0128	.0152ᵃ		
		.0129	.0161		
		.0138	.0171ᵃ		
		.0141	> .03		

ᵃ Equilibrated by decarburization of previously carburized samples.

r_1 against carbon content is a straight line, but intersects the abscissa at 0.004% carbon for the electrolytic and at 0.0008% carbon for the carbonyl iron. Similar samples of both irons treated in either wet or dry hydrogen for periods up to forty-eight hours likewise analyzed 0.004% and 0.0008% carbon, respectively, though the analysis[2] of either metal shows no appreciable amount of any element which would form a highly stable carbide. If the source of this discrepancy were some hydrocarbon in the hydrogen or a blank

(6) R. W. Gurry and H. Trigg, *Ind. Eng. Chem., Anal. Ed.*, **16**, 248 (1944).

(7) R. W. Gurry, *Trans. Am. Inst. Mining Met. Engrs.*, **150**, 147 (1942).

(8) Brower, Larsen and Schenk, *ibid.*, **113**, 61 (1934).

error of the analysis train, the residual carbon in both types of iron should be the same.

This slight difference may be ascribed to some slight difference between the final equilibrated iron phases—for example, in extent of distortion of the unit cube brought about by interstitial solution of an element such as oxygen, or possibly by prior cold work. With respect to the latter, there is clear evidence from other sources that a sojourn of several days at a temperature even of 800° removes only partially the effect of cold work.

Whatever the reason for the difference, the two sets of measurements at 800° are in good agreement if the appropriate residual carbon is subtracted from the experimental results. Figure 2 shows a comparison of these two sets, as thus corrected, together with values calculated from the data of Dünwald and Wagner[9] for equilibrium with a series of CO–CO_2 atmospheres at 800°.
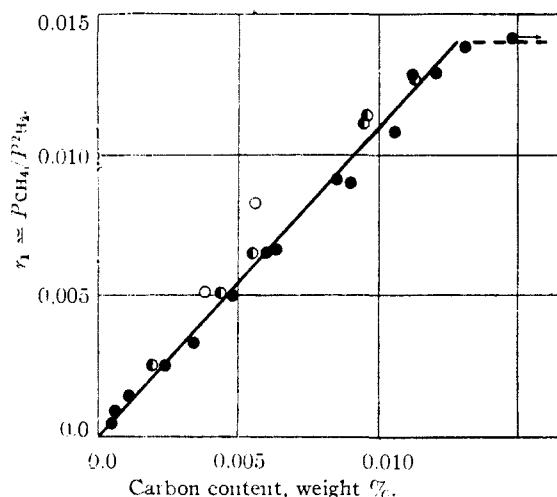

Fig. 2.—Carbon content of ferrite at 800° in relation to $r_1 = P_{CH_4}/P^2_{H_2}$: ● Smith, electrolytic iron; ◐ Smith, carbonyl iron; ○ calculated from Dünwald and Wagner data on $r_2 = P^2_{CO}/P_{CO_2}$.

At 800°, the transition of ferrite to austenite occurred when the ratio, r_1 was between 0.0138 and 0.0141. If 0.0140 is taken as the limiting value, the solubility of carbon in ferrite (line GP of Fig. 1) at 800°, as read from Fig. 2, is 0.0128% by weight. The relation between the ferrite and austenite equilibria at 800° is indicated in Fig. 3. At 750° the value of r_1 for this transition was between 0.053 and 0.055; the solubility of carbon in ferrite at $r_1 = 0.054$, as read from a curve similar to Fig. 2, is 0.020%. There are few data with which to compare these measured solubilities, which are about 30% lower than those generally accepted.[10] The curve drawn through the tem-

(9) Dünwald and Wagner, Z. anorg. allgem. Chem., 199, 321 (1931). The ratio r_1 was calculated from the given ratio r_2 by equations (1a) and (2a) and the values of the equilibrium constants K_3 and K_4 of Table IV derived from this investigation.

(10) Epstein, "Alloys of Carbon and Iron," McGraw-Hill Book Co., Inc., New York, N. Y., 1936.

perature of the α-γ transformation[10] for pure iron, G, Fig. 1, and the above solubilities intersects the isothermal line at 723° (P, Fig. 1) at 0.025% carbon. This is the solubility of carbon in ferrite at the iron–cementite eutectoid; it compares favorably with the value 0.03% carbon found microscopically by Whitely.[11]

EXPERIMENTAL MEASUREMENTS OF EQUILIBRIUM OF CH_4–H_2 MIXTURES WITH AUSTENITE: $r_1 = P_{CH_4}/P^2_{H_2}$, WHERE P IS IN ATMOSPHERES

800°		1000°	
r_1	Final carbon content % by weight	r_1	Final carbon content % by weight
0.0159	0.356[a]	0.00154	0.326
.0209	.454[a]	.00151	.331
.0228	.484[b]	.00157	.338
.0241	.516[a]	.00254	.534
.0267	.567[a]	.00304	.631
.0316	.654[a]	.00355	.729
.0361	.733[a]	.00462	.880
0367	.736[a]	.00512	.974
.0396	.790[a]	.00540	1.015
.0410	.803	.00647	1.160
.0438	.852	.00722	1.258
.0444	.872	.00746	1.274
.0449	.877	.00910	1.440
		.00926	1.476

[a] Equilibrated by decarburization. [b] The primary mixture for this sample was 10% CH_4, that for the others at 800° was 60% CH_4.

Equilibrium with Austenite.—Table II gives the experimental results for the equilibrium of electrolytic iron with various CH_4–H_2 mixtures for the temperatures 800 and 1000°. The consistency of these results is illustrated in Fig. 3 where r_1 is plotted against observed carbon content at 800°. For a given carbon concentration the value of r_1 in Fig. 3 is roughly half that given by Schenk.[12] The best curve through these points intersects the value of r_1 for the ferrite-austenite equilibrium at 800° (C, Fig. 1 and 3), at 0.315% carbon, which is identical with the value determined by Mehl and Wells[13] from dilatometric measurements. This agreement, though gratifying, is not an absolute check on the accuracy of our results because any consistent error in gas composition will not affect the carbon content at this intersection.

The consistency of the results at 1000° is similar to that at 800° shown in Fig. 3. At 1000°, however, there is a slight reduction of silica in the furnace tube by the gas, part of the silicon so produced vaporizes and is absorbed by the sample. For samples of about 1.4% carbon the increase in silicon was about 0.011% per day, but the extent of this reaction is not sufficient to change the gas

(11) J. H. Whitely, J. Iron & Steel Inst., 116, 293 (1927).

(12) R. Schenk, F. Kurzen and H. Wesslock, Z. anorg. allgem. Chem., 203, 159 (1932).

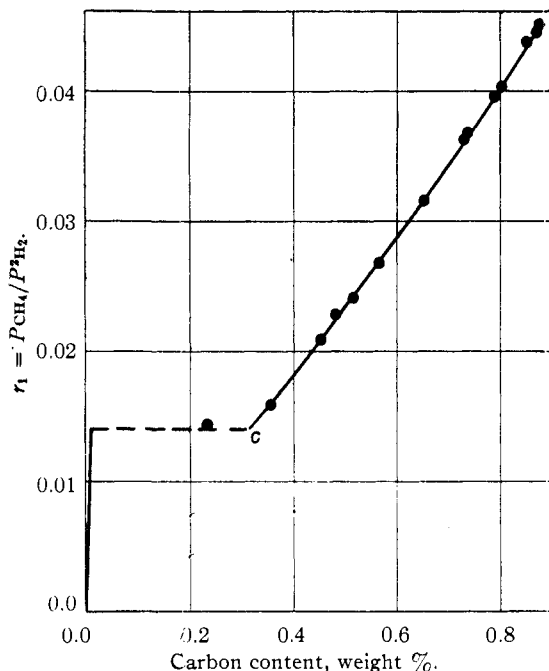(13) Robert F. Mehl and Cyril Wells, Am. Inst. Min. Met. Engrs., 125, 429 (1937).

Fig. 3.—Carbon content of austenite at 800° in relation to $r_1 = P_{CH_4}/P^2_{H_2}$: point C is lower limit of stable austenite at 800°.

composition appreciably. A few measurements were made with CH_4–H_2 mixtures at 1200° but they were not continued because the silicon pick-up proved to be about ten times greater than at 1000°.

Table III gives the experimental results obtained with electrolytic iron and CO–CO_2 mixtures for the temperatures 800, 1000, and 1200°.

A typical example of the reproducibility of these measurements is illustrated in Fig. 4 where r_2 is plotted against carbon content at 1000°. Figure 4 also provides a comparison of these results with those of the later previous investigations.[9,14,15,16,17] The data of Dünwald and Wagner[9] are in good agreement, the others in poor agreement, with the results of this investigation. The accord with the data of Dünwald and Wagner is illustrated better in Fig. 5, where log r_2 for a number of carbon concentrations is plotted against $1/T$, the reciprocal of the absolute temperature, for our results at 800, 1000, 1200° and for theirs at 940, 1000 and 1070°; the values of r_2 were read from a large scale graph similar to Fig. 4. In general their results, for a given carbon concentration and temperature, give a value of r_2, slightly higher than this investigation; the difference could be accounted for by an uncertainty of about 1° in measured temperature. Since the variation in tem-

(14) Arthur Bramley and Harry Dennis Lord, *J. Chem. Soc.*, 1641 (1932).

(15) A. Johansson and R. Von Seth, *J. Iron Steel Inst.*, **411**, 295 (1926).

(16) M. L. Becker, *ibid.*, **121**, 337 (1930).

(17) G. Takahashi, *Science Reports, Tohoku Imp. Univ.*, **15**, 157 (1926).

TABLE III

EXPERIMENTAL MEASUREMENTS OF EQUILIBRIUM OF CO–CO_2 MIXTURES WITH AUSTENITE: $r_2 = P^2_{CO}/P_{CO_2}$, WHERE P IS IN ATMOSPHERES

800°		1000°		1200°	
	Final carbon content, % by		Final carbon content, % by		Final carbon content, % by
r_2	weight	r_2	weight	r_2	weight
2.25	0.343	1.98	0.0360	3.75	0.0148
2.46	.356	2.49	.0487	3.80	.0141
2.65	.377	3.12	.0563	5.83	.0217
2.85	.405	4.21	.0740	7.14	.0252
3.11	.443	7.29	.133	7.23	.0273
3.12	.453	13.8	.242	12.46	.0450
3.63	.522	27.4	.455	30.3	.109
4.21	.568	43.4	.655	61.4	.215
4.50	.608	56.2	.810	122.5	.416
4.87	.647	70.8	.963	123.1	.413
5.11	.661	84.1	1.081	243.6	.738
5.54	.726	99.4	1.206	352.2	.942
5.64	.726	113.3	1.321		
6.07	.765	130.2	1.462		
6.55	.815	131.7	1.466		
6.75	.831	132.4	1.471[b]		
6.81	.838[a]				
6.89	.836				
7.24	.875				
7.31	.878				
7.32	.898				
7.52	.911				
7.75	.929				
7.77	.916				

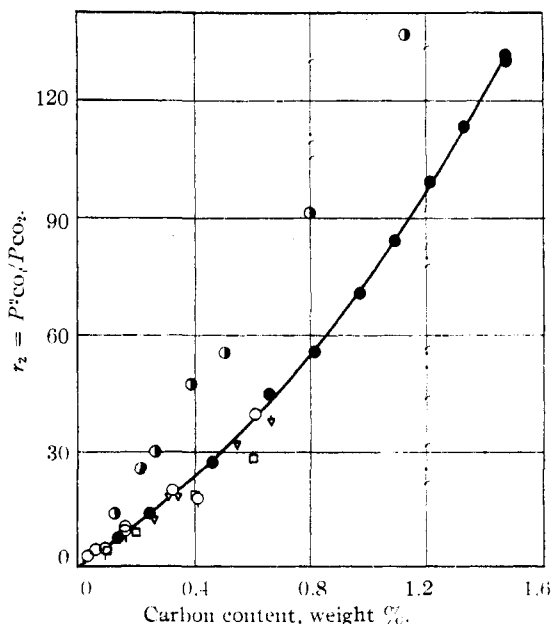[a] Carbonyl iron. [b] Sample ten times thicker and one half weight of other samples.

Fig. 4.—Carbon content of austenite at 1000° in relation to $r_2 = P^2_{CO}/P_{CO_2}$: ● Smith; ○ Dünwald and Wagner; ◑ Bramley and Lord; ♀ Becker; □ Johansson and Von Seth; ▽ Takahashi.
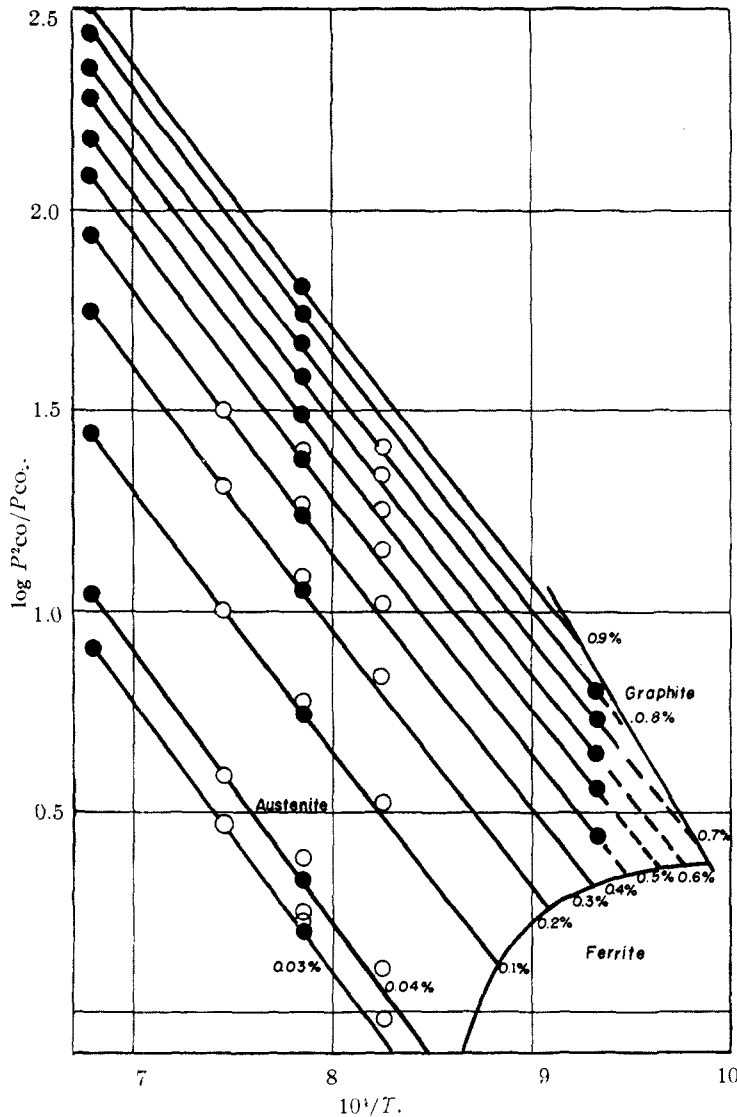
Fig. 5.—Plot of log r_2 against $10^4/T$ for even increments of carbon content: ● Smith; ○ Diinwald and Wagner.

perature of their furnace was $\pm 7°$, and their

For samples equilibrated with CO–CO_2 mixtures at 800°, the austenite–ferrite transition occurred at a value of r_2 between 2.18 and 2.25, which corresponds to 0.323% carbon at point C of Fig. 1. This is slightly greater than the value (0.315%) for the CH_4–H_2 mixtures, also given by Mehl and Wells.[13]

Equilibrium with Graphite; the Constants K_3 and K_4.—The constants K_3 and K_4 at 800 and 1000° were determined by direct measurement of the equilibrium of graphite with each pair of gases, and indirectly from the austenite equilibria and graphite solubility by the method outlined in the introduction. For the direct measurement, the gas composition at equilibrium was determined graphically from the gain or loss of weight in unit time, for a number of gas mixtures at fixed total rate of flow, of a block of Acheson graphite impregnated with a small amount of iron to serve as catalyst. A typical series for each pair of gases at 1000° is plotted in Fig. 6. There is a slight scatter, as is to be expected in such a measurement, but the partial pressure of CO_2 or CH_4 at which the weight remained unchanged can be determined by interpolation with a precision of ± 0.2 at 1000° and $\pm 0.4\%$ at 800°.

The indirect determination requires a knowledge of the carbon content of austenite in equilibrium with graphite and a short extrapolation (always less than 0.06% C) of our austenite equilibrium data to the carbon content corresponding to saturation with graphite. The solubility of graphite in austenite at 800 and 1000° determined by interpolation of the data given by Wells[18] at 738 and 840°, and by Gurry[19] at temperatures near 950 and 1100° was 0.88% and 1.50%, respectively.

Table IV brings together values of the constants K_3 and K_4 for equilibrium with graphite at 800 and 1000° derived: (1) from direct measurements of r_1' or r_2' in equilibrium with graphite, (2) by extrapolation of the experimental curve for r_1 or r_2 to the carbon content corresponding to saturation with graphite, (3) by interpolation of the recently published constants derived from

(18) Cyril Wells, Trans. Am. Soc. Metals, 26, 289 (1938).

(19) R. W. Gurry, Trans. Am. Inst. Mining Met. Engrs., 150, 147 (1942).

TABLE IV

VALUES OF THE EQUILIBRIUM CONSTANT K_3 AND K_4, WHERE P IS IN ATMOSPHERES

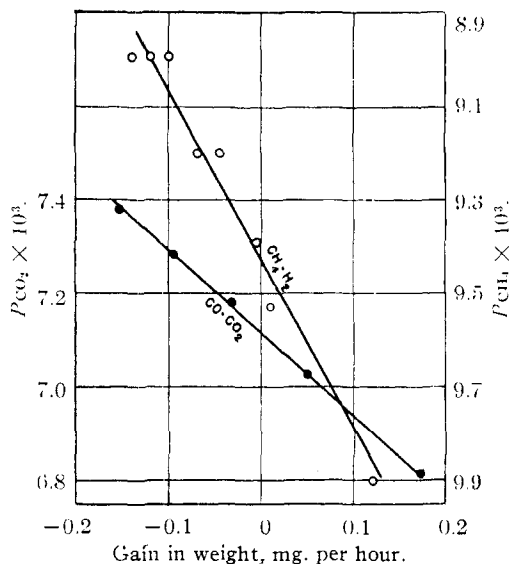| t, °C.	1 Direct measurement	2 Extrapolation of r	3 From spectroscopic and calorimetric data	4 As given by Chipman
		$K_3 = P_{CH_4}/P_{H_2}^2$		
800	0.0453	0.0456	0.0469	0.051
1000	0.00962	0.00950	0.00949	0.0102
$\Delta H'_3$	−21,000	−21,330	−21,700	−21,850
		$K_4 = P_{CO}^2/P_{CO_2}$		
800	7.33	7.28	7.68	6.22
1000	138.6	137.2	151	117
$\Delta H'$	39,900	39,970	40,300	39,830

Fig. 6.—Weight change of a block of Acheson graphite in relation to the partial pressure of either CO_2 or CH_4: ● CO-CO_2 mixtures, ○ CH_4-H_2 mixtures.

Fig. 7.—Activity (a_c) of carbon relative to graphite (mean from two sets of measurements) at 1000° in relation to atom fraction carbon in iron.

calorimetric and spectroscopic data.[20] (4) from Chipman's summary of the data then available.[21] The agreement between our direct and indirect measurements (columns 1 and 2) is excellent; but it may be noted that this is not an entirely independent check, since the same gas mixtures were used in both and any error in gas composition would affect both equally. This table also includes values of the heat of reaction $\Delta H'_3$, $\Delta H'_4$ as calculated from each pair of values of K_3 or K_4 at 800 and 1000°, respectively. The heats in column 3 are in better agreement with those of columns 1 or 2 than are the equilibrium constants upon which they are based.

An attempt to make an independent determination of this graphite solubility at 1000° by passing CO-CO_2 mixtures, of compositions near that for equilibrium with graphite, over samples of electrolytic iron packed in graphite containing a small amount of ferric oxide, was not successful; the carbon content of the sample changed with change in gas ratio although to a less extent than when no graphite was present. However, the intersection of the lines obtained by plotting r_2 against carbon content for these results and those for the austenite equilibrium should give the graphite solubility; the value thus derived is 1.497% carbon in good agreement with that (1.50%) determined from the direct measurements of Wells and Gurry.

It should be possible to determine graphite solubility, and equilibrium constant, by a method similar to that used to fix the carbon concentration at which ferrite begins to transform to austenite. A few measurements of this type were

(20) Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *Bur. Standards J. Research*, **34**, 143 (1945).

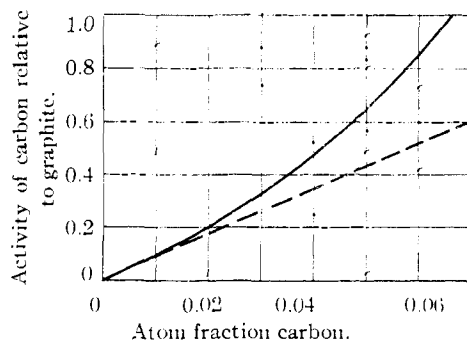(21) John Chipman, *Ind. Eng. Chem.*, **24**, 1013 (1932).

made with CO-CO_2 mixtures at 800°, but the results indicated that the system tends to follow the metastable austenite equilibrium. For instance, the samples (Table III) with 0.916 and 0.929% carbon contain considerably more carbon than corresponds to the graphite solubility at this temperature, yet these points are in accord with the austenite equilibrium. Samples with 0.95 to 0.975% carbon (analysis by gain in weight) were in accord with the austenite equilibrium after being in the gas mixture for 24 hours; however, after being quenched and returned to the furnace the carbon increased as would be expected if the graphite phase were then present in the sample.

The Activity of Carbon Relative to Graphite.—The activity of carbon, at a given concentration, relative to graphite, may be calculated from the measurements with either gas mixture by equation (1a) or (2a) and the data in Tables II, III and IV. The results of such calculations, based on values of r_1 and r_2 interpolated from the experimental curve for regular increments of carbon content, and of K_3 or K_4 given in column 2, Table IV, are presented in Table V. It is to be noted that for a given carbon content, the activity of carbon is only half as great at 1000 as at 800°, corresponding to the lower saturation concentration of graphite in austenite at the lower temperature; also that at both temperatures the activity as calculated from r_1 is greater than that from r_2. These two calculated activities would be identical only if (1) the ratio of the selected values of K_3 and K_4 is exact, (2) the measurement of r_1, r_2 and the carbon content at equilibrium are equally accurate in both cases, (3) the final iron phase is identical and contains only carbon or, at most, identical small amounts of other elements, (4) the gases are equally ideal, an assumption which seems unlikely to introduce an appreciable error. The extent to which these conditions were fulfilled is discussed below.

(1) That the difference between the two sets of activities is not entirely due to mutually inconsistent values of the constants K_3, K_4 is indicated by the fact that the ratio r_2/r_1, which would be

<div align="center">TABLE V</div>

<div align="center">ACTIVITY OF CARBON IN AUSTENITE RELATIVE TO GRAPHITE AT 800 AND AT 1000°</div>

Carbon content weight %	Temperature 800°					Temperature 1000°				
			a_c					a_c		
	r_1	r_2	r_1/K_3	r_2/K_4	$r_2/r_1 = K$	r_1	r_2	r_1/K_3	r_2/K_4	$K \times 10^{-2} = r_2/r_1 \times 10^{-2}$
0.1						0.00047	5.6	0.050	0.041	119
.2						.00092	11.1	.097	.081	121
.3	0.0132	2.04	0.290	0.280	155	.00137	17.4	.144	.127	127
.4	.0181	2.80	.397	.385	155	.00185	23.7	.195	.173	128
.5	.0232	3.61	.509	.496	156	.00235	30.9	.247	.225	132
.6	.0287	4.47	.630	.614	156	.00286	38.7	.301	.282	135
.7	.0344	5.40	.753	.742	157	.00344	46.8	.362	.341	136
.8	.0405	6.42	.888	.882	158	.00403	55.7	.424	.406	138
.88	.0456	7.28	1.000	1.000	160	....	...	...	...	...
.9						.00467	65.0	.491	.447	139
1.0						.00535	75.0	.563	.547	140
1.1						.00607	85.8	.639	.626	141
1.2						.00684	97.2	.720	.709	142
1.3						.00766	109.7	.806	.800	143
1.4						.00854	122.8	.899	.896	144
1.50						.00950	137.2	1.000	1.000	144

the equilibrium constant, K, for the reaction $CO + CH_4 = 2CO + 2H_2$ shows a regular trend with carbon content covering a range of about 3% at 800° and 18% at 1000°. In each case this K is lower than that computed from spectroscopic and calorimetric data but approaches it as the carbon content increases. The agreement between the two sets of activities is not improved by using the constants given in column 3, Table IV, instead of those of column 2.

(2) The values of r_1 and r_2 should be consistent within a few per cent. The value of r_2 may have been somewhat more accurate than that of r_1 since the preparation of the CO–CO_2 mixtures was more direct. The difference between our two sets of measurements is shown better in the very sensitive plots (Fig. 8 and 9) of log $(r\ n_1/n_2)$ against n_2/n_1, where n_2/n_1 is the ratio of the number of atoms of carbon to iron; if they were consistent over the entire range of carbon content the slope of both lines in each figure should be the same. At each temperature the slope of the curve for CO–CO_2 mixtures is greater than for the CH_4–H_2 mixtures, but the difference in slope is practically identical. Anything which would tend to make the true value of r_1 smaller (than the analyzed value of the input gas) at low carbon content, or that of r_2 smaller at high carbon content, would account for the discrepancy between the two sets of measurements. Since the proportion of methane is small for samples of low carbon content, while that of carbon dioxide is small for samples of high carbon content, the discrepancy could be due to a tiny leak of oxygen into either gas mixture. However, a low value of r_2 at high carbon
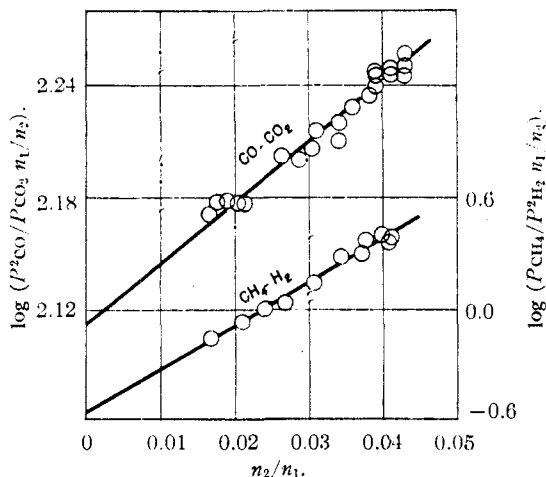

Fig. 8.—Plot of log $(r_m n_1/n_2)$ against n_2/n_1, the atom ratio of carbon to iron, for the two sets of measurements at 800°.
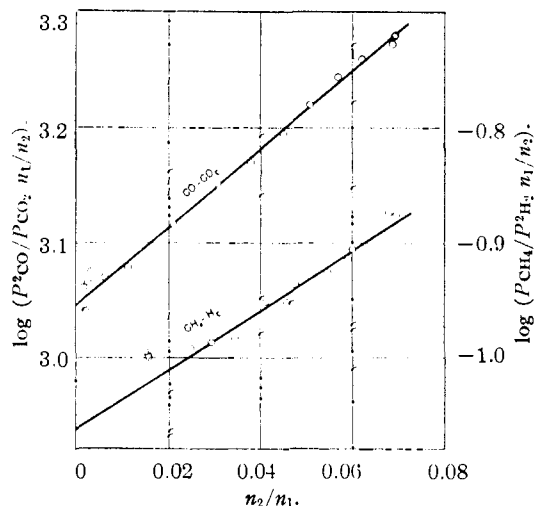

Fig. 9.—Plot of log $(r_m n_1/n_2)$ against n_2/n_1, the atom ratio of carbon to iron, for the two sets of measurements at 1000°.

content would lower K_4 and K and thus increase the difference between our results and those calculated from spectroscopic and calorimetric data. A leak of about 0.01% oxygen into the CH_4–H_2 mixtures at 1000° would account for the difference in slope (oxygen reacts almost exclusively with methane rather than hydrogen) of the pair of lines of Fig. 9; but, since at 800° the relative amount of methane is ten times as great as at 1000°, the same proportion of oxygen would produce a relatively small effect and hence would not account for the discrepancy in slope at this lower temperature. Moreover, in view of the great pains taken to secure a tight system, the hypothesis of such a leak does not seem satisfactory unless the data point clearly in this direction—which they do not.

The accuracy of the carbon determination was the same in both cases. However, there may be a difference in the measured equilibrium carbon content (for a given carbon activity of the gas phase) if there were appreciable reaction of the sample with the gas atmosphere during quench, the CO–CO_2 mixtures then tending to carburize, and the CH_4–H_2 mixtures to decarburize the specimen. Several lines of evidence indicate that the error from this source is not appreciable, at least at high carbon content. First a sample (b, Table III) ten times as thick and half as heavy as the others gave a concordant result. Second, the agreement of the pairs of values of K_3 and K_4 (Table IV, 1 and 2) is within the expected experimental error although the type of sample in the two measurements was quite different; moreover correction for a change in carbon during quench would bring closer the pair of values of K_4 but more apart those of K_3. Third, the data of Dünwald and Wagner,[9] who weighed the sample at temperature on a special balance, are not subject to this possible error; and Fig. 5 shows that they agree with the present data better at the higher temperatures, which is contrary to expectation if reaction during cooling were appreciable. The small difference between these data and our measurements at 1000° (Fig. 5) is in the direction of such an error but could be attributed equally well to other causes.

(3) The iron samples were initially identical, but when equilibrated, there was a slight difference in the amount of elements other than carbon, especially with respect to oxygen, silicon and hydrogen. The initial oxygen content was 0.02%; for equilibrium with CO–CO_2 mixtures it is less than 0.01%[9] (the agreement of the analysis by gain in weight and by combustion of previously deoxidized samples would indicate that it was considerably less than 0.01% at 1000°); for samples equilibrated with CH_4–H_2 mixtures it is 0.0 to < 0.02% (see equilibration period). The silicon content of samples treated with CH_4–H_2 mixtures may be greater than for those treated with CO–CO_2 mixtures by 0.03% (see equilibrium with

austenite) and their hydrogen content may be greater by 0.0006%.[22] For liquid iron the sign of the differential $(\partial a_0/\partial\%C)_{\%O}$ is negative,[23] a_0 being the activity of oxygen; if this is assumed to be likewise true for austenite, the sign of the differential $(\partial\%O/\partial\%C)_{a_0}$ is positive; that is, increase of oxygen at fixed activity should increase carbon content at equilibrium. On the other hand, the presence of silicon would tend to lower carbon content[24] at equilibrium; the decrease in carbon is, however, only about one-tenth the increase in silicon. Both of these effects are in the direction of the observed discrepancy; but since the amount of these elements is always small, it does not seem reasonable that they can entirely account for it.

The precise source of this lack of complete accord between the results calculated from different data is thus still an open question that can probably not be answered except by additional painstaking investigations which would require an effort hardly justified by the importance of the matter.

Heat of Solution of Carbon in Ferrite.—If the activity (a_c) of carbon relative to graphite is known for a number of temperatures in the region of stability of ferrite, the heat of solution ΔH_s of graphite in ferrite may be determined by the equation

$$\Delta H_s = 4.5755\,[\partial \log a_c/\partial 1/T]_{\%C} \qquad (5)$$

At 0.01% carbon at 800° a_c may be calculated directly from the data of Table I and the constant K_3; at 750° from Table I and a value of K_3 extrapolated from the results at 800 and 1000°; at 738°, the temperature of the iron–graphite eutectoid (P', Fig. 1), by extrapolation of the limiting solubility to this temperature and the assumption that at this low concentration a_c is proportional to carbon content. The values of a_c, at 0.01% C, thus obtained are 0.242, 0.365 and 0.454, respectively. From the slope of the best straight line on a plot of log a_c vs. $1/T$, ΔH_s is 20,000 cal. The result is not appreciably different if K_3, as derived from spectroscopic measurements, is used in the calculation. If it is assumed that the properties of δ-iron and α-iron are similar because their structure is similar, a value of a_c in α-iron at 1490° may be calculated from the equilibrium of δ with γ-iron and liquid iron, as given by Adcock,[25] and values of r_2 for equilibrium with liquid iron as given by Marshall and Chipman.[25] The value of ΔH_s derived with this additional datum is 26,000 cal.

Heat of Transfer of Carbon from the Gas Mixtures to Austenite, and the Heat of Solution of Graphite in Austenite.—The equilibrium con-

(22) Sieverts, Zapf and Moritz, Z. physik. Chem., **A183**, 19 (1938).
(23) Shadburn Marshall and John Chipman, Trans. Am. Soc. Metals, **30**, 69 (1942).
(24) "Alloys of Iron and Silicon," Griener, Marsh and Stoughton, McGraw-Hill Book Co., Inc., New York, N. Y.
(25) Frank Adcock, J. Iron Steel Inst., **135**, 281 (1937).

stants for reactions (1) and (2) may be written

$$K_m = r_m/a \qquad (6)$$

where the subscript m is 1 or 2 and a is the activity of carbon in austenite at the equilibrium concentration relative to its value at some chosen fixed concentration. The heat of transfer of carbon from the particular gas to austenite of a given concentration is given by

$$-\Delta H_n/4.5755 = [\partial \log K_m/\partial 1/T]_{\%C} = [\partial \log r_m/\partial 1/T]_{\%C} - [\partial \log a/\partial 1/T]_{\%C} \quad (7)$$

where the subscript m is 1 or 2. The first term on the right side of this equation is the heat of transfer of carbon from the gas to austenite at the fixed concentration, and the second term that from austenite at the fixed concentration to austenite of the equilibrium concentration. If the latter is small compared to the former, and if ΔH_m does not change appreciably with temperature over the temperature range considered, the curves obtained by plotting $(\log r_m)_{\%C}$ vs. $1/T$ should be straight lines and the slope should be the same for all concentrations and equal to $-\Delta H_m/4.5755$. That these conditions are fulfilled within the experimental error is illustrated in Fig. 5. Further evidence that the second term on the right of equation (7) is small will be given in the appendix. The value of ΔH_1 and ΔH_2 calculated from our measurements is $-31,000$ cal. and $29,600$ cal., respectively; ΔH_2 calculated from the data of Dünwald and Wagner[9] is 28,800 cal., that given by Bramley and Lord[11] is 29,950 cal.

Likewise the heat of reactions (3) and (4) is given by

$$-\Delta H'_m/4.5755 = d \log K_m/d1/T \qquad (8)$$

where the subscript m is 3 or 4. The difference $\Delta H'_m - \Delta H_m$ is the heat of solution of graphite in austenite. If $\Delta H'_m$ is taken as the mean of the values obtained from the equilibrium measurements (Table IV) and ΔH_m as given above, the heat of solution of graphite in austenite from the measurements with $CO-CO_2$ mixtures is 10,300 cal. and that from the CH_4-H_2 mixtures is 9,940 cal.

Appendix[26]

An Approximate Solution Law for Carbon in α-Iron and the Heat of the $\alpha-\gamma$ Transformation. —It seemed desirable to express in analytical form the results of the foregoing measurements of the activity of carbon in austenite. By analogy with liquid solutions it might be guessed, as a first approximation, that Henry's law would be obeyed, that the activity of carbon a_c would be proportional to its atom fraction. However, it is obvious from Fig. 7 that such proportionality holds, within the experimental error, over a very limited range; if the proportionality constant is chosen to satisfy the measurements at low con-

(26) This appendix is contributed by Dr. L. S. Darken and R. P. Smith.

centrations, those at higher concentrations depart from the proportional values by more than 50%.

An artifice which has sometimes been adopted to circumvent such departure from the solution laws is to assume the presence of molecular species; for instance, austenite has been considered as an ideal solution of Fe_3C in iron,[27,28] whence by consideration of the homogeneous equilibrium $C + 3Fe = Fe_3C$ the activity of carbon would be proportional to N_{Fe_3C}/N_{Fe}^3, where each N represents the mole fraction calculated on the above basis. Actually the data do not fit this proportionality well either, although the agreement is markedly better than on the assumption of Henry's law. In any case this type of treatment is quite unsatisfactory from the theoretical viewpoint since no meaning can be attached to molecular species in a solid solution.

A relation which has been found useful for a variety of binary liquid solutions, sets the logarithm of the activity coefficient of one component proportional to the square of the mole fraction of the other (the pure liquid being selected as standard state)

$$\log \gamma_1 = \alpha N_2^2; \quad \log \gamma_2 = \alpha N_1^2$$

A variety of derivations by the methods of statistical mechanics[29,30,31,32,33] reduce to this form under certain simplifying conditions. The data of the present investigation fit this type of relationship quite well; but this representation must be regarded as entirely empirical in this case since the statistical derivations are based on concepts applicable to the liquid state and to substitutional solid solutions. It is questionable whether there is any basis whatsoever for its application to interstitial solid solutions such as carbon in iron.

It seemed that the type of relation to be anticipated, as well as a little insight into the nature of this solid solution, might be gained from a consideration of its structure. In austenite the iron atoms are arranged in a close-packed face-centered cubic lattice, and the carbon atoms occupy a limited number of the octahedral interstices which are located at the centers and at the mid-points of the edges of the unit cubes—these two positions being crystallographically equivalent.[31] A clearer picture is obtained from the relationship to the sodium chloride type of lattice to which a theoretical austenite with all interstitial positions filled would belong. Thus every carbon atom has as nearest neighbors six iron atoms, and the nearest interstitial sites to it are twelve in number; the total number of interstitial sites is equal to the number of iron atoms.

(27) K. K. Kelly, Bureau Mines Bulletin 407.

(28) J. B. Austin, Metals and Alloys, **4**, 49 (1933).

(29) Hildebrand and Wood, J. Chem. Phys., **1**, 817 (1933).

(30) Scatchard, Chem. Rev., **8**, 321 (1931).

(31) Rushbrooke, Proc. Roy. Soc. (London), **A166**, 296 (1938).

(32) Kirkwood, J. Phys. Chem., **43**, 94 (1939).

(33) Guggenheim, Proc. Roy. Soc. (London), **A148**, 304 (1935).

(34) Petch, J. Iron and Steel Inst., **145**, 110 (1942).

To derive the isothermal expression for the free energy of such a system it is convenient to make use of the partition function $f = \Sigma g_i e^{-\epsilon_i/kt}$, where g_i is the number of distinguishable arrangements of the atoms on the appropriate sites in such manner that the total energy is ϵ_i. For the present purpose the only energy levels considered for a given atom are those arising from its position relative to neighboring atoms, i.e., each atom is considered to have the average energy of all atoms of the same kind which are similarly situated. Considering a system of n_1 iron atoms, n_1 sites appropriate thereto, and n_1 interstitial positions of which n_2 are occupied by carbon atoms, it is clear that there is only one distinguishable arrangement of the iron atoms, and that the evaluation of the partition function hinges on a counting of the number of distinguishable arrangements of the carbon atoms possible for each energy level. As a direct attack on this problem appears prohibitively difficult, attention may first be focused on an individual carbon atom. Since the position of iron atoms relative to it is always the same, the only distinguishable difference in its surroundings depends on whether or not nearby interstitial sites are occupied by other carbon atoms—i.e., its energy depends on how the other carbon atoms are distributed about it. If we limit our consideration to reasonably dilute solutions (where the number of carbon atoms having more than one nearest neighbor is negligibly small) and introduce the approximation that the energy is influenced only by the presence of another carbon atom in one of the twelve nearest neighbor sites, only two energy levels need be taken into account—i.e., the given carbon atom may have no nearest neighbor carbon atom or it may have one.

Regarding the alloy as being formed by addition, one at a time, of carbon atoms to an initially pure iron, the partition function for each carbon atom will contain two terms corresponding to the two energy levels—the first involving the number of ways the atom can be added such that it has no nearest neighbors (approximately $n_1 - 13$ times the number of carbon atoms already present) and the second involving the number of ways it can be added such that it has one nearest neighbor (approximately 12 times the number of carbon atoms already present). The partition function of the first, second, third, and final (n_2th) carbon atoms are given approximately by the following expressions:

$$f_1 = n_1\theta_1 \tag{9}$$

$$f_2 = (n_1 - 13)\theta_1 + 12\theta_2 \tag{10}$$

$$f_3 = (n_1 - 26)\theta_1 + 24\theta_2 \tag{11}$$

$$f_{n2} = [n_1 - 13(n_2 - 1)]\theta_1 + 12(n_2 - 1)\theta_2 \tag{12}$$

where $\theta_1 = e^{-\epsilon_1/KT}$ and $\theta_2 = e^{-\epsilon_2/kT}$; ϵ_1 is the energy to bring a carbon atom to a site with no nearest neighbor, ϵ_2 is the energy to bring a carbon atom into a nearest neighbor site; k is the Boltz-

man constant and T the absolute temperature. For higher values of n_2 the value of f_{n_2} given by equation (12) will be too large. The partition function for the assemblage is $f = f_1 f_2 f_3 \cdots f_{n_2}/n_2!$ To establish a standard energy level, we may arbitrarily assign the value zero to ϵ_1. The partition function for the assemblage then becomes

$$f = n_1(n_1 - 13 + 12\theta_2)(n_1 - 26 + 24\theta_2)\ldots/n_2!$$

$$= \left(\frac{13 - 12\theta_2}{n_2!}\right)^{n_2}\left(\frac{n_1}{13 - 12\theta_2}\right)\left(\frac{n_1}{13 - 12\theta_2} - 1\right)$$
$$\left(\frac{n_1}{13 - 12\theta_2} - 2\right)\cdots$$

$$= \frac{(13 - 12\theta_2)^{n_2}\left(\frac{n_1}{13 - 12\theta_2}\right)!}{\left(\frac{n_1}{13 - 12\theta_2} - n_2\right)!\,n_2!} \tag{13}$$

or by Stirling's approximation

$$\ln f = n_2 \ln (13 - 12\theta_2) + \frac{n_1}{13 - 12\theta_2} \ln \frac{n_1}{13 - 12\theta_2} -$$
$$\left(\frac{n_1}{13 - 12\theta_2} - n_2\right) \ln \left(\frac{n_1}{13 - 12\theta_2} - n_2\right) - n_2 \ln n_2 \tag{14}$$

differentiating with respect to n_2 and dropping constant terms

$$\left(\frac{\partial \ln f}{\partial n_2}\right)_{n_1,\,T,\,V} = \ln [1 - (13 - 12\theta_2)n_2/n_1] - \ln n_2/n_1 \tag{15}$$

$$= - \ln n_2/n_1 - (13 - 12\theta_2)n_2/n_1 - \ldots \tag{16}$$

The Helmholtz free energy, A, is given by

$$A = - RT \ln f$$

also

$$\left(\frac{\partial A}{\partial n_2}\right)_{T,\,V,\,n_1} = \left(\frac{\partial F}{\partial n_2}\right)_{P,\,T,\,n_1} =$$
$$- RT \left(\frac{\partial \ln f}{\partial n_2}\right)_{T,\,V,\,n_1} = RT \ln a_2 + I \tag{17}$$

where a_2 is the activity of carbon. Equations (16) and (17) give

$$I' + \ln a_2 \cong \ln n_2/n_1 + (13 - 12\theta_2)n_2/n_1 \tag{18}$$

and

$$I' + \ln a_2 n_1/n_2 \cong (13 - 12\theta_2)n_2/n_1 \tag{19}$$

At 1.5 weight per cent. carbon the second term in the expansion of $\ln [1 - (13 - 12\theta_2)n_2/n_1]$ of equation (15) is about 20% of the first term; but the error caused by neglecting it is at least partly compensated by the fact that f as given by equation (13) becomes too large as n_2 increases.

The activity of carbon is proportional (isothermally) to r_1 or r_2; therefore if equation (19) is satisfactory, a plot of $\ln (r_1 n_1/n_2)$ or $\ln(r_2 n_1/n_2)$ vs. n_2/n_1 should be a straight line with a slope equal to $(13 - 12\theta_2)$ and an intercept equal to $\Delta F°/RT$ where $\Delta F°$ is the free energy of transfer of carbon from the gas phase to the metal phase when all reactants and products are in their standard state. That equation (19) represents the equilibrium measurements within the experimental error is illustrated in Figs. 8 and 9. The

two sets of measurements give an average slope of 6.3 at 800° and 6.9 at 1000°. The term θ_2 of equation (19) was defined as $e^{-\epsilon_1/kt}$; this may also be written $e^{-\Delta E/RT}$ where ΔE is the energy required to bring two gram atoms of carbon into nearest neighbor sites, and ΔE corresponding to each slope given above is 1300 and 1700 cal. Since there is no reason to believe that ΔE should vary appreciably with temperature over the temperature range considered, in all calculations involving equation (19) ΔE will be considered constant and equal to 1500 cal.

If $\epsilon_1 = \epsilon_2 = 0$, or $\theta_2 = 1$, equations (15) and (17) reduce to the equation $\ln a_2 = \ln n_2/n_1/(1 - n_2/n_1) + I''$ mentioned by Dünwald and Wagner.[9] If this equation were valid throughout the range of carbon content, the slope of the lines in Fig. 8 and 9 would each be $1/2.3$ instead of 6.0 to 7.0 which reproduces our experimental results.

The product of $\Delta E/2$ and the fraction of carbon atoms paired for a given carbon concentration is approximately the partial molal heat of carbon relative to the infinitely dilute solution. The probability that for a given carbon atom any one of its 12 nearest neighbor sites is occupied by another carbon atom is approximately $12n_2/n_1 e^{-\Delta E/RT}$; this is also equal to the fraction of n_2 carbon atoms which are paired. The energy associated with nearest neighbor pairs per gram atom of carbon is $\left(12\dfrac{n_2}{n_1}e^{-\Delta E/RT}\right)\dfrac{\Delta E}{2}$. If ΔE is 1500 cal. the partial molal heat of dilution of carbon in iron at a concentration of 0.9% carbon is -210 cal. This (divided by 4.575) is an approximation of the value of the second term on the right of equation (7) and is less than the precision of ΔH_2 determined from the slope of the curves of Fig. 5.

Thus the qualitative conclusion is reached that the carbon atoms in austenite may be regarded as exerting a slight repulsive force on each other, so that they enter adjacent interstitial positions only about one third as frequently as would be the case if their distribution were random; the change of distribution with temperature is small.

Heat of Transformation of α- to γ-Iron.—With the aid of equation (18) from the previous section and the Gibbs–Duhem equation, the activity of iron in austenite may be evaluated over the composition and temperature range covered. As shown in Fig. 1, the temperature range of equilibrium between α- and γ-iron in the iron–carbon system extends from 723 to 910°. Hence the heat of transformation of α- to γ-iron may be calculated if the thermodynamic equilibrium constant can be evaluated over this range. This may be done from a knowledge of the equilibrium compositions since the activity of iron is now known as a function of composition. The equilibrium constant for the reaction Fe (α) = Fe (γ) is

$$K_5 = a_\gamma/a_\alpha \qquad (20)$$

where a_γ and a_α represent respectively the activity of iron in austenite relative to its value in pure γ-iron and in ferrite relative to its value in pure α-iron. The heat of transformation is then

$$\Delta H_5 = -Rd \ln K_5/d\left(\frac{1}{T}\right) \qquad (21)$$

The activity in γ-iron, by equation (19) and the Gibbs–Duhem equation, is

$$\ln a_\gamma = -\left(\frac{n_2}{n_1}\right)_\gamma - \left(\frac{13 - 12e^{-\Delta E/RT}}{2}\right)\left(\frac{n_2}{n_1}\right)_\gamma^2 \qquad (22)$$

Since the concentration of carbon in ferrite is always low, the solution may be considered ideal and therefore

$$\ln a_\alpha \cong -(n_2/n_1)_\alpha \qquad (23)$$

From the composition of austenite in equilibrium with ferrite, as given by Mehl and Wells and the corresponding compositions of ferrite from this investigation, values of $\ln a_\gamma$ and $\ln a_\alpha$ were computed, and are given in Table VI.

TABLE VI

EQUILIBRIUM OF α- AND γ-IRON

t, °C.		γ-iron			α-iron		
	% C	n_2/n_1	$-\ln a_\gamma$		% C	$-\ln a_\alpha$	$-\ln K_5$
910	0	0	0		0	0	0
849	0.135	0.0063	0.0064		0.0069	0.0003	0.0061
842	.160	.0075	.0076		.0077	.0004	.0072
809	.280	.0131	.0136		.0117	.0005	.0131
802	.302	.0141	.0148		.0127	.0006	.0142
801	.310	.0145	.0152		.0128	.0006	.0146
770	.458	.0214	.0230		.0170	.0008	.0222
765	.487	.0227	.0245		.0177	.0008	.0237
755	.544	.0254	.0276		.0193	.0009	.0267
752	.579	.0271	.0296		.0198	.0009	.0285
741	.663	.0310	.0343		.0216	.0010	.0332
742	.665	.0312	.0345		.0214	.0010	.0335
723	.80	.0375	.0423		.0250	.0012	.0411

The heat of transformation of α-iron to γ-iron determined from the slope of a plot of log K_5 vs. $1/T$ is given in Table VII, column 2, and column 3 is the heat of transformation as computed by Austin[35] by collation of calorimetric data.

TABLE VII

HEAT OF α. γ-TRANSFORMATION

t, °C.	$\Delta H_5{}^a$	$\Delta H_5{}^b$
905		218
910	215	
850	330	292
800	495	434
750	825	693
723	1000	

a Smith, from equilibrium measurements. b Austin, from calorimetric measurements.

The values at 910° summarized by Cleaves and Thompson[36] range from 160 to 375 cal. Of the values determined by direct measurement at 910° those of Klinkhardt[37] and of Awbery and

(35) J. B. Austin, Ind. Eng. Chem., **24**, 1225 (1932).

(36) "The Metal Iron," McGraw-Hill Book Co., New York, N. Y., 1935.

(37) H. Klinkhardt, Ann. Physik, ser. 4, **84**, 167 (1927).

Griffiths[38] appear to be the best; they give 216 and 218 cal. per gram atom, respectively. The agreement between these directly determined values and that computed from the equilibrium measurements is surprisingly good; the discrepancy (shown by Table VII) at the lower temperatures is felt to be due in large part to the great uncertainty in the heat capacity of the two forms of iron in this region.

The heat of solution of graphite in γ-iron may also be determined with the aid of equation 19 and the relation

$$\Delta H_s = - 4.575 \, d \log a_2/d \, (1/T)$$

where a_2 is activity of carbon in the austenite in equilibrium with graphite and is relative to a standard state such that $a_2 = n_2/n_1$ at infinite dilution. A plot of $\log a_2$ vs. $1/T$ for the experimentally determined values of the solubility of graphite is shown in Fig. 10. The slope of this line corresponds to a heat of solution of 9800 cal. in satisfactory agreement with the value (10,100 cal.) obtained previously by a different method.

Summary

By determination of the carbon content of an iron phase which had been definitely equilibrated with one of a series of gas mixtures, each of constant composition, the following equilibria were measured: CH_4-H_2 mixtures with ferrite at 750 and 800°, with austenite at 800 and 1000°, and with graphite at 800 and 1000°; CO-CO_2 mixtures with austenite at 800, 1000 and 1200°, and with graphite at 800 and 1000°.

The limiting solubility of carbon in ferrite at 750 and 800° was found to be 0.020 and 0.0128 weight per cent., respectively, both of which are lower than the data commonly accepted hitherto. Austenite at its lower limit of stability at 800° contains 0.319 ± 0.004% carbon, in good accord with the results of dilatometric measurements.

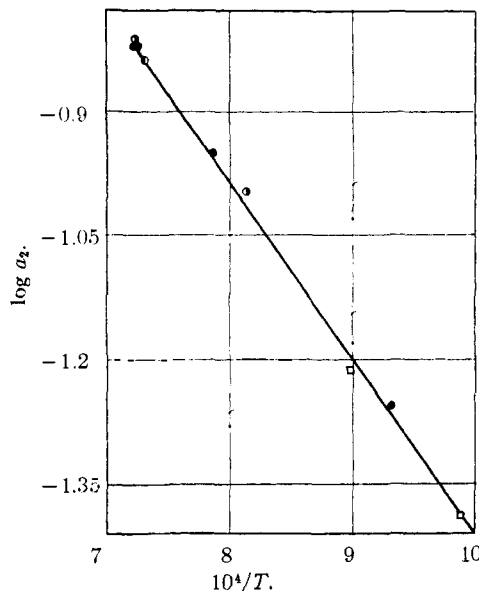(38) J. H. Awbery and E. Griffiths, Proc. Roy. Soc. (London), 174, 1 (1940).

Fig. 10.—Plot of logarithm of activity of carbon in austenite at equilibrium with graphite against $10^4/T$. based on the following solubility measurements: ● Smith, average value of carbon content, determined from plot of austenite equilibria, at which $r_1 = r_1'$ and $r_2 = r_2'$: □ Wells: ◐ Gurry, equilibrium with graphite: ◓ Gurry, equilibrium with carbon from toluene.

The experimental results permitted direct calculation of the activity of carbon in austenite relative to graphite as unity and of the heat of solution of graphite in ferrite and in austenite. There is a slight apparent difference in activity according as it is calculated from the results with one or the other pair of gases; its source is still uncertain.

In the appendix an analytic expression, based on statistical considerations, is developed which reproduces satisfactorily the measurements of activity of carbon in solid solution in γ-iron, austenite, as a function of its concentration.

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The Polarography of Uranium. II. Polarography in Strongly Acid Solution[1]

BY I. M. KOLTHOFF AND W. E. HARRIS

In a previous paper[2] the polarography of hexavalent uranium in 0.01 to 0.2 N hydrochloric acid was discussed. Two reduction waves were obtained, the first one corresponding quantitatively to the reduction of hexavalent uranium to the pentavalent state and the second to the reduction to the trivalent state.

(1) From a thesis submitted by W. E. Harris to the graduate school of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, June, 1944.

(2) W. E. Harris and I. M. Kolthoff, THIS JOURNAL, 67, 1484 (1945).

Herasymenko[3] briefly states that a high concentration of strong acid in the uranyl solution changes the relative magnitudes of the reduction waves obtained. He attributes this to a decomposition of pentavalent uranium into hexavalent and tetravalent uranium, the hexavalent uranium formed being reduced at the dropping electrode. We have made a systematic study of the effect of acidity on the polarographic waves of uranyl uranium. The first diffusion current

(3) P. Herasymenko, Trans. Faraday Soc., 24, 272 (1928).