220. *The Equilibria between Mixtures of Carbon Monoxide and Carbon Dioxide at Various Pressures in Contact with Steels of Different Carbon Concentrations at* 750—1150°.

By Arthur Bramley and Harry Dennis Lord.

It is well known that carbon monoxide has a carburising action when in contact with iron or steel at a sufficiently high temperature, and that the dioxide has the reverse effect. Mixtures of these two gases may act in either way according to circumstances and, for a given set of conditions, a definite equilibrium must exist, which is determined by the following factors : pressure, temperature, composition of the steel. The object of the present investigation was to study the effects of varying each of these factors.

The problem has already received the attention of a number of investigators, notably, among earlier workers, of Baur and Glaessner (*Z. physikal. Chem.*, 1903, **43**, 354) and Matsubara (*Trans. Amer. Inst. Min. Met. Eng.*, 1920—1922, **67**, 3), who were chiefly concerned with the equilibria of gases in contact with solids in which some oxide of iron formed a constituent phase. Schenck and his co-workers (Schenck, Semille, and Falcke, *Ber.*, 1907, **40**, 1704; Schenck, *Z. anorg. Chem.*, 1927, **161**, 287; **164**, 145, 314; **166**, 113; **167**, 253, 315) have carried out an extensive series of researches, in which, in addition to mixtures of carbon monoxide and dioxide, mixtures of hydrogen and methane were used. More recently, the equilibrium between austenite and the oxides of carbon has been studied by Takahashi (*Sci. Rep. Tohôku Imp. Univ.*, 1926, **15**, 159), and Johansson and von Seth (*J. Iron Steel Inst.*, 1926, II, 295) have investigated this problem with special reference to the surface carburisation and decarburisation of steel. In both these investigations certain details of apparatus and experimental method appear to be open to criticism.

When the present investigation was well advanced, a paper by Becker (*ibid.*, 1930, I, 337) appeared bearing on the same subject, but again, apparatus and methods are not free from objection.

Reactions Involved.—The chief reactions with which the present investigation is concerned are the following :

$$2CO \rightleftharpoons C + CO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$Fe_3C \rightleftharpoons 3Fe + C \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Consideration of these equations, all of which represent balanced actions, shows that (*a*) reaction (1) is concerned only with the composition of the gaseous phase, (*b*) reaction (2) determines whether the gas mixture possesses carburising or decarburising properties, (*c*) reaction (3) represents an equilibrium in solid solutions only.

In considering the present problem, reaction (3) is of the utmost importance, and its significance should be clearly understood. Austenite may be regarded as a solid solution of carbon and iron carbide in γ-iron, and for any given set of conditions its constitution is governed by this reaction. Accordingly, the greater the total concentration of carbon, the greater will be the concentration of free carbon in the solution. It may be expected that, since there is an assumed immeasurable but nevertheless definite pressure of carbon vapour present in reaction (1), the composition of the gaseous phase in equilibrium with a steel will be governed by the concentration of free carbon in the steel, as represented by reaction (3). This is only assuming the application of some form of the partition law, an assumption which is shown later to be fully justified.

Previous Investigations.—The composition of the gas in equilibrium with a given steel has hitherto been determined by either dynamic (streaming) or static methods. Both methods were used by Schenck, and from his earlier experiments, in which mixtures of carbon monoxide and dioxide were used, he concluded that oxidation of the steel was unavoidable; later, he substituted mixtures of hydrogen and methane as the gaseous phase. In all cases the weight of iron or steel used was very small, and the composition of the end product does not appear to have been obtained very satisfactorily. It is very doubtful whether Schenck's conclusions regarding the oxidation of the steel by the oxides of carbon were correct (see p. 1667).

A dynamic method was adopted by Takahashi but the scope of this work was rather limited and the results obtained appear to be somewhat uncertain. Johansson and von Seth also used the streaming method. A large quantity of gas of known composition was passed slowly over a small quantity of steel millings in a magnesia boat, heated in a silica tube. After equilibrium had been attained, the concentration of carbon in the steel was determined by analysis. The duration of these experiments was of the order of 6—8 hours, even at temperatures as low as 700°, and, as shown later, this is insufficient to give equilibrium at these temperatures, especially in view of the slow rate of diffusion of carbon and the low concentration gradient. Further, it is almost invariably found that when a steel containing any appreciable quantity of carbon is cooled in an atmosphere of carbon monoxide and dioxide, surface decarburisation takes place. Hence, the analysis of the steel, which can only represent the average composition, may not necessarily be the same as that of a steel which is in equilibrium with the gas used. The presence of nitrogen in the gas mixture also introduces an unnecessary complication.

The static method was used by Becker, who, instead of analysing the gases in equilibrium with the steel, deduced their composition by measuring the total pressure of carbon dioxide and monoxide, and making use of the known dissociation pressures of strontium carbonate at the temperatures concerned, some of this substance being placed in the reaction tube close to the steel. It is doubtful whether this ingenious method is more reliable than a carefully conducted direct gas analysis. This is especially the case when the design of Becker's apparatus is taken into consideration. The temperature control would need to be within close limits: a fall in temperature would lead to absorption of carbon dioxide which, in turn, would intensify error due to dead space. The period of 3 minutes, which Becker allowed for equilibrium to be attained before making his measurements, was certainly far too short, for reasons which have already been mentioned.

In all the experiments carried out by previous investigators, few if any precautions have been taken to limit the variation in the composition of the steels to the carbon only. Steels of the requisite carbon concentration have been used without regard to the amount of other elements present: it is highly probable that some of these had an appreciable effect on the gaseous equilibrium.

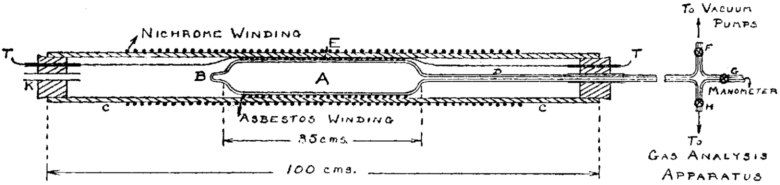
EXPERIMENTAL.

Methods and Apparatus.—It was decided to use a series of steels in which the concentrations of all the elements except carbon were not only constant but very low. To obtain these a very pure Swedish charcoal iron of the following composition was used: C, 0·03; Si, trace; Mn, 0·08; S, 0·010; P, 0·008%. From this, steels of approximately the required carbon concentrations were prepared in the following manner. A bar of the iron (approximately 20 cm. long and 3·5 cm. in diameter) was carburised by gaseous cementation with pure carbon monoxide until a suitable weight of carbon had been introduced. The bar was afterwards reheated in a stationary atmosphere of carbon monoxide until, as a result of diffusion, the concentration of the carbon had become uniform to a depth of at least 4 mm. After removal of a thin skimming of the metal from the bar by turning in a lathe, successive layers of approximately 0·5 mm. thickness were removed in the form of thin spiral turnings and each of these was analysed. The concentration of carbon in the first six layers did not vary by more than 0·01%, and these, after being mixed, constituted the metal used in one series of experiments. Steels of other carbon concentrations were prepared in a similar manner.

After careful consideration, the " static " method was adopted, and, as it was important that the composition of the metal used should not change during a series of experiments, a much larger weight of steel than that generally employed by previous investigators was used. Further, it was necessary to have a considerable volume of gas in the reaction vessel in order that a sufficient quantity could be withdrawn for analysis after equilibrium had been established. The volume analysed was usually about 50 c.c., and even in the experiments at 0·25 atm. it was never less than 15 c.c.

The apparatus used is shown in Fig. 1. The reaction vessel *A* consisted of a 600-c.c. transparent silica bulb approximately 35 cm. long, and of 3·5 cm. internal diameter. Attached to one end was a tube *D*, 50 cm. long, 9 mm. external diameter, and 1 mm. bore; at the other end was a tube *B*, 4 cm. long and 6 mm. internal diameter. The bulb was filled through the open end of *B* with the steel turnings, and was then sealed with the oxy-hydrogen blow-pipe. The bulb *A* was wound from end to end with asbestos string, and placed centrally in a tube furnace *C*. The purpose of the asbestos winding was partly to hold the bulb *A* concentrically in *C*, and partly to act as a heat insulator, and so damp out any slight fluctuations in temperature which might occur in the furnace tube itself. The latter consisted of a large Vitreosil tube, 100 cm. long and 6 cm. internal diameter, wound with nichrome wire and packed with asbestos in a case. The winding and packing were so arranged that the temperature did not vary by more than 2—3° throughout the central 40 cm. of its length. The temperature of the reaction vessel was measured by means of a platinum–platinum-rhodium thermocouple (junction at *E*) and an indicator supplied by the Cambridge Instrument Co.

FIG. 1.



The open end of the capillary *D* was connected to a cross-piece, also of capillary tubing, fitted with three perfectly gas-tight stopcocks. The branch *F* was sealed to a mercury-vapour pump which was followed by a Sprengel pump, and *G* was sealed to a mercury manometer whilst *H* was connected to a water-jacketed gas burette of the type given by Travers ("Study of Gases," Fig. 59, p. 67). This apparatus was used for measuring and introducing the gases into the reaction vessel and for the analysis of the gases withdrawn from the tube after equilibrium had been attained.

The carbon monoxide was prepared by the action of concentrated sulphuric acid on a concentrated solution of formic acid, and a mixture of carbon monoxide and dioxide from pure oxalic acid with concentrated sulphuric acid. These gases were stored in reservoirs over concentrated sulphuric acid. A 40% solution of caustic potash was used to absorb the carbon dioxide, and periodically the carbon monoxide was estimated by absorption with ammoniacal cuprous chloride solution. In no case was any residual gas found after removal of these two oxides.

Each series of experiments was carried out in the following manner. The bulb containing the steel turnings, having been placed in position in the furnace, was evacuated at room temperature until the pressure was reduced to *ca.* 0·0001 mm. The furnace was then heated to about 1100°, and the pumps were kept working until all the dissolved gases had been removed. Stopcock *F* having been closed, a measured volume of gas of known composition was introduced, and the temperature of the furnace adjusted and maintained constant until equilibrium at the required pressure had been attained. If necessary, gas was introduced or taken out in order to adjust the pressure to that required. Equilibrium was regarded as established when the gas pressure had remained constant for about 3 hours. Then, a sample of the gas was withdrawn as rapidly as possible for analysis. The rapidity of the removal of this gas is of great importance, since the lowering in pressure produced within the bulb causes a consequent change in the equilibrium value. When the bulb was being charged with gas the latter was sometimes richer and sometimes poorer in carbon dioxide than the mixture which was found to be in equilibrium with the steel. Thus equilibrium was approached from both sides. The volumes of the two oxides of carbon put into and withdrawn from the reaction vessel were carefully measured and adjusted so as to avoid any variation in the concentration of the carbon in the steel throughout a series of experiments. At the end of each series, analysis of the steel showed no change in the concentration of the carbon, and there was no sign of oxidation.

In the first experiment, it was found that, during the evacuation at the high temperature used, the bulb which had walls of about 1·5 mm. thickness collapsed inside the furnace. Consequently bulbs with thicker walls, *ca.* 4 mm., were used in all subsequent experiments. To reduce further the risk of such collapse, the pressure inside the furnace itself was lowered by evacuation at *K*.

In order to obtain strictly comparable results, in each series of experiments the equilibria were determined at pressures increasing by exactly 0·25 atm. from 0·25 to 2 atm. and at temperatures increasing by 50° intervals between the required limits.

Results.

The percentages of carbon dioxide present in the mixtures of carbon monoxide and dioxide which are in equilibrium with the steels used at the temperatures and pressures indicated are recorded in the following tables.

Carbon Dioxide in Gaseous Phase, %.

Press. (atmos.).	Temperature.							
	750°.	800°.	850°.	900°.	950°.	1000°.	1050°.	1100°.
	Series A.	C = 0·125%; weight of steel in bulb = 103·1 g.						
2·00	—	32·50	29·02	22·27	16·02	11·25	7·85	5·40
1·75	—	29·42	27·78	20·35	13·88	10·11	7·14	4·75
1·50	—	27·99	24·72	18·52	12·75	9·27	5·95	4·28
1·25	—	24·20	22·65	15·94	11·20	7·85	5·18	3·61
1·00	—	21·48	18·59	13·88	9·00	6·10	4·16	2·85
0·75	—	18·26	15·24	11·13	7·18	4·90	3·24	2·27
0·50	—	13·18	11·26	7·60	5·13	3·25	2·28	1·38
0·25	—	7·48	6·59	4·42	2·60	—	—	—
	Series B.	C = 0·210%; weight of steel in bulb = 103·1 g.						
2·00	34·23	33·42	22·32*	16·40	11·32	7·07	5·48	—
1·75	—	30·82	20·22*	14·58	9·93	6·60	4·55	3·16
1·50	—	27·70	18·39*	13·22	8·45	5·48	3·26	2·80
1·25	26·67	25·77	16·20*	10·95	7·69	4·07	2·62	2·12
1·00	23·66	22·99	13·70*	9·27	6·02	3·61	1·88	—
0·75	—	17·95	9·42*	7·27	4·57	2·78	—	—
0·50	—	13·40	8·03*	4·95	2·96	1·69	—	—
0·25	—	8·60	4·51*	2·28	—	—	—	—
	Series C.	C = 0·260%; weight of steel in bulb = 102·3 g.						
2·00	—	29·88	21·16	14·19	9·57	6·23	4·77	—
1·75	—	27·91	19·20	12·80	8·38	5·39	4·15	2·92
1·50	—	25·65	17·42	11·49	7·15	4·32	3·58	2·29
1·25	—	22·70	14·93	9·65	6·06	3·47	2·81	1·96
1·00	—	19·55	12·32	7·90	5·02	2·77	2·25	1·60
0·75	—	16·21	9·65	6·63	3·95	2·28	1·75	—
0·50	—	12·15	6·93	4·68	2·74	1·62	0·99	—
0·25	—	7·14	3·81	2·57	1·69	—	—	—
	Series D.	C = 0·385%; weight of steel in bulb = 154·8 g.						
2·00	—	22·05	15·75	9·60	6·77	4·02	2·54	—
1·75	—	20·58	14·02	8·75	5·72	3·61	2·39	—
1·50	—	18·68	13·00	7·91	4·73	2·87	2·02	—
1·25	—	15·98	10·96	6·89	4·21	2·59	1·81	—
1·00	—	13·52	9·05	5·29	3·42	2·02	1·35	—
0·75	—	11·08	7·14	4·18	2·62	1·38	1·00	—
0·50	—	8·15	5·02	2·64	1·68	1·03	0·65	—
0·25	—	4·30	2·92	1·61	—	—	—	—
	Series E.	C = 0·500%; weight of steel in bulb = 131·0 g.						
2·00	—	20·89	13·37	9·19	5·80	3·42	—	1·54
1·75	—	18·62	11·83	7·95	4·95	2·75	—	1·22
1·50	—	16·78	10·86	6·62	4·28	2·55	—	—
1·25	—	14·80	9·49	5·59	3·47	2·26	—	—
1·00	—	12·95	7·53	4·34	2·74	1·74	—	0·80
0·75	—	10·34	6·01	2·93	2·01	1·30	—	0·59
0·50	—	6·91	4·02	1·80	1·27	0·93	—	—
0·25	—	3·99	2·38	0·89	—	—	—	—

* These experiments were conducted at 860° instead of 850° because the latter is very close to the transition temperature for this steel.

Press. (atmos.).	Temperature.							
	750°.	800°.	850°.	900°.	950°.	1000°.	1050°.	1100°
Series F.	C = 0·795%; weight of steel in bulb = 167·5 g.							
2·00*	26·07	16·03	9·68	5·40	3·36	2·21	—	—
1·75	22·75	13·93	7·91	4·86	3·03	2·09	—	0·87
1·50	21·72	12·29	6·96	4·21	2·43	1·68	—	0·78
1·25†	18·18	10·58	6·57	3·26	1·95	1·19	—	—
1·00	16·33	8·78	5·04	2·72	1·52	0·82	—	0·43
0·75	12·41	6·71	4·00	1·90	1·01	0·83	—	—
0·50	8·83	4·66	2·77	1·37	0·88	0·63	—	—
0·25	5·33	2·55	1·26	—	—	—	—	—
Series G.	C = 1·120%; weight of steel in bulb = 144·7 g.							
2·00	—	11·99	7·40	3·93	2·44	1·59	—	—
1·75	—	10·43	6·26	3·51	1·84	1·43	—	—
1·50	—	8·84	5·50	2·88	1·56	1·00	—	—
1·25	—	8·68	4·49	2·15	1·45	0·91	—	—
1·00	—	6·68	3·47	1·73	1·13	0·72	—	—
0·75	—	5·56	2·36	1·39	0·98	0·43	—	—
0·50	—	3·70	1·72	1·01	—	—	—	—
Series H.	C = 1·550%; weight of steel in bulb = 184·6 g.							
2·00	21·50	11·72	6·24	3·11	1·81	0·96	0·68	—
1·75	20·24	10·41	5·65	2·64	1·64	0·86	0·50	—
1·50	17·92	8·98	4·82	2·21	1·21	0·73	0·54	—
1·25	15·99	7·81	3·79	2·01	1·08	0·79	0·53	—
1·00	13·25	6·60	3·30	1·53	0·77	0·58	0·36	—
0·75	10·98	4·81	2·41	1·02	0·62	0·35	0·25	—
0·50	7·65	3·73	1·32	0·91	0·48	0·27	0·18	—
0·25	4·24	1·88	0·81	0·42	—	—	—	—
Series K.	C = 2·050%‡; weight of steel in bulb = 129·7 g.							
2·00	—	11·70	6·47	3·13	1·98	0·93	—	—
1·75	—	10·50	5·62	2·74	1·37	—	—	—
1·50	—	9·36	4·83	2·13	1·07	0·76	—	—
1·25	—	7·51	3·90	1·78	1·14	0·60	—	—
1·00	—	6·41	3·11	1·48	0·97	0·48	—	—
0·75	—	4·57	2·17	1·37	0·65	—	—	—
0·50	—	3·84	1·58	0·85	0·41	—	—	—
0·25	—	1·90	0·75	0·42	—	—	—	—

* At 1150° and 2 atmos., $CO_2 = 0·56\%$.

† At 1150° and 1·25 atmos., $CO_2 = 0·28\%$.

‡ As it was not possible to prepare a steel of much higher carbon concentration than the one used in Series H by the cementation process, a steel of the following composition was used for this series of experiments : C, 2·05; Si, 0·07; Mn, 0·15; S, 0·02; P, 0·02%.

The results in Series A are represented graphically in Figs. 2 and 3. In Fig. 2, the relationship between the percentage of carbon dioxide and pressure at the temperatures indicated is shown, whilst in Fig. 3 the connexion between per cent. of carbon dioxide and temperature at various pressures is indicated. A similar set of curves is obtained when the results given in Series B are plotted. The experimental figures obtained in Series C—K give curves of the same type as those shown in Figs. 4 and 5, which refer to Series E.

Figs. 6 and 7 represent the results obtained with the highest-carbon steel.

FIG. 2. FIG. 3.

Series A. Carbon = 0·125%.

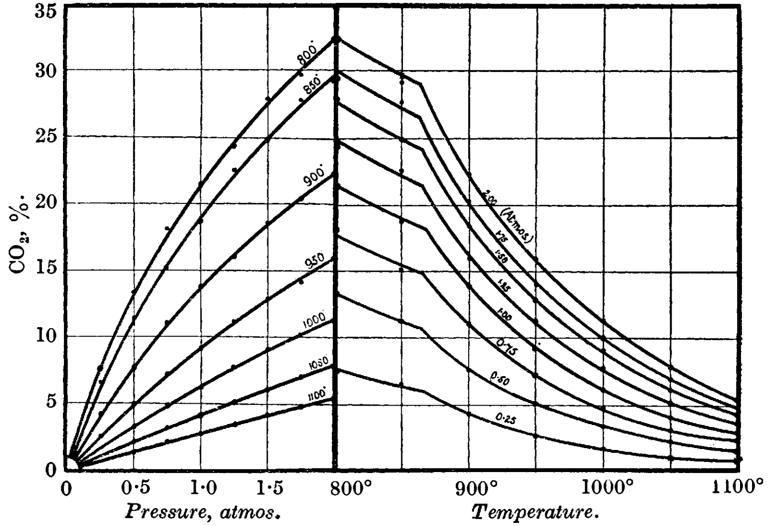
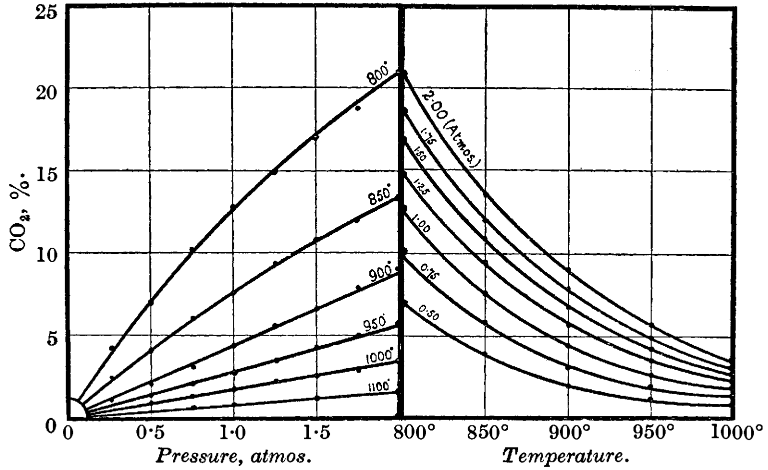


FIG. 4. FIG. 5.

Series E. Carbon = 0·500%.



Only a few results at 750° are recorded in the foregoing tables, owing to the limitations imposed by the time required for equilibrium to be established at this temperature (60—70 hours). Further, on account of the difficulty of accurately analysing gas mixtures containing less than 1% of carbon dioxide, the number of experiments at the higher temperatures was also limited.

FIG. 6. FIG. 7.

Series K. Carbon = 2·050%.

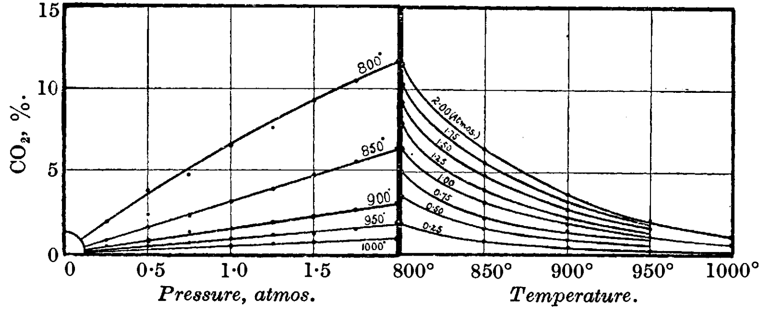
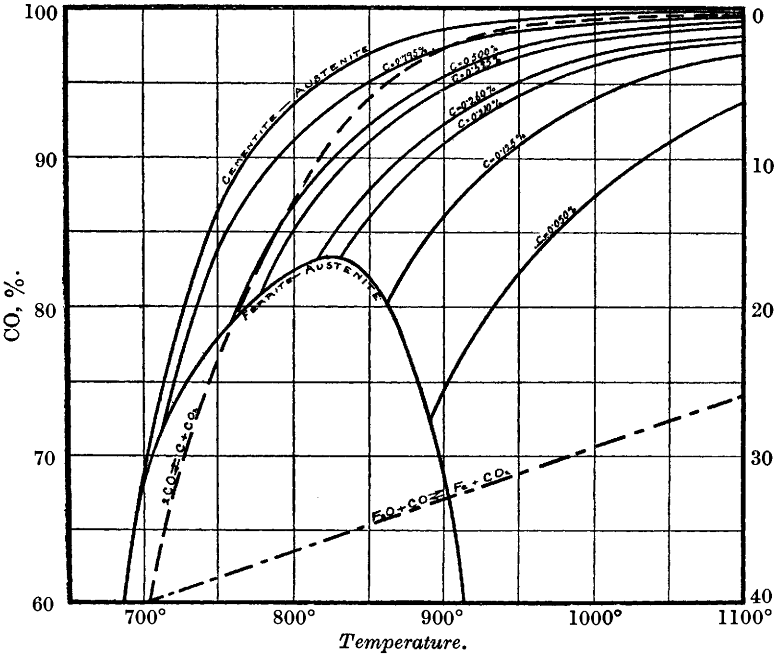


FIG. 8.

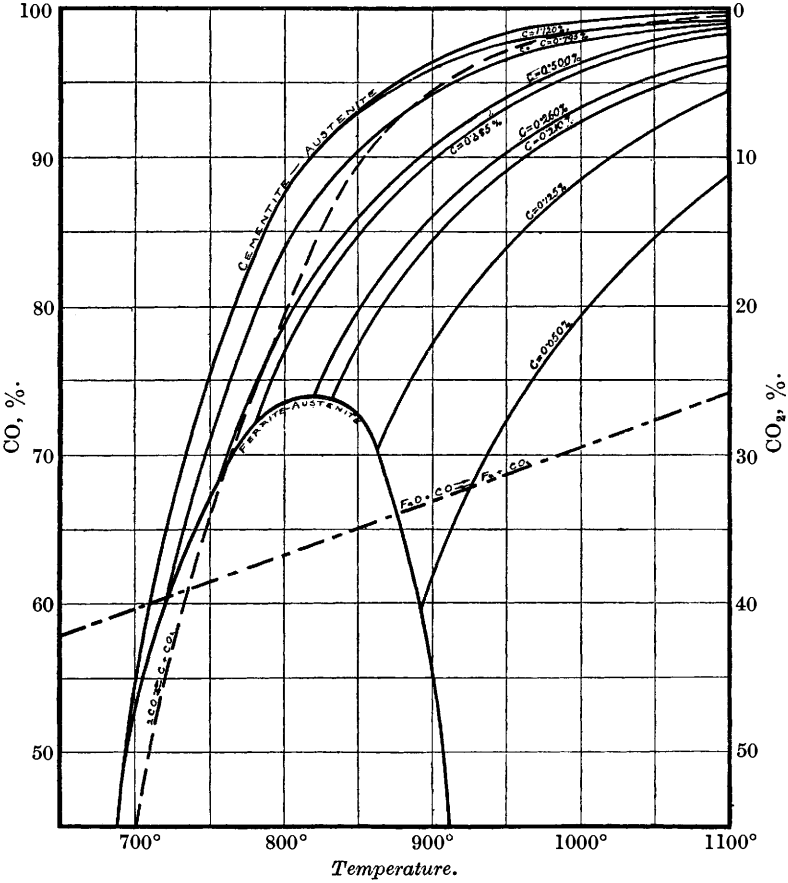


The following table shows the average times taken for equilibrium to be established at the temperatures indicated; throughout the various series of experiments, this time at any one temperature was approximately constant.

Temp. ………	750°	800°	850°	900°	950°	1000°	1050°	1100°	1150°
Time, hrs. …	66	33	22	18	14·5	12	10	8	6

The original Swedish iron was not used because the results obtained from such a set of measurements would probably be of little value for the following reasons: (*a*) On account of the very small weight of carbon actually present in the steel used, a slight variation of this quantity would have a comparatively large effect on the equilibrium value of the gas in contact with it. For example, if at any time during the series of experiments, 10 c.c. of carbon dioxide in excess of the quantity necessary for equilibrium were introduced, this would remove one-sixth of the total quantity of carbon present. (*b*) It is known that steel dissolves an appreciable quantity of carbon monoxide, and if the carbon concentration is very low the effect of this dissolved gas may not be negligible.

FIG. 9.



(*c*) It will be obvious from the position of the iron–iron oxide curve in Figs. 8 and 9 that, for a steel containing 0·03% of carbon at temperatures below 950°, oxidation will take place. (*d*) As will be seen later, the results of such a series of experiments would not add materially to the value of the deductions made from those already obtained.

Discussion of Results.

Equation (1) (p. 1642) represents a balanced action which has been studied extensively by previous investigators, and its equilibrium constant k_1 can be expressed as $k_1 = [CO]^2/[C][CO_2]$. If the partial pressures are represented by p_{CO}, p_{CO_2}, and p_C respectively, and the total pressure is P, then, since p_C is negligibly small compared with the other two, $p_{CO} + p_{CO_2} = P$, and the equilibrium constant can be represented thus :

$$k_1 = \frac{x^2P^2}{[C](1-x)P} = \frac{x^2P}{[C]\,.\,(1-x)} \quad . \quad . \quad . \quad (1a)$$

where x and $(1-x)$ are the fractions of monoxide and dioxide respectively in the equilibrium mixture. For all cases in which solid carbon is present, [C] has a definite value, $[C_1]$, for each temperature irrespective of the total pressure. Hence, for any particular temperature

$$K_1 = k_1[C_1] = x^2P/(1-x) \quad . \quad . \quad . \quad . \quad (1a')$$

In the absence of free carbon in the solid phase, however, [C] is a variable quantity. Since a mixture of carbon monoxide and dioxide carburises or decarburises a given steel according to conditions of temperature and pressure, it follows that the reaction involved is a balanced one which may be represented by equation (2). An examination of the analytical results obtained from this investigation has shown that, for any given steel at constant temperature

$$x^2P/(1-x) = K_2 \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

in which K_2 is a constant. The figures given in Table I, which refer to the experiments made at 800° in Series D, illustrate this point :

TABLE I.

P (atmos.).	x.	$(1-x)$.	K_2.	P (atmos.).	x.	$(1-x)$.	K_2.
2·00	0·7795	0·2205	5·51	1·00	0·8648	0·1352	5·53
1·75	0·7942	0·2058	5·36	0·75	0·8892	0·1108	5·36
1·50	0·8132	0·1868	5·32	0·50	0·9185	0·0815	5·18
1·25	0·8402	0·1598	5·52	0·25	0·9570	0·0430	5·32

All the results obtained have been treated in a similar manner, and in every case a constant of the type represented by K_2 in equation (2*a*) has been found (mean values of these are shown in Table II).

Before considering equation (3), it is necessary to summarise the views concerning the constitution of austenite :

(*a*) Many workers regard austenite as a solid solution of free, atomically dispersed carbon in γ-iron. When an austenitic solution is cooled, for every g.-mol. of iron carbide deposited at the Ar_1 point there are 7000 calories of heat evolved (see p. 1665) in addition to that given out by the iron during its transition from the γ- to the α-state. On the theory stated, this would represent the heat of formation of iron carbide from its elements, *i.e.*, iron carbide would be an exothermic compound, which is certainly not the case.

(*b*) Van 't Hoff's law connecting the lowering of the freezing point of a solvent with the concentration of a solute has been applied by Bramley (private communication) to the depression of the A_3 and A_2 transition temperatures resulting from the addition of carbon to iron. It was shown that, on the assumption that the carbon in austenite is present as iron carbide, the calculated loci of the transition temperatures agree with those found experimentally. On the other hand, the carbon being assumed to be free and atomically dispersed, the calculated loci are considerably higher. The former assumption is therefore more probably correct.

(*c*) If all the carbon in austenite is free, then the separation of cementite from such a solution and under such well-defined conditions as indicated by the A_{cm} line is not easily comprehended. On the other hand, if all the carbon is combined as iron carbide, the separation of graphite according to the graphite solubility line cannot be explained satisfactorily. To assume that cementite is unstable at the temperatures at which graphite is deposited from austenite removes one difficulty only to raise another, for if such were the case, the dissociation of iron carbide into iron and graphite would proceed to completion before equilibrium was established. The recent work of Bramley and Allen (*Eng.*, 1932, **133**, 305) has shown that this is not the case. It thus appears most probable that austenite contains both free carbon and iron carbide, each exerting a certain osmotic pressure, and, for any given temperature between certain limits, each having its own characteristic solubility. Judging from the position of the calculated loci of the transition points A_3 and A_2, it would appear that by far the greater portion of the carbon present is in the form of carbide.

(*d*) The assumption of the presence of both free and combined carbon in austenite affords a simple explanation of the mechanism of the diffusion of carbon into steel during the process of cementation. This solid-diffusion theory has received additional support recently from Day (*Trans. Amer. Soc. Steel Treating*, 1926, **9**, ii, 247) and from Takahashi (*Sci. Rep. Tohôku Imp. Univ.*, 1928, **17**, 761), both of whom were unable to explain their experimental results by the alternative theory of gaseous diffusion.

In accordance with the foregoing views, the carbon in austenite is partly free and atomically dispersed and partly combined as iron carbide, and there exists between the two a balanced action which is represented by equation (3), for which the equilibrium constant may be expressed as $K_3' = [\mathrm{Fe_3C}]/[\mathrm{Fe}]^3[\mathrm{C}_s]$, where $[\mathrm{C}_s]$ represents the concentration of free, atomically dispersed carbon, and the other symbols have their usual significance.

Since the concentration of free iron is very nearly constant, the above equation may be expressed as

$$K_3 = K_3'[\mathrm{Fe}]^3 = [\mathrm{Fe_3C}]/[\mathrm{C}_s] \quad . \quad . \quad . \quad . \quad (3a)$$

Application of Henry's Law.—Since the composition of the mixture of carbon monoxide and dioxide which is in equilibrium with steel at a given temperature and pressure has been found to vary with the percentage of carbon in the steel, it follows that the concentration of carbon in the gaseous phase must be controlled in some way by that of the carbon in the steel.

From equations (1*a*) and (2*a*), which may be expressed as

$$K_2 = k_1[\mathrm{C}_2] = x^2P/(1 - x) \quad . \quad . \quad . \quad . \quad (2a')$$

it follows that the concentration of carbon vapour $[\mathrm{C}_2]$ in the gas which is in equilibrium with a given steel at a certain temperature is fixed and independent of pressure.

If all the carbon in austenite is free and atomically dispersed, we have $[\mathrm{C}_2]/[\mathrm{C}_s] = K_2/k_1[\mathrm{C}_s] = \text{constant}$. If, on the other hand, it is partly free and partly combined as indicated in equation (3), we have, from equations (2*a*′) and (3*a*), $[\mathrm{C}_2]/[\mathrm{C}_s] = (K_2/k_1)/([\mathrm{Fe_3C}]/K_3) = \text{constant}$. Thus, in either case, Henry's law is obeyed.

On the assumption that the whole of the carbon in austenite is combined as iron carbide, it is difficult to conceive how the vapour pressure of carbon in the gaseous equilibrium mixture in contact with it is fixed by such a solution.

The foregoing results have an interesting bearing on the molecular condition of carbon in the vapour state. Since Henry's law is obeyed, it follows that the uncombined carbon in the austenitic solid solution must be in the same molecular condition as that in the gaseous phase. Furthermore, the persistence of this relationship throughout the temperature interval concerned, *i.e.*, 800—

1100°, suggests that there is no change in the molecular complexity of the carbon molecules over this range of temperature. It has been shown by one of the authors (private communication) that there is very good reason for assuming that the free carbon in austenite is monatomic; therefore the conclusion is drawn that the molecules of carbon in the vapour state also contain only one atom under these conditions.

It has been shown by Kohn and Guckel (*Z. Physik*, 1924, **27**, 305) that, at the temperature of the electric arc, carbon vapour is monatomic, and the present investigation indicates that this condition persists down to 800°.

Application of Results to the Iron–Carbon Equilibrium Diagram.

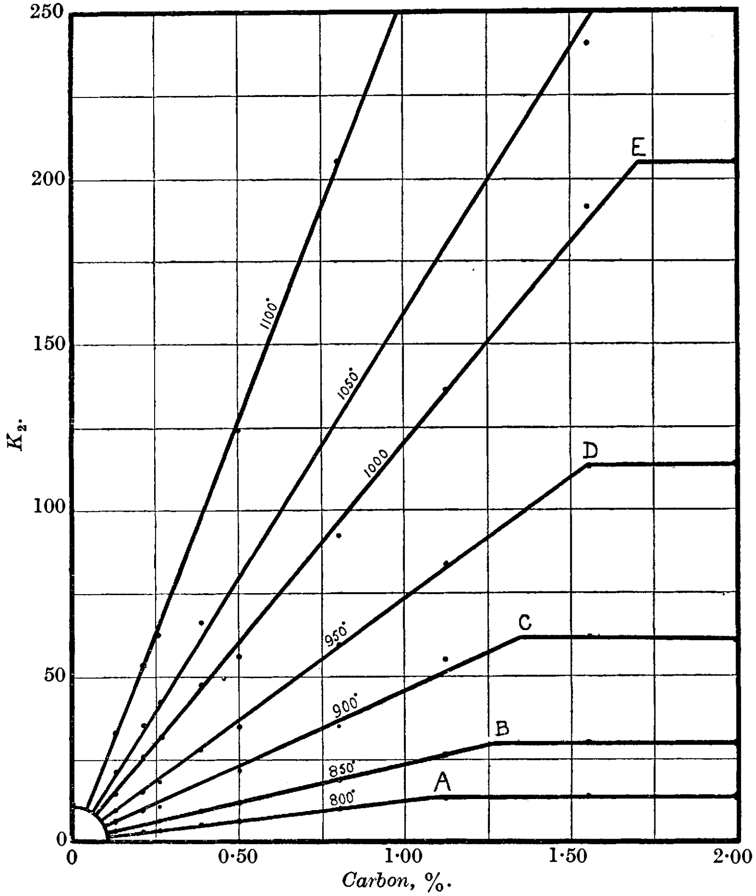
Following the method of previous investigators for purposes of comparison, the results obtained in this investigation at 1 and 2 atmos. pressure have been represented in Figs. 8 and 9 respectively, the curves for a 0·05% carbon steel having been calculated by the aid of results represented in Fig. 10.

According to Johansson and von Seth (*loc. cit.*), the graphite line crosses the ferrite–austenite line at 730° and the cementite–austenite line at about 800°, and above this temperature the proportion of carbon dioxide in equilibrium with graphite is lower than that in equilibrium with cementite. On the other hand, Becker (*loc. cit.*) found that the graphite line crossed the first line at about 720° but did not cross the second line at all. The results of the present investigation (Figs. 8 and 9) show that the graphite line crosses the ferrite–austenite line at 760°, but remains throughout its length on the same side of the cementite–austenite line. This is in accordance with the view that the vapour pressure of carbon above cementite is greater than that above graphite throughout the range of temperature investigated. In the experiments with the 2·05% carbon steel, analysis showed that, contrary to expectation, no precipitation of carbon had taken place. For a total pressure of 1 atm., the proportions of carbon dioxide in the equilibrium mixtures in contact with steels of given carbon concentrations are, according to Becker's measurements, considerably lower than those determined by Johansson and von Seth. The results shown in Fig. 8 are slightly lower than those of Becker. This difference is discussed later.

The results enumerated in cols. 1 and 2 of Table II are represented graphically in Fig. 10, from which it will be seen that, for each temperature there exists a linear relationship between the constant K_2 and the concentration of carbon in the steel up to a certain point, beyond which the value of the constant remains fixed.

It has been shown in equation ($2a'$) that the constant K_2 is directly proportional to $[C_2]$, the concentration of carbon vapour in the gas which is in equilibrium with a given steel. Thus, so far as the inclined portions of the lines in Fig. 10 are concerned, it follows that the concentration of carbon vapour in the gaseous mixture in equilibrium with a steel is directly proportional to the concentration of carbon in the latter. Further, since Henry's law is applicable, the concentration of atomically dispersed carbon in the steel is also proportional to the total concentration of carbon in it.

FIG. 10.



It will be seen from Fig. 10 that at 800° K_2 reaches its maximum value at the point A, when the concentration of carbon in the steel

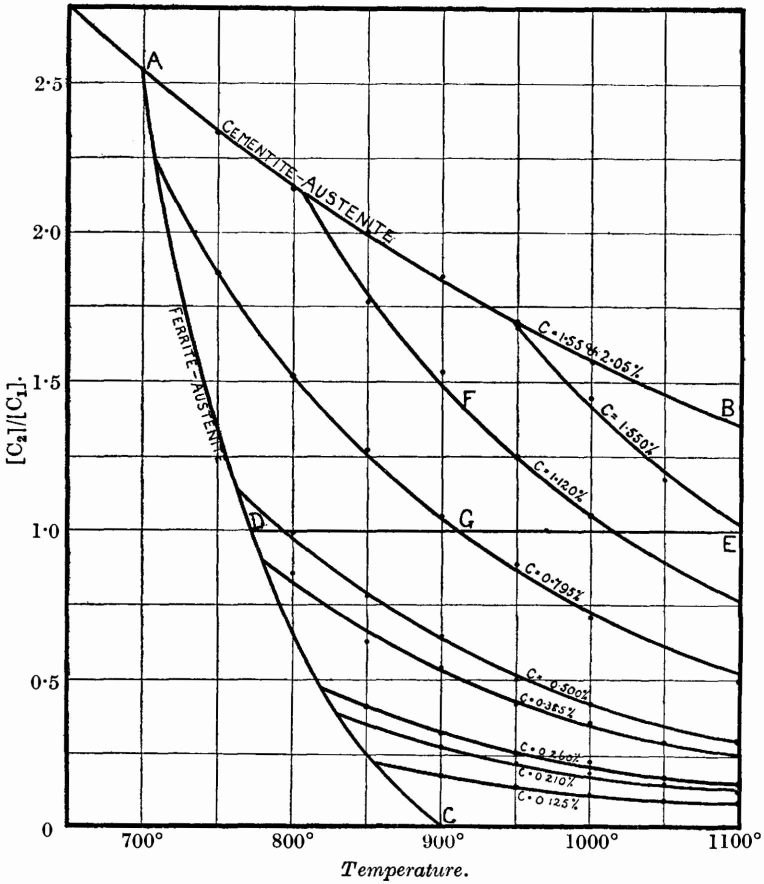
TABLE II.

C, %, in steel.	K_2.	$K_2/K_1=$ $[C_2]/[C_1]$.	K_2/K_1.
Temp., 800°; $K_1 = 6{\cdot}19$.			
0·125	2·86	0·46	
0·210	2·72	0·44	
0·260	3·23	0·52	
0·385	5·38	0·87	0·83
0·500	6·17	1·00	0·98
0·795	9·40	1·52	1·51
1·120	12·85	2·08	2·16
1·550	13·31	2·15	2·16
2·050	13·32	2·15	2·16
Temp., 850°; $K_1 = 14{\cdot}80$.			
0·125	3·41	0·23	
0·210			0·35
0·260	6·08	0·41	0·41
0·385	9·02	0·61	0·66
0·500	11·34	0·77	0·78
0·795	18·11	1·22	1·26
1·120	26·00	1·76	1·79
1·550	29·84	2·01	1·99
2·050	29·83	2·01	1·99
Temp., 900°; $K_1 = 32{\cdot}57$.			
0·125	5·40	0·17	0·17
0·210	8·82	0·27	0·28
0·260	10·13	0·31	0·33
0·385	17·95	0·55	0·54
0·500	20·99	0·65	0·63
0·795	34·61	1·06	1·02
1·120	50·58	1·55	1·50
1·550	61·83	1·90	1·84
2·050	60·98	1·86	1·84
Temp., 950°; $K_1 = 67{\cdot}30$.			
0·125	8·99	0·13	0·13
0·210	14·62	0·22	0·22
0·260	17·10	0·25	0·26
0·385	27·42	0·41	0·43
0·500	33·76	0·50	0·51
0·795	60·12	0·89	0·87
1·120	84·43	1·25	1·25
1·550	113·10	1·68	1·69
2·050	113·90	1·70	1·70
Temp., 1000°; $K_1 = 131{\cdot}0$.			
0·125	14·00	0·11	0·11
0·210	25·66	0·20	0·18
0·260	31·09	0·24	0·21
0·385	47·51	0·36	0·36
0·500	55·34	0·42	0·42
0·795	91·20	0·71	0·73
1·120	136·80	1·05	1·06
1·550	192·35	1·47	1·42
2·050	204·70	1·56	1·57
Temp., 1050°; $K_1 = 242{\cdot}7$.			
0·125	21·63	0·09	0·09
0·210	35·72	0·15	0·15
0·260	40·23	0·17	0·18
0·385	71·71	0·30	0·30
0·500			0·35
0·795			0·61
1·120			0·89
1·550	231·45	1·16	1·20
2·050			1·46
Temp., 1100°; $K_1 = 427{\cdot}0$.			
0·125	32·94	0·08	0·08
0·210	52·96	0·12	0·12
0·260	60·16	0·14	0·15
0·385			0·26
0·500	123·60	0·29	0·30
0·795	204·60	0·48	0·53
1·120			0·77
1·550			1·03
2·050			1·36

is 1·08%. For steels containing a higher concentration of carbon, the value of K_2 does not alter. Thus, the point A represents the saturation value of carbon in austenite which is in equilibrium with cementite; A, therefore, is a point on the A_{cm} line in the iron–carbon equilibrium diagram. In the same way, the points B—E also represent points on the A_{cm} line at the temperatures indicated.

It has been shown in equation ($1a'$) that for a mixture of carbon monoxide and dioxide in equilibrium with graphite, for each temperature there is an equilibrium constant $K_1 = k_1[C_1]$, where $[C_1]$ is the carbon vapour pressure above graphite. Similarly, for a mixture of these gases in equilibrium with a given steel, there is an equilibrium constant for each temperature, which, according to equation ($2a'$), is given by $K_2 = k_1[C_2]$, where $[C_2]$ is the pressure of carbon vapour above the steel. Hence, we have $K_2/K_1 = [C_2]/[C_1]$, *i.e.*, the equilibrium constants of reactions (2) and (1) stand in the same relation to one another as the carbon vapour pressures above steel and graphite respectively at the same temperature. The values of K_1 as deduced by Tigerschiöld (*Jernkontorets Ann.*, 1923, 67), together with the corresponding ratios K_2/K_1, are included in col. 3 of Table II, and in Fig. 11 these have been plotted against temperature for each steel.

FIG. 11.



Below the horizontal line DE through the ordinate 1·0 in Fig. 11, the carbon vapour pressure above steel is less than that in equilibrium with graphite, whilst above this line the opposite is the case. Since the curve AB, which refers to steels containing free cementite, is, throughout its length, considerably above the line DE, it follows that, at any rate between 700° and 1100°, the carbon vapour pressure above cementite is greater than that above graphite. This result is in agreement with the observations of Schenck and of Becker but not with those of Matsubara or of Johansson and von Seth. The line AC represents the lower temperature limits of austenitic solid solutions. At the point A, ferrite, austenite, and cementite are in equilibrium with one another; thus, it corresponds to the eutectoid point S on the iron–carbon equilibrium diagram. The temperature corresponding to the point A in Fig. 11 is 697°, which is in good agreement with the accepted value.

The position of the line DE is of great practical importance in the annealing of steel in the presence of free graphite. If a steel, in a condition represented by any point below this line, is subjected to the action of an atmosphere containing carbon monoxide and dioxide in the presence of free graphite, it will undergo further carburisation; on the other hand, if it is represented by any point above the line DE, it will be partially decarburised in a similar atmosphere. For example, if a steel containing 1·12% of carbon is annealed at 910° in the presence of free graphite, it will pass from the condition represented by the point F in Fig. 11 to that indicated by the point G, *i.e.*, the concentration of carbon (in the surface layers, at any rate) will be reduced to 0·80%.

The figures given in the last column of Table II have been read off the curves in Fig. 11, and have been used to construct the diagram in Fig. 12, in which the relationship between the ratio $[C_2]/[C_1]$ and the concentration of carbon in the various steels is plotted for each temperature. At 800°, the horizontal line NO corresponds to a constant vapour pressure of carbon above the equilibrium mixtures of ferrite and austenite having a composition indicated by the point O. Between the extreme limits of composition of austenite at this temperature, the variation of the vapour pressure of carbon with its concentration in the solid solution is indicated by the straight line OA. For total concentrations of carbon greater than that indicated by point A, free cementite is present, and the horizontal line AP thus represents the constant vapour pressure of carbon above the equilibrium mixture of austenite and cementite. It will be seen that O indicates the position of a point on the A_1 line, and the same applies to the point R. It is of interest that points on the A_1 line can be obtained from Fig. 3 and a corresponding figure for Series B. The two sets of curves intersect at a constant temperature, which, with the corresponding carbon concentration, gives a point on the A_1 line. In Fig. 12, A, B, C, D, E, and F correspond to points on the A_{cm} line at the temperatures indicated.

Johansson and von Seth represented their results in the same way as those in Fig. 12, but their curves fell very much lower than the corresponding curves in this figure. Further, the points of intersection of the inclined and horizontal lines in their diagram would lead to an A_{cm} line in the iron–carbon equilibrium diagram far removed from that generally accepted, *e.g.*, at 1000° their results would fix a point on the A_{cm} line corresponding to 0·75% of carbon. In view of the results obtained in the present investigation and shown in Fig. 12, there appears to be no justification for their assumption that the inclined lines merge gradually into the horizontal ones instead of intersecting them at definite points.

FIG. 12.

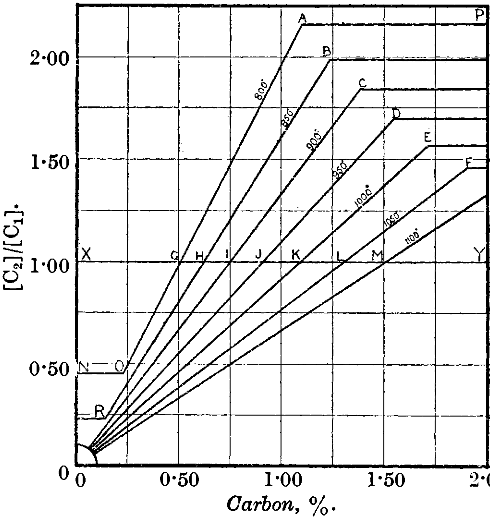
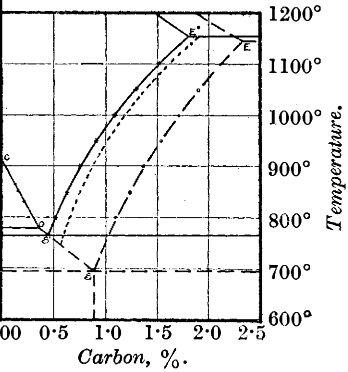


FIG. 13.

Iron–carbon equilibrium diagram.



At 800°, the point G, where the line OA and the horizontal line XY drawn through the ordinate 1·0 intersect, indicates the concentration of carbon in an austenitic solution having the same carbon vapour pressure as that above graphite. Thus the position of G fixes a point on the graphite solubility line in the iron–carbon equilibrium diagram. In the same way, the concentrations of carbon corresponding to H—M fix other points on the graphite solubility line at the temperatures indicated. Table III gives the positions of points on this equilibrium diagram obtained as indicated from Fig. 12 (or, for 830°, from the results of Series B).

TABLE III.

Points on the A_1 line.		Points on the A_{cm} line.		Points on the graphite line.	
Temp.	C, %.	Temp.	C, %.	Temp.	C, %.
800°	0·24	800°	1·09	800°	0·51
830	0·21	850	1·23	850	0·62
850	0·15	900	1·38	900	0·75
865	0·125	950	1·54	950	0·91
		1000	1·72	1000	1·09
		1050	1·90	1050	1·30
				1100	1·51

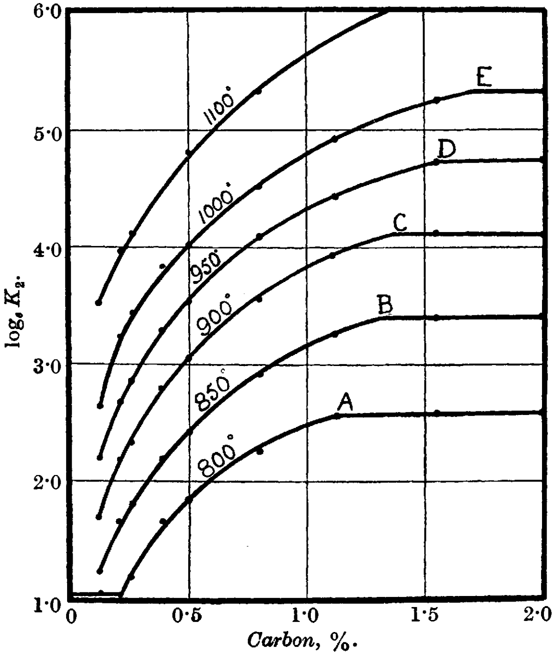
In Fig. 13 the lines GO, OS, and SE are identical with those given by Carpenter and Keeling (*J. Iron Steel Inst.*, 1904, I, 224). The points on the A_1 line enumerated in Table III are indicated by dots, and those on the A_{cm} line by circles : in both cases, the results are in very good agreement with those of the above authors.

The position of the graphite solubility line is indicated by the curve S′E′, which has been plotted from the results given in Table III. In a recent investigation by Bramley and Allen (*loc. cit.*), a carbon solubility line was determined by an entirely different method, and its position is represented by the broken line in Fig. 13; throughout its length, this line lies very close to, but slightly to the right of, the line S′E′.

At first sight, it would appear that the position of this line should be independent of the method of determination, but consideration shows that this is not necessarily the case. When, as a result of annealing, carbon is precipitated from a high-carbon steel or from white cast iron, as in the production of malleable iron castings, it is probably amorphous and is in a very different state from the lenticular flakes of graphite present in grey cast iron. Attention has already been drawn to this by Hatfield ("Cast Iron in the Light of Recent Research," p. 270), who refers to it as annealing carbon. In the work of Bramley and Allen, the equilibrium between austenite and solid carbon was determined by direct precipitation from a high-carbon steel as a result of prolonged heating at different temperatures, and the precipitated carbon appeared to be amorphous. It has been shown by Dent and Cobb (J., 1929, 1903) that the vapour pressure of carbon above graphite is lower than that above any other form of carbon at 800°. It follows, therefore, that the solubility of graphite is lower than that of any other form of carbon at that temperature, and there is no apparent reason why it should be otherwise over the range of temperature covered by this investigation. These considerations indicate that the solubility curve of carbon in equilibrium with graphite lies to the left of that obtained when austenite is in equilibrium with any other form of carbon. Thus the relative positions of the two carbon solubility curves in Fig. 13 are accounted for.

It is noteworthy that Becker's results, represented by him in a figure similar to Figs. 8 and 9, would fix the position of the graphite solubility line very close to the A_{cm} line and considerably to the right of the broken line in Fig. 13. This would indicate that the solubility of graphite is considerably greater than that of amorphous carbon, which is not the case.

FIG. 14.



Becker (*loc. cit.*, Fig. 6) gives a series of curves showing the relationship between log K_3 and the concentrations of carbon in the steels used for various temperatures. For purposes of comparison, our results have been represented similarly in Fig. 14, in which K_2 has the same meaning as Becker's K_3. Each of his graphs, like those given in Fig. 14, consists of two distinct parts, but the curved portion in every case shows a marked inflexion in the curvature near the point of intersection with the straight-line part. In no case in Fig. 14 is there any sign of inflexion in the curvature of the middle portions of the curves. The points A, B, C, D, and E correspond to points on the A_{cm} line, and their positions are in good agreement with the accepted values. It would appear that Becker deduced the positions of similar points from the A_{cm} line, thus necessitating an inflexion of his curves, similar to that described above, in all cases. From the positions of the experimental points alone, as given by Becker, there appears to be no justification for drawing his curves with inflexions : smooth curves without inflexions can be drawn through the points, but these intersect the horizontal lines at points which correspond to concentrations of carbon appreciably greater than those required by the A_{cm} line.

Thermochemical Relationships.

Determination of the Heat of the Reaction $Fe_3C + CO_2 = 3Fe + 2CO$.—It has already been shown that for this reaction there exists an equilibrium constant, $K_2 = [CO]^2/[CO_2]$, the value of which is independent of the pressure; the values of K_2 for various steels and temperatures have been given in Table II. By application of van 't Hoff's isochore, we have, if the heat effect of the reaction remains constant over the range of temperature concerned, $d \log_e K_2/dT = - Q/RT^2$ or

$$\log_e K_2 = Q/RT + I \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where Q is the heat evolved by the reaction and I is an integration constant.

The values of $\log_e K_2$ have been plotted against the reciprocals of the absolute temperatures in Fig. 15 for all the steels used, from which it will be seen that in each case the relationship is linear. It follows, therefore, that equation (4) is obeyed, and the heat effect of the reaction is constant for a given steel within the limits of experimental accuracy, over the range of temperature considered.

It follows from equation (4) that

$$Q = R\,(\log_e K_2' - \log_e K_2'')/(1/T' - 1/T'') \quad . \quad . \quad (5)$$

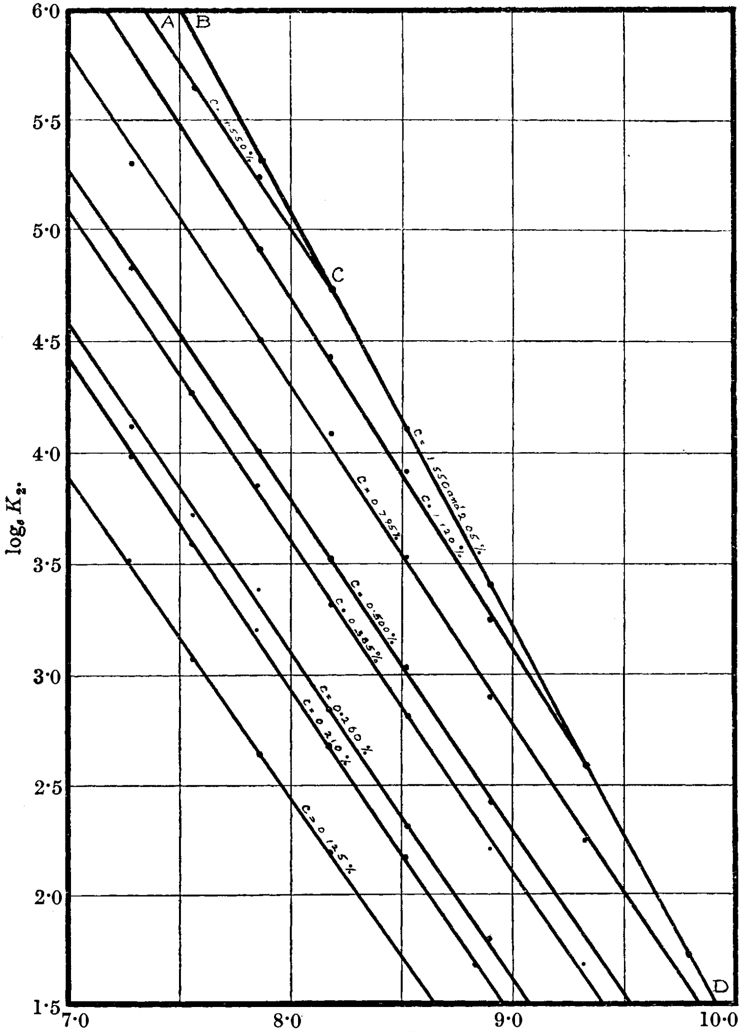
in which K_2' and K_2'' are the equilibrium constants corresponding to the temperatures T' and T'' respectively. The values of Q, together with the corresponding values of I, have been calculated for each steel by the aid of equation (5) and are as follows :

C, %.	Q, cals.	I.	C, %.	Q, cals.	I.
0·125	– 28,820	11·39	0·795	– 30,600	16·61
0·210	– 29,750	14·92	1·120	– 31,390	17·34
0·260	– 29,430	14·95	1·550	– 30,420	17·25
0·385	– 29,610	15·53	1·550 2·050	– 36,950	19·94
0·500	– 29,590	15·70			

The mean of the first 8 values of Q is – 29,950 cals. Two values are given for Q for the 1·550% carbon steel, for the following reason.

Above 950°, this steel is entirely in the austenitic state and the value — 30,420 cals. given above was deduced from the line AC in Fig. 15, which represents the results obtained with the steel in that condition. In the same steel below 950°, free cementite was always present, and its values of $\log_e K_2$ for the lower range of temperature fall on the same straight line BCD as those for the 2·05% carbon steel. The value — 36,950 cals. was deduced from this line.

FIG. 15.



For steels in the austenitic condition, the given values of Q are approximately constant, and taking the mean, we obtain the equation

$$3\mathrm{Fe}(\gamma\text{-}) + 2\mathrm{CO} = \mathrm{Fe_3C}\ (\text{dissolved}) + \mathrm{CO_2} + 29{,}950\ \text{cals.} \quad (6)$$

The iron carbide formed by the action of carbon monoxide on γ-iron dissolves in the excess of the latter with the formation of austenite.

For the case in which free cementite is present, we have

$$3\mathrm{Fe}(\gamma\text{-}) + 2\mathrm{CO} = \mathrm{Fe_3C}\ (\text{precipitated}) + \mathrm{CO_2} + 36{,}950\ \text{cals.} \quad (7)$$

By subtracting equation (6) from (7), we get

$$\mathrm{Fe_3C}\ (\text{dissolved}) = \mathrm{Fe_3C}\ (\text{precipitated}) + 7{,}000\ \text{cals.}$$

Hence, it follows that the heat of solution of iron carbide in austenite is — 7000 cals. per g.-mol. By an entirely different method, a closely agreeing value of — 6200 cals. per g.-mol. was deduced by Bramley (unpublished) for this quantity.

Determination of the Heat of Formation of Iron Carbide.—The direct determination of this quantity involves great experimental difficulties, and its value can only be ascertained by indirect methods. Previous attempts to solve the problem are summarised, together with the results, in Table IV. There is an enormous variation, and the actual value is not yet known with any certainty.

TABLE IV.

Heat of Formation of Iron Carbide.

Q, cals. per g.-mol. of $\mathrm{Fe_3C}$.	Method.	Investigators.
+ 8,494	Calorimetric.	Campbell, *J. Iron Steel Inst.*, 1901, I, 211.
+ 8,940	Equilibria.	Schenck, Semiller, and Falcke, *loc. cit.*
+ 2,270	Calorimetric.	Jermiloff, *J. Russ. Met. Soc.*, 1911, 351.
0	,,	Baykoff, *Metall. Mem.*, 1911, **8**, 315.
— 15,300	,,	Ruff and Gersten, *Ber.*, 1912, **45**, 63; 1913, **46**, 314.
— 13,580	,,	Brodie, Jennings, and Hayes, *Trans. Amer. Soc. Steel Treating*, 1926, **10**, 615.
— 19,162	Equilibria.	Maxwell and Hayes, *J. Amer. Chem. Soc.*, 1926, **48**, 584.
— 15,405	,,	Schenck, *loc. cit.*
— 4,800	Calorimetric.	Watasé, *Sci. Rep. Tohôku Imp. Univ.*, 1926, **17**, 1091.
— 5,400	,,	Roth, *Arch. Eisenhüttenw.*, 1929—30, **3**, 343.

It is possible, from the results of the present investigation, to calculate the heat of formation of iron carbide by two independent methods :

(I) Consider the three free-energy equations :

$$2\mathrm{CO}(g) = \mathrm{C}\ (\text{graphite}) + \mathrm{CO_2}(g)\text{; free-energy change} = \Delta F_1 \quad (8)$$

$$3\mathrm{Fe}(\gamma\text{-}) + 2\mathrm{CO}(g) = \mathrm{Fe_3}(s) + \mathrm{CO_2}(g) \quad ,, \quad ,, \quad = \Delta F_2 \quad (9)$$

$$3\mathrm{Fe}(\gamma\text{-}) + \mathrm{C}\ (\text{graphite}) = \mathrm{Fe_3C}(s) \quad ,, \quad ,, \quad = \Delta F_3 \quad (10)$$

By subtracting equation (8) from equation (9), we have

$$\Delta F_2 - \Delta F_1 = \Delta F_3$$

but (compare equation 2*a*) $\Delta F_2 = RT \log_e K_2$
and (compare equation 1*a*′) $\Delta F_1 = RT \log_e K_1$

Hence $$\Delta F_3 = RT (\log_e K_2 - \log_e K_1) \quad . \quad . \quad . \quad (11)$$

The values of K_2, the equilibrium constant for equation (9), have been ascertained from the results obtained with the 2·05% carbon steel, and the logarithms of these quantities have been read off the corresponding line BCD in Fig. 14. These, together with the values of $\log_e K_1$ deduced from Tigerschiöld's data, are given in Table V. This particular steel was selected because this is the only case in which free cementite is present throughout the whole range of temperature concerned. The values of ΔF_3 have been calculated for each temperature with the aid of equation (11) and the results are included in Table V.

TABLE V.

Temp.	$\text{Log}_e K_1$.	$\text{Log}_e K_2$.	ΔF_3 (cals.).	ΔH (cals.).
800°	1·823	2·61	1678	4639
850	2·695	3·39	1551	4665
900	3·484	4·10	1439	4677
950	4·210	4·74	1288	4651
1000	4·875	5·32	1126	4667

The rate of change of free energy with temperature is approximately constant between 800° and 1000°, and its value is given by

$$d(\Delta F_3)/dT = (1126—1678)/200 = -2·76 \text{ cals. per degree.}$$

The heat effect of reaction (10) may be calculated from the above results by application of the Gibbs-Helmholtz equation

$$d(\Delta F)/dT = (\Delta F - \Delta H)/T \quad . \quad . \quad . \quad . \quad (12)$$

in which ΔF = free-energy change, ΔH = heat absorbed by the reaction, and T = absolute temperature. Hence, by substitution in equation (12), the value of ΔH for the reaction indicated by equation (10) may be calculated :

$$\Delta H_{800^\circ} = 1678 + 2·76 \times 1073 = 4639 \text{ cals.}$$

The values of ΔH for the other temperatures, similarly calculated, are given in the last column in Table V. They are approximately constant, and the mean value for the heat of formation of iron carbide from γ-iron and graphite between 800° and 1000° is — 4660 cals. per g.-mol.

(II) For the action of carbon monoxide on a steel in the austenitic condition, we have, from equation (6)

$$3\text{Fe}(\gamma\text{-}) + 2\text{CO} = \text{Fe}_3\text{C (dissolved)} + \text{CO}_2 + 29{,}950 \text{ cals.} \quad . \ (6a)$$

The heat effect of the reaction $2CO = C + CO_2$ has been deduced from Tigerschiöld's results, which give 41,650 cals. Maxwell and Hayes (*loc. cit.*), from consideration of the results obtained by Rhead and Wheeler (J., 1910, **97**, 2178; 1911, **99**, 1140), concluded that the best value was 41,950 cals. In both cases the heat effect was found to be practically independent of temperature. Taking the mean of these two figures, we have

$$2CO = C + CO_2 + 41{,}800 \text{ cals.} \quad . \quad . \quad . \quad (13)$$

By subtracting equation (13) from (6*a*) we get

$$3Fe(\gamma\text{-}) + C = Fe_3C \text{ (dissolved)} - 11{,}850 \text{ cals.} \quad . \quad . \quad (14)$$

Taking the heat of precipitation of iron carbide from austenite as 7000 cals. per g.-mol. (p. 1665), we have

$$Fe_3C \text{ (dissolved)} = Fe_3C \text{ (precipitated)} + 7000 \text{ cals.} \quad . \quad . \quad (15)$$

On adding equations (14) and (15), we obtain

$$3Fe(\gamma\text{-}) + C = Fe_3C \text{ (precipitated)} - 4850 \text{ cals.}$$

Thus, the results obtained independently for the heat of formation of iron carbide are in excellent agreement. Taking the mean value, we have

$$3Fe(\gamma) + C \text{ (graphite)} = Fe_3C - 4750 \text{ cals.} \quad . \quad . \quad (16)$$

The heat of transition from α- to γ-iron is given by

$$3Fe(\alpha\text{-}) = 3Fe(\gamma\text{-}) - 2200 \text{ cals.} \quad . \quad . \quad . \quad (17)$$

Addition of equations (16) and (17) gives

$$3Fe(\alpha\text{-}) + C \text{ (graphite)} = Fe_3C - 6950 \text{ cals.}$$

This result is not very different from that obtained by Roth (*loc. cit.*) in the most recent calorimetric determination of this quantity.

Schenck (*loc. cit.*), in referring to his earlier determination of this value, which was deduced from a study of the equilibria between carbon monoxide, carbon dioxide, and steel, concluded that it was vitiated by oxidation of the metal. Later, he sought to avoid this complication by studying the equilibria between mixtures of methane, hydrogen, and steel.

The results obtained in the present investigation and represented in Figs. 8 and 9 indicate that, with mixtures of carbon monoxide and dioxide, oxidation can be avoided. The recent work of Wheeler and Wood (*Fuel*, 1930, **9**, 567) has shown that in the presence of steel or silica, methane when heated above 650° gives rise to a variety of products including a number of higher hydrocarbons. These observations would tend to show that the result obtained by Schenck in his later work is also of doubtful value.

Summary.

1. A critical survey of the work carried out by previous investigators has been given.

2. The equilibria between mixtures of carbon monoxide and dioxide and steels, with carbon concentrations ranging from 0·1 to 2·0% at temperatures between 750° and 1150°, have been determined for total pressures of 0·25—2·0 atmos. A static method of establishing equilibrium was used.

3. All the steels, with the exception of that containing 2·0% of carbon, were prepared from the same bar of Swedish charcoal iron by direct gaseous cementation, thus restricting the effects on the equilibria to a variation in the concentration of carbon only.

4. It has been found that the concentration of carbon vapour in the gaseous equilibrium mixture in contact with steel is governed by its concentration in the steel in a way indicating that Henry's law is applicable to this case; also evidence has been obtained which indicates that carbon vapour is monatomic at temperatures in the region of 1000°.

5. It has been shown that the carbon vapour pressure above cementite is greater than that above graphite at all temperatures between 700° and 1100°, thus indicating that, within this range, cementite is metastable with respect to graphite. This inference is in agreement with the conclusions of Schenck and of Becker, but is contrary to those of Matsubara and of Johansson and von Seth.

6. The conditions under which carbon steels will undergo decarburisation when annealed in the presence of graphite have been determined.

7. Points on the A_1 and the A_{cm} lines in the iron–carbon equilibrium diagram have been deduced and are in good agreement with the results obtained by Carpenter and Keeling.

8. The position of the graphite solubility line in this equilibrium diagram has been determined: it lies approximately parallel to the A_{cm} line and slightly to the left of that obtained by Bramley and Allen for amorphous carbon. This is consistent with the fact that graphite is the more stable form of carbon over the range of temperatures concerned.

9. The thermochemical relationships of the reactions involved have been considered, and the following results obtained:

(*a*) $3Fe(\gamma\text{-}) + 2CO = Fe_3C$ (dissolved) $+ CO_2 + 29{,}950$ cals.

(*b*) $3Fe(\gamma\text{-}) + 2CO = Fe_3C$ (precipitated) $+ CO_2 + 36{,}950$ cals.

(*c*) The heat of solution of iron carbide in γ-iron with the formation of austenite is $-$ 7000 cals. per g.-mol.

(*d*) The heat of formation of iron carbide from γ-iron and graphite is given by the equation

$$3\text{Fe}(\gamma\text{-}) + \text{C} = \text{Fe}_3\text{C} - 4750 \text{ cals.}$$

and from α-iron and graphite by the equation

$$3\text{Fe}(\alpha\text{-}) + \text{C} = \text{Fe}_3\text{C} - 6950 \text{ cals.}$$

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