that it is improbable that our $\Delta T = 0$ or 30° would be the unique temperature at which $a = 1$ for mercury atoms. It would be our guess that a determination for mercury with T_w at a higher setting than 30° would likewise give $a \rightarrow 1$ as $\Delta T \rightarrow 0$. Evidence for the independence of "a" on ΔT is the curve for hydrogen of Rowley and Bonhoeffer[9] (partially plotted in Fig. 5). T_f is allowed to go from 109° K. to above 400° K. with the wall at 88° K. for T_f to 200° K., wall at 193° K. for T_f from 200° K. to 300° K., and wall at 273° K. for T_f above 300° K. No breaks occur in the curve between the points where T_w is shifted much nearer to T_f.

It is quite evident that much more experimental work, carefully controlled with respect to filament surface condition, purity of gases, and accuracy of measurement, must be done before knowledge of the quantitative behavior of the accommodation coefficient is satisfactory. The theory of accommodation coefficients on saturated surfaces is no doubt closely tied to adsorption theory and may in some cases involve primarily interaction of gas molecules with like molecules in an adsorbed condition rather than with the surface of the solid itself. This would lead one to suspect that the addition of the "$a\Lambda$" terms of Table I to get the total heat conductivity for mixtures of gases at low pressure would not be permissible unless proved so experimentally. Preferential adsorption of the molecules of one gas could well alter the accommodation coefficients of the other gases. We would hazard the opinion that with further development the study of accommodation coefficients may have considerable potentiality as a means of expanding the present knowledge of the field concerned with adsorption of gases on solids.

Summary

The temperature distributions over an electrically heated filament in vacuum and in gas are discussed and reasons for the desirability of having uniform temperature throughout the length of the filament for accommodation coefficient measurements are pointed out. A tube designed to give this condition is described and accommodation coefficients for eight gases obtained with this tube over a range of temperature are reported and compared with existing values.

COLUMBIA, MO. RECEIVED JANUARY 27, 1943

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

The Solubility of Hydrogen at Low Pressure in Iron, Nickel and Certain Steels at 400 to 600°

BY MARION H. ARMBRUSTER

Although several investigators have measured the solubility of hydrogen at 1 atmosphere pressure in various samples of iron and steel, there is considerable discrepancy between their results, particularly at the lower temperatures, probably because of the small magnitude of the solubility and the lack of consistency of the method used. There was, however, no information on the solubility at low partial pressures, such as are much more likely to be met with in practice, and little on how the solubility in steel is influenced by changes in composition of the steel. Accordingly, the measurements, described in this paper, at a hydrogen pressure ranging from about 0.001 mm. to 1.5 mm., on substantially pure iron and nickel, and on a number of steels at the temperature levels 400, 500, 600° were undertaken; on iron at 600° the pressure range was extended subsequently up to 350 mm. At each temperature, the measured solubility s is accurately represented, within the experimental error, by the linear equation $s/p^{1/2} = \alpha$, p being the pressure of hydrogen; and the values at all three temperatures are reproduced by the linear relation $\log(s/p^{1/2}) = A/T + B$. Extrapolation by means of this expression to a pressure of 1 atmosphere yields values in excellent accord with the mean data of previous investigators, at temperatures up to 900°. The results show that, within the range of pressure and at the three temperature levels investigated, the solubility in a ferritic steel does not differ greatly from that in pure iron; whereas in an austenitic steel the solubility is four or five times as great, and about the same as in pure nickel. There are, however, individual differences, which are quite reproducible, between steels; these seem to be due to differences in content of non-metallic elements, other than carbon, rather than of metallic elements.

Experimental

Apparatus.—Since over the temperature and pressure range covered the amount of hydrogen dissolved in iron is very small, high vacuum technique affords the most sensitive and accurate mode of measurement. The procedure and the method of calculation is identical with that described in a previous paper[1] dealing with adsorption of gases on a mica surface; a weighed sample of the metal, in the form of thin strip, being exposed to a known quantity of hydrogen until the residual pressure remained unchanged; equilibrium was approached from lower as well as from higher pressure, with identical results. The apparatus used for measurements in the pressure range 0.001 to 1.5 mm. is identical with that described previously,[1] except that the Pyrex[2] sorption bulb was replaced by one of vitreous silica, its volume being about 250 cc.

For the pressure range 3 to 350 mm. the apparatus was designed for similar precision considering that the measurement of solubility at higher pressure is dependent on a smaller difference between two large pressure readings. The system for this pressure range differed from that used over the lower range in the following respects: (a) the total volume was reduced from about 1000 to 100 cc., that of the main part of the system being 45.85 cc., of the absorption bulb section 53.61 cc.; (b) mercury U-seals were replaced by stopcocks with oblique bore, and the liquid air traps were eliminated; (c) the pressure was read on a McLeod gage with three bulbs (covering the ranges 2-30, 15-150 and 50-650 mm.) on a linear scale, due correction being made for the pressure-volume changes during the reading. This correction was large when pressure was read with the stopcock connecting gage to absorption bulb closed (as was the case in actual measurement to obviate alteration of the amount dissolved while the gage was being read) because of the relatively smaller volume of the system, an essential feature to cut down dead space; accordingly this correction was checked by reading the same pressure of a larger volume, *i. e.*, with the stopcock open between gage and absorption bulb. The pressure was read with an accuracy of 0.5%, of which 0.1% is uncertainty in reading and the remainder is due to variation in the capillary depression of the mercury column which is less marked than estimated from available data[3,4]; the effect was least erratic when a standard procedure of raising the mercury in the gage with hard tapping and of waiting for its level to recede was followed. The corrections for adsorption of hydrogen on the walls of the system and for diffusion through the wall of the heated silica bulb were determined; both proved to be negligible.

During measurements the temperature of the specimen bulb was observed regularly and held within ±2° of the stated level; the pressure was measured within a precision of 1% over the range 0.001 to 2 mm. and of 0.5% from 3 to 350 mm., corresponding to within 0.04 micromole hydrogen over the lower, and 0.4 over the higher, pressure range. Since the amount dissolved by the metal was derived by difference, the precision of the result is less, the solubility being reproducible within 0.1 and 1 micromole, respectively, over the two pressure ranges.

Procedure.—The metal sample, usually in the form of thin strip, after treatment with alcohol and ether to degrease it, was placed in the bulb and treated, to reduce surface oxide, at 650° for a minimum of twenty-four hours, with carefully purified hydrogen[5] introduced through a tube extending to the bottom of the bulb; it was then sealed up in a hydrogen atmosphere. Subsequent outgassing, at 650° and at a pressure of 10^{-6} mm., was continued, over a period of at least twenty-four hours, until there was no build-up of pressure when the pump was cut off from the system. In the case of the carbonyl iron, this criterion necessitated alternate treatment with hydrogen and outgassing, all at 650°, for a period of three weeks; presumably because, as other experience has indicated, the last trace of carbon monoxide is very difficult to remove from iron.

Some of the steels had to be put through this cycle of alternate treatments a number of times before the solubility measurements were consistent from one run to another. The fact that such pretreatments are necessary if the hydrogen is to be absorbed rapidly, reversibly, and reproducibly illustrates the difficulty of cleaning up the surface, and removing the last traces of adsorbed, possibly also of dissolved and entrapped, gas from a steel. On the other hand, one should not overlook the possibility that these repeated treatments may have reduced impurities such as oxides or sulfides and to that extent have altered the metal below its surface. Incidentally, it may be mentioned that in one case, as the result of an accident, mercury came in contact with a specimen and wetted it, an observation which proves the absence at that time of any barrier film on the steel (apart, however, from a single instance, a "stainless" steel with 13% chromium, discussed later).

After the pretreatment, spectroscopically pure commercial hydrogen was admitted into the system, and the several series of measurements were then made, beginning with the highest temperature; at each temperature, two or three independent sets of measurements, both on rising and on falling pressure, were made. Under these conditions, pressure equilibrium was attained in fifteen minutes. This is in line with expectation; for, on the basis that the diffusion coefficient of hydrogen in iron at 400° is[6] 0.92×10^{-4} sq. cm./sec., the time required for hydrogen at constant pressure to diffuse into a strip 0.34 mm. thick to the extent that the iron as a whole is 99.9% saturated, is about ten seconds.[7]

Correction of Measured Pressure for Thermal Transpiration.—Since the amount of hydrogen dissolved is a function of its pressure (p) at temperature in the absorp-

---

(1) Armbruster and Austin, This Journal, **60**, 467 (1938); **61**, 1117 (1939).

(2) Apparently even at 400° there is some slight attack on Pyrex by hydrogen, the degree of attack depending upon the pressure; the results of the solubility determinations made in Pyrex were therefore slightly higher than those in the silica bulb.

(3) W. Carwood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 514 (1934).

(4) Glazebrook, "Dictionary of Applied Physics," Vol. III, p. 159.

(5) Tank hydrogen had been passed through the train sulfuric acid, calcium chloride, hot platinized asbestos, activated alumina, phosphorus pentoxide to remove traces of water and oxygen.

(6) This value for the diffusivity is obtained from the rate of diffusion determined by Smithells and Ransley, *Proc. Roy. Soc.* (London), **150**, 187 (1935), and the solubility measurements of Sieverts, *Z. physik. Chem.*, **75**, 598 (1911); **A183**, 19 (1938).

(7) As calculated from the expression given by Johnston and Andrews, This Journal, **46**, 640 (1924).

TABLE I

SOLUBILITY OF HYDROGEN IN IRON AT 600°

A. Lower pressure range: wt. of iron = 517 g.; v_i = 521.8 cc.; V = 956.6 cc.; $\Sigma v/RT$ = 57.03 micromoles/mm.

Pressure of hydrogen, mm.			Amount of hydrogen (micromoles)		Solubility s (micromoles/100 g.)		
Measured,			total	residual	observed	calculated	
p_i	p[a]	$p^{1/2}$	$n_i = p_i v_i/RT_i$	n[b]	s	$s_c = 1.93p^{1/2}$	$\Delta = s - s_c$
0.0305	0.0038	0.062	0.87	0.20	0.13	0.12	+0.01
.0502	.0088	.093	1.43	0.55	.17	.18	− .01
.164	.0455	.215	4.68	2.59	.41	.41	.00
.328	.110	.332	9.36	6.27	.60	.64	− .04
.485	.177	.420	13.84	10.09	.73	.81	− .08
.548	.199	.446	15.64	11.35	.83	.86	− .03
.985	.387	.621	28.11	22.07	1.17	1.20	− .03
1.730	.720	.849	49.37	41.06	1.61	1.64	− .03
2.604	1.120	1.057	74.32	63.87	2.02	2.04	− .02
3.180	1.390	1.179	90.76	79.27	2.22	2.27	− .05
B. Higher pressure range: wt. of iron = 449 g.; v_i = 45.85 cc.; V = 99.46 cc.; $\Sigma v/RT$ = 4.13 micromoles/mm.							
18.88	6.30	2.51	0.0466×10^3	0.0260×10^3	4.6	4.8	− 0.2
22.53	7.54	2.75	.0556	.0311	5.5	5.3	+ .2
27.32	9.80	3.13	.0674	.0405	6.0	6.0	.0
29.66	11.05	3.32	.0731	.0456	6.1	6.4	− .3
35.74	13.56	3.68	.0881	.0560	7.1	7.1	.0
60.38	25.27	5.00	.1489	.1044	9.9	9.7	+ .2
75.66	32.62	5.72	.1866	.1347	11.6	11.0	+ .6
80.40	34.97	5.92	.1983	.1444	12.0	11.4	+ .6
123.95	58.23	7.63	.3057	.2405	14.5	14.7	− .2
140.4	66.47	8.15	.3462	.2745	16.0	15.7	+ .3
144.35	68.61	8.28	.3560	.2834	16.2	16.0	+ .2
149.8	70.97	8.42	.3694	.2931	17.0	16.3	+ .7
260.4	131.4	11.46	.6421	.5427	22.1	22.1	.0
296.1	150.1	12.25	.7302	.6199	24.6	23.6	+ 1.0
298.1	151.65	12.31	.7351	.6263	24.2	23.8	+ 0.4
338.6	175.25	13.24	.8351	.7238	24.8	25.6	− .8
438.35	228.4	15.12	1.081	.9433	30.7	29.2	+ 1.5
621.0	331.2	18.20	1.531	1.368	36.3	35.1	+ 1.2
624.0	334.5	18.29	1.539	1.382	35.0	35.3	− 0.3
629.0	335.5	18.37	1.551	1.386	36.7	35.5	+ 1.2

[a] Above 0.08 mm., p (pressure in absorption bulb) = p_f observed; below 0.08 mm., p is p_f corrected for thermal transpiration effect. [b] $n = p_f \Sigma v/RT$, in which the quantity, $\Sigma v/RT$, is a constant except below 0.08 mm. where it varies with p_f, as determined by separate experiment,[1] on account of thermal transpiration.

tion bulb, the final pressure (p_f) observed on the gage, at room temperature, at equilibrium within the system has to be corrected for thermal transpiration at pressures less than 0.08 mm., above which limit the correction was negligible. It was determined, as described in the papers cited,[1] from a blank experiment with hydrogen in absence of the metal sample, and the known temperatures and volumes of the several parts of the system.

Calculation of the Amount Dissolved

The mass of hydrogen absorbed is the difference between the total number of micromoles[8] (n_i) of hydrogen introduced into the system and the residual number (n) in the gas phase at equilibrium with the metal. The former (n_i) was derived from the measured pressure (p_i) of the hydrogen initially introduced into a part of the system of accurately known volume (v_i) at room temperature (T_i); that is, $n_i = p_i v_i/RT_i$. The residual amount (n) was calculated from the observed final pressure (p_f) at equilibrium in the system of volume V (its total volume, as measured at room temperature, less that of the sample) taking into account the effect of (1) thermal transpiration, where necessary, (2) the actual temperature distribution in the system upon the effective volume (or pressure) of the gas phase at equilibrium throughout the system. This temperature distribution depends not only on the temperature differences in the system (bulb 400 to 600°, trap −183° in low-pressure system only, remainder at 20 and 25° in low- and high-pressure systems, respectively) but differs according as the heat-conducting sample is or is not present. Accordingly calculation based on a blank experiment,

---

[8] This unit of mass (one millionth mole or 2×10^{-6} g.) is used thoughout, as the most appropriate; on this basis, with pressure in millimeters and volume in milliliters, the gas constant R has the value 0.0624.

either allowing for the volume of the specimen or replacing the specimen by a closed silica tube of like volume, leads to incorrect results; this is more readily discussed by reference to the results of the several measurements, on iron, at 600°, as presented in detail in Table I for the pressure range (A) 0.004 to 1.4 mm., (B) 6 to 335 mm.

In this table the first column is the initial measured pressure (p_i) of hydrogen in volume (v_i). The second column lists p, the observed final pressure (p_f) corrected where necessary for thermal transpiration; the third is $p^{1/2}$. The fourth and fifth columns list, respectively, n_i the total, and n the residual number of micromoles of hydrogen; n was calculated from the expression $p_f \Sigma v/RT$, the significance of which will be discussed immediately. In the sixth and seventh columns are the values of the observed solubility (s) and of s_c, as calculated from the equations $s_c = 1.93\, p^{1/2}$. The last column shows, by means of the differences $s - s_c$, which are in no case greater than the estimated precision of the measurements, how closely the whole series of observations at 600° are in accord with this simple linear relation.

Determination of n in a System with Temperature Gradients.—When n was calculated in the usual way from the measured pressure p_f and the total volume (V) of the system at room temperature throughout, in combination with the results of a blank experiment which was identical except that the iron sample was absent, and was designed to compensate for the effects of thermal transpiration and of temperature differences upon p_f, a plot of the solubility so derived against $p^{1/2}$ proved to curve upward slightly (A, Fig. 1). On the other hand, when the blank experiment was identical except for the presence in the specimen bulb of a closed silica tube of the same volume as the specimen, and this result was made use of to calculate n, the plot curved slightly downward (B, Fig. 1).

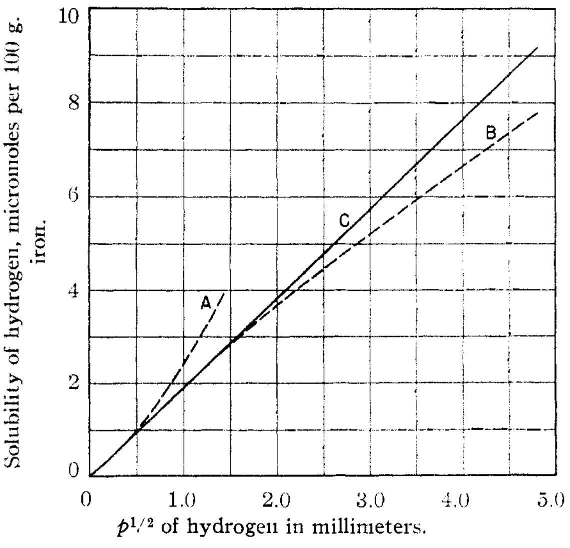

Fig. 1.—Dependence of calculated solubility of hydrogen in iron at 600° on the method of determining effective volume of gas phase: curve A, using hydrogen blank without sample and correcting for its volume (low pressure system); curve B, using hydrogen blank replacing sample with closed silica tube of same volume (higher pressure system); curve C, using argon blank in presence of sample or using intercept of data plotted in terms of n_i/p against $1/p^{1/2}$.

This lack of concordance led to the deduction that there is a difference in temperature distribution in the bulb according as the metal specimen is or is not there; and this proved to be so. For calculation based on a third type of blank, identical with the solubility determinations except that hydrogen was now replaced by argon, which dissolves only to a negligible extent in iron at this temperature, then yielded a straight line (C, Fig. 1). Attention is specifically called to this difference of temperature distribution depending upon whether a conducting specimen is present or absent; it seems to have been left out of account in determinations of similar equilibria, and its neglect may in other cases have exerted an appreciable influence upon the final result desired, particularly where this is measured as a difference between two relatively large quantities of a gas phase. Thus a *proper* blank experiment leads to a correct determination of the amount of residual hydrogen, and hence to a solubility which bears the expected linear relation to $p^{1/2}$ within the precision of the measurements themselves.

The fact of this linear relation between s and $p^{1/2}$, when n is calculated properly, combined with the very reasonable assumption that the temperature distribution remains unaltered throughout the measurements in a given apparatus at any one temperature level, offers a means of deriving n directly from the measurements themselves, thus obviating the necessity of making a proper blank experiment in each case. For, under the foregoing assumption, $n = \Sigma pv/RT$ where v is the element of volume of each part of the system at its actual temperature T. Now s is, by definition, proportional to $n_i - n$, that is to $n_i - \Sigma pv/RT$; but it is also, by measurement, proportional to $p^{1/2}$.

By combining these two relations, and rearranging, we have

$$\frac{n_i}{p} = \frac{\alpha}{p^{1/2}} + \Sigma \frac{v}{RT} \qquad (1)$$

which, if the premises are valid, is a linear relation between the measured variables (n_i/p) and $(1/p^{1/2})$, with slope α and intercept $\Sigma v/RT$. When each series of measurements in Table I was plotted in this way, as shown in Fig. 2, the resulting graph was in each case linear over the whole pressure range, within the expected precision of the measurements; and the value of $\Sigma v/RT$ so derived (for example, 4.14 micromoles per mm. in upper section, Fig. 2), agrees excellently with that (4.12) based on the blank experiment with argon in the same apparatus at the same temperature. Thus this mode of calculation leads to a result identical with that determined from a proper blank experiment.

This relation therefore can be used to determine n $(= p\Sigma v/RT)$ the number of micromoles of hydrogen in the gas phase at equilibrium[9] from the measured values of n_i and p; though indeed its value is now not explicitly needed because the slope of the line so drawn is the same as that of the solubility line $s = \alpha p^{1/2}$ which, by definition, passes through the point $s = 0$. Accordingly, instead of troubling to make a proper blank in each case, all series of measurements on each metal specimen were treated in this way, with the results presented in the several tables. It may be thought that the resulting linearity of solubility with the square root of pressure is a necessary consequence of its assumption in deriving the linearity of (n_i/p) with $(1/p^{1/2})$; the experimental justification for so doing is that the measurements, when interpreted by means of the argon blank, do in fact validate it. This linearity however does not preclude the possibility of the solubility following a quadratic relation of the type $s = \alpha p^{1/2} + \beta p$; if this were so, the plot of s against $p^{1/2}$ would deviate markedly from a straight line at high pressure but not at low, a departure not observed and hardly to be anticipated since the law is usually regarded as holding accurately at high, but possibly not at low, pressure. The linear relation observed between n_i/p and $1/p^{1/2}$ definitely indicates that the law is followed down to the lowest pressures, except for the possibility of error in the correction for thermal transpiration.

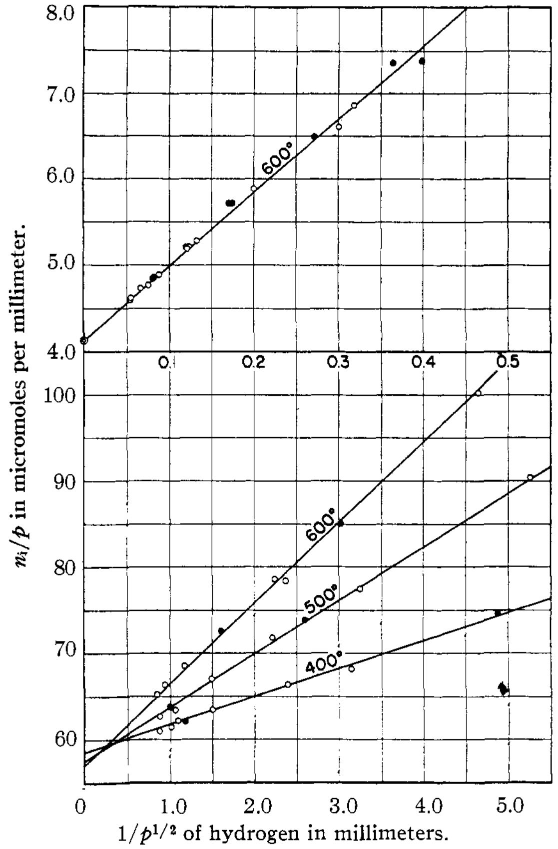

Fig. 2.—Plot of data in form of n_i/p against $1/p^{1/2}$ for iron: upper section at 600°, higher pressure range; and lower section at 600, 500, 400°, lower pressure range. Open and closed circles designate measurements with increasing and decreasing pressure, respectively; double circle is value of intercept as determined by a blank measurement with argon.

Solubility of Hydrogen in Pure Iron (initially carbonyl iron).—The specimen of iron was cut from a strip 0.34 mm. thick of carbonyl iron, containing initially about 0.01% carbon, and weighed 516 g. in all measurements in the lower pressure range, and 448.7 g. in the higher range. The ratio of volume to geometric area was 65 cm. The results at 600° have been presented in Table I; those at 500 and 400° are given in Table II, which is completely analogous to Table I and includes all necessary details.

The data at all three temperatures are closely reproduced by the single equation

$$\log (s/p^{1/2}) = -1454/T + 1.946 \qquad (2)$$

where s is solubility in micromoles per 100 g. of metal, p is pressure in millimeters, and T is absolute temperature, as is evident from the following comparison

---

[9] It should be noted that below 0.08 mm. thermal transpiration being appreciable $n(= p_f\Sigma v/RT)$, in which the quantity $\Sigma v/RT$ varies with p_f as determined by separate experiment.[1]

TABLE II

SOLUBILITY OF HYDROGEN AT LOW PRESSURE IN IRON AT 500 AND 400°

A. 500°: $s_c = 1.16\ p^{1/2}$; $\Sigma v/RT$ = 57.56 micromoles/mm.; other constants same as in Table IA.

Pressure of hydrogen, mm. Measured, p_i	p	$p^{1/2}$	Amount of hydrogen (micromoles) total $n_i = p_i v_i/RT_i$	residual n	Solubility s (micromoles/100 g.) observed s	calculated s_c	$\Delta = s - s_c$
0.0215	0.0039	0.062	0.61	0.14	0.09	0.07	+0.02
.114	.036	.190	3.25	2.01	.24	.22	+ .02
.258	.095	.308	7.36	5.47	.36	.36	.00
.382	.148	.384	10.90	8.52	.46	.45	+ .01
.512	.203	.450	14.61	11.68	.57	.52	+ .05
1.018	.433	.658	29.05	24.92	.80	.76	+ .04
1.958	.881	.939	55.88	50.71	1.00	1.09	− .09
2.218	.992	.996	63.30	57.10	1.20	1.16	+ .04
2.832	1.290	1.136	80.83	74.24	1.27	1.32	− .05

B. 400°: $s_c = 0.60\ p^{1/2}$; $\Sigma v/RT$ = 58.60 micromoles/mm.; other constants same as in Table IA.

p_i	p	$p^{1/2}$	n_i	n	s	s_c	$\Delta = s - s_c$
0.022_5	0.0065	0.081	0.64	0.33	0.06	0.05	+0.01
.110	.0422	.205	3.14	2.47	.13	.12	+ .01
.241	.101	.317	6.88	5.92	.19	.19	.00
.402	.173	.416	11.47	10.14	.26	.25	+ .01
.978	.440	.663	27.91	25.78	.41	.40	+ .01
1.555	.715	.846	44.38	41.90	.48	.51	− .03
1.805	.828	.910	51.51	48.52	.58	.55	+ .03
2.089	.970	.985	59.62	56.84	.54	.59	− .05
2.778	1.300	1.140	79.28	76.18	.60	.68	− .08

t	T	$s/p^{1/2}$ from Tables 1, 11	Equation 2
400	673	0.60	0.61
500	773	1.16	1.16
600	873	1.93	1.91

Thus this single equation expresses all the data within the precision of the measurements, and it may, therefore, be used to calculate the solubility of hydrogen at any pressure in iron at any temperature within and near the range covered.

TABLE III

COMPARISON OF MEASUREMENTS OF THE SOLUBILITY OF HYDROGEN AT 1 ATM. IN IRON AT 300 TO 900°

Form of sample	Solubility s (micromoles/100 g.) 300°	400°	500°	600°	700°	800°	900°	ΔH (cal./g. mole)	Investigator
Carbonyl iron sheet 0.34 mm.	7.06	16.8	32.0	52.6	78.0	107	140	13,300	Armbruster[10]
Wire 2 mm.	. . .	15.2	29.4	50.4	73.4	96.8	138	13,900	Pihlstrand[11]
Wire 0.3 mm. and powder	. . .	15.6	26.8	53.5	80.3	106	134	13,700	Sieverts & Zapf-Moritz[12]
Chips	4.4	8.9	29.0	51.3	78.0	105	129	13,800	Luckemeyer-Hasse & Schenck[13]
Sheet 0.3 mm.	. . .	8.0	26.3	53.1	78.1	103	125	12,300	Martin[14]
Tubing, 6.2 mm. wall	18.5	29.9	44.6	59.8	80.3	110	138	11,300	Andrew, *et al.*[15]
Electrolytic (sheet)	. . .	27.6	51.3	81.2	113.0	169	223	13,500	Baukloh & Müller[16]
Electrolytic (block)	. . .	11.2	33.4	57.1	91.0	125	163	14,500	Baukloh & Müller[16]
Reduced iron	. . .	13.4	44.6	78.0	110.0	145	195	13,000	Baukloh & Müller[16]
Electrolytic iron	. . .	. .	22.3	44.6	71.4	96.8	125	14,400	Iwasé & Fukusima[17]
Reduced iron	. . .	8.9	31.2	62.4	84.7	114	143	11,400	Iwasé & Fukusima[17]

A number of other investigators have measured this solubility, all by the so-called isobaric method at a pressure of about 1 atm. though over a wide range of temperature; but they give so little information on experimental details or on what corrections, if any, they applied, that it is difficult to assess their accuracy. Values at 1 atm. pressure for round values of temperature, interpolated from plots, in terms of log s against $1/T$, of the data of other investigators are brought together in Table III with corresponding extrapolated values computed from our data by means of equation (2). Although a considerable spread is apparent at the

---

(10) Extrapolated by equation (2) from data at 0.004 to 350 mm. and 400–600°.

(11) Pihlstrand and Jernkontorets, *Ann.*, **121**, 219 (1937).

(12) Sieverts, *Z. physik. Chem.*, **75**, 598 (1918); Sieverts and Zapf-Moritz, *ibid.*, **A183**, 19 (1938).

(13) Luckemeyer-Hasse and Schenck, *Arch. Eisenhüttenw.*, **6**, 210 (1932).

(14) Martin, *ibid.*, **3**, 411 (1929).

(15) Andrew, Lee and Quarrell, *J. Iron Steel Inst.*, (1942).

(16) Baukloh and Müller, *Arch. Eisenhüttenw.*, **11**, 513 (1937–8).

(17) Iwasé and Fukusima, *Science Reports Tôhoku Imp. Univ.*, **27**, 162 (1938).

TABLE IV

SOLUBILITY OF HYDROGEN AT LOW PRESSURE IN NICKEL AT 600, 500 AND 400°

A. 600°: $s_c = 9.83\ p^{1/2}$; wt. of nickel = 378 g.; v_l = 484.9 cc.; V = 939.4 cc.; $\Sigma v/RT$ = 54.00 micromoles/mm.

Pressure of hydrogen, mm. Measured, p_i	p	$p^{1/2}$	Amount of hydrogen (micromoles) total $n_i = p_i v_i/RT_i$	residual n	Solubility s (micromoles/100 g.) observed s	calculated s_c	$\Delta = s - s_c$
0.0895	0.0035	0.059	2.37	0.10	0.60	0.58	+0.02
.273	.0254	.159	7.24	1.08	1.63	1.56	+ .07
.6275	.0978	.313	16.64	5.28	3.00	3.08	− .08
1.218	.251	.501	32.30	13.55	4.96	4.93	+ .03
2.390	.631	.795	63.38	34.07	7.75	7.82	− .07
3.526	1.032	1.016	93.51	55.73	9.99	9.99	.00
4.120	1.251	1.118	109.26	67.55	11.03	10.99	+ .04
5.552	1.800	1.342	147.24	97.20	13.24	13.19	+ .05
B. 500°: $s_c = 7.94\ p^{1/2}$; $\Sigma v/RT$ = 55.39; other constants same as in Table IV A.							
0.043	0.0013	0.036	1.14	0.10	0.28	0.29	−0.01
.175	.0161	.127	4.64	0.68	1.05	1.01	+ .04
.343	.0477	.218	9.10	2.54	1.74	1.72	+ .02
.686	.134	.367	18.19	7.42	2.85	2.90	− .05
1.578	.407	.638	41.85	22.54	5.11	5.04	+ .07
3.091	.958	.979	81.97	53.06	7.65	7.73	− .08
4.135	1.349	1.162	109.66	74.72	9.24	9.18	+ .06
C. 400°: $s_c = 5.93\ p^{1/2}$; $\Sigma v/RT$ = 57.03; other constants same as in Table IV A.							
0.0245	0.00076	0.028	0.65	0.04	0.16	0.17	−0.01
.109	.0105	.102	2.89	0.33	0.68	0.61	+ .07
.2885	.0484	.220	7.65	2.52	1.36	1.31	+ .05
.6135	.140	.374	16.27	7.98	2.19	2.22	− .03
1.612	.476	.691	42.75	27.15	4.13	4.10	+ .03
2.046	.640	.800	54.26	36.50	4.70	4.74	− .04
2.988	1.000	1.000	79.24	57.03	5.88	5.94	− .06

lower temperatures, in which range the plot in most cases ceases to be linear, above 500° the agreement is fairly good. Specifically, (except for the last two pairs of investigators, who report a solubility differing with the form of sample used) at 800° the variation is about 12% compared with a four-fold variation at 400°; and this is as would be expected from the relatively greater experimental error at the lower temperature. Since our investigation involves measurements at pressure down to 0.004 mm. where the volume of gas absorbed is large compared to that measured at 1 atm., the inherent accuracy of the method is considered greater; moreover our results are within 5 to 10% of those of Pihlstrand[11] and of Sieverts[12] over the whole temperature range.

The mean molal heat (ΔH) of solution of hydrogen in alpha-iron (body-centered iron lattice, stable up to 910°) derived from equation (2) is 13,300 calories. This is identical with the mean value calculated from the linear, and presumably more accurate, portion of the plot, in terms of log s against $1/T$, of the data of all the other workers; and it is most nearly in agreement with those the graph of which is linear over the longest temperature range.

Solubility in Nickel

The specimen of nickel,[18] a strip 0.14 mm. thick, weighed 337.7 g.; the ratio of volume to geometric area was 152 cm. A typical series of measurements at each temperature over the pressure range 0.001 to 1.8 mm. is given in Table IV, which is completely analogous to Tables I and II. The last column shows that the deviations from the straight line, $s = \alpha p^{1/2}$, are not greater than the precision of the experiment.

The isothermal relations at the three temperatures are expressed by the single equation

$$\log (s/p^{1/2}) = -645/T + 1.732 \qquad (3)$$

as indicated by the following comparison

t	T	$s/p^{1/2}$ from Table IV	Equation (3)
400	673	5.93	5.94
500	773	7.94	7.91
600	873	9.83	9.84

Smittenberg,[19] using the same method of measurement at low pressure, but wire instead of sheet (the ratio of surface to volume being 15-fold greater than in the present measurements),

---

(18) Analysis indicated 99.52% Ni, 0.13% C, 0.13% Mn, 0.09% Fe, 0.06% Cu; these small proportions of other elements would, presumably, not measurably affect the amount of hydrogen dissolved.

(19) Smittenberg, *Rec. trav. chim.*, **53**, 1065 (1934).

TABLE V

COMPARISON OF MEASUREMENTS OF THE SOLUBILITY OF HYDROGEN AT 1 ATM. IN NICKEL AT 300 to 900°

Form of sample	Solubility s (micromoles per 100 g.) 300°	400°	500°	600°	700°	800°	900°	ΔH (cal./g. mole)	Investigator
Sheet 0.14 mm.	111	164	218	271	323	373	419	5900	Armbruster[21]
Wire 0.02 mm.	135	183	244	297	349	393	436	5300	Smittenberg[22]
Wire 0.5 and 3 mm.; powder chips	105	161	186	245	301	356	411	6100	Sieverts[20]
	89	112	145	192	251	312	381	4300 (300–500°) 9000 (500–900°)	Luckemeyer Hasse and Schenck[12]

TABLE VI

DESCRIPTION OF SAMPLES

Number	Sample Designation	Composition of Samples C	Mn	S	P	Si	Cr	Ni	etc.	Weight, g.	Thickness, mm.	$\frac{\text{Area}}{\text{Volume}}$ (cm.$^{-1}$)
1	Carbonyl iron	0.011								516.6	0.34	65
2	Mild steel	.39	0.73	0.032	0.022	0.19	0.048	0.012		439.6	2.45	10
3	Mild steel	.39	.70	.049	.016	.128				382.1	0.076	255
4	Mild steel	12	.47	.041	.016	.003				366.7	.038	530
5	Mild steel	.10	.39	.032	.015	.007				499.5	.27	80
6	1.5% Mn steel	.20	1.46	.022	.027	.205				510.7	.26	82
7	3% Si steel	.05	0.23	.013	.010	3.17			Al 0.27 Al_2O_3 0.03	624.9	.28	74
8	4% Ni steel	.32	.64	.020	.023	0.245	...	3.64		504.7	.26	78
9	13 Cr 0.3 C, ferritic	.32	.47	...	...	.28	12.78			508.3	.74	28
10	16% Cr steel	.09	.46	.014	.012	.395	15.60	0.33		552.3	.25	80
11	28% Ni steel	.025	.18		...	.06	...	27.88		475.5	0.15	137
12	13% Mn steel	1.40	12.98	.019	.048	.32				523.8	.96	22
13	13 Cr 0.3 C, austenitic	0.32	0.47	...	...	.28	12.78			508.3	.74	28
14	18Cr–8Ni steel	.07	.37	.005	.006	.47	18.30	9.92		362.2	.097	209
15	Nickel	.13	.13	...	...	.04	...	99.52	Cu 0.06 Fe 0.09	377.7	.14	152

determined the solubility isotherm at 300 and at 600° up to 1.0 mm., and an isobar at 0.1 mm. from 20 to 600°. His results fit the same types of linear relation but are about 10 to 15% higher than ours, as is evident from the following comparison at 0.1 mm. pressure

Micromoles/100 g. at 0.1 mm. in nickel 400°	500°	600°	Investigator
2.1	2.8	3.4	Smittenberg
1.8	2.5	3.1	Armbruster

The only other measurements on nickel are by Sieverts and Hagenacker[20] and by Luckemeyer-Hasse and Schenck,[13] all at 1 atmosphere over the range 300 to 900°; these are compared at 1 atmosphere with values extrapolated from the low pressure data in Table V, which is completely analogous to Table III for iron. Our results fall between those of Smittenberg and Sieverts, being 2 to 15% higher than those of the latter; those of Luckemeyer-Hasse and Schenck are as much as 30% lower. The reason for the somewhat higher values extrapolated from measurements at low pressure is not clear, but, in consideration of the inherent lower accuracy of determinations at 1 atmosphere and the considerable extrapolation, the agreement is satisfactory. The mean molal heat of solution, within this temperature range, derived from the data of Smittenberg and of Sieverts agrees within 5% with our value (5900 cal.) from equation (3).

Comparison of the solubility in nickel with that in iron shows that, within the temperature and pressure range investigated, the corresponding solubility in nickel is 5 to 9 times as great as in alpha-iron; this at 910° transforms to gamma-iron which has the same face-centered lattice, and is then capable of dissolving about as much hydrogen as nickel. In both cases, the solution is quite "dilute"—for instance, in nickel at 600° and 1 mm. pressure there is in solution 1 atom hydrogen to 80,000 atoms nickel, and the "ideal" solubility law is followed closely.

Solubility in Certain Steels.—The steels included in this investigation are listed in Table VI, which gives, besides the composition as determined by chemical analysis, the thickness of the strip, the weight of the sample used, and the approximate ratio of the geometric area of its surface (sq. cm.) to its volume (cc.), the volume being obtained from mass and density. This ratio is in all cases so small as to preclude the intervention of any adsorption effect such as might cause difficulty in interpreting the results

---

(20) Sieverts, *Z. physik. Chem.*, **60**, 129 (1907); **77**, 591 (1911); Sieverts and Hagenacker, *Ber.*, **42**, 338 (1909).

(21) Extrapolated by eqn. (3) from data at 0.001 to 1.5 mm. and 400 to 600°.

(22) Extrapolated from isobaric data of Smittenberg[19] at 0.1 mm. and 20 to 600°.

if it were very large—as it might be, for instance, if a very fine powder were used as sample. That disturbing adsorption effects on the metal were in fact absent was shown by special experiments.

Anomalies of Behavior.—In the group of steels there were two which in presence of hydrogen exhibited a special behavior worthy of mention. One of these was the 13% chromium 0.3% carbon steel (No. 13), which took hours, instead of minutes, to come to equilibrium with hydrogen. This rate was measured, but the data afforded no definite clue to the reason for this exceptional slowness. Calculations from the rate of diffusion and the solubility of hydrogen in such a steel, as measured by Naumann[23] and Sieverts,[24] respectively, indicate that the period required for 99% saturation of a piece of this thickness at 400° would be of the order of five minutes. Likewise, the diffusivity derived from the measured rate by a procedure[25] which takes into account the variable pressure at the gas–metal interface—again on the basis of equilibrium between metal surface and gas—is so far off that one is forced to conclude that the metal surface was not in equilibrium with the gas. On the original sample there was a barely visible film, presumably of oxide, which was not reduced by treatment with pure hydrogen,[26] and accordingly remained on the sample throughout the measurements, and there is little question that this film is the relatively impervious barrier which hinders so surprisingly the passage of hydrogen and is the presumable source of the "stainlessness" of the steel.

If rate of passage of hydrogen through this film is the limiting factor in the over-all rate of absorption, it may reasonably be supposed to be proportional to the concentration gradient of hydrogen through the film, therefore (for constant thickness of film) to the difference in partial pressure, Δp, between the outer and inner surfaces of the film. This difference was measured approximately by observing, after several periods of exposure of the specimen at 400° to hydrogen, the gage pressure and thence, from the amount absorbed, computing the "virtual" pressure of hydrogen in the metal, that is, the pressure that would be in equilibrium with the hydrogen concentration in the metal if the total hydrogen content were uniformly distributed, which is an admissible assumption because diffusion in the metal is in this case much more rapid than diffusion through the film to the metal. On the basis just outlined

$$\Delta p = k \frac{dq}{dt}$$

where q is the amount of hydrogen which has entered the metal at time t and k is a constant; and the experimental data are in reasonable accord with this relation, as is shown by Table VII. Moreover the same numerical value of k was valid when the metal was austenitic as when it was ferritic; and the time for attainment of equilibrium with the austenitized sample was about fourfold that for the same sample when ferritic, corresponding to the fourfold greater solubility of hydrogen in austenite than in ferrite. It seems likely that this is not mere coincidence, but that the identical film was present in both, *i. e.*, that the film was little, if any, affected by the austenitizing treatment (about ten minutes at 1100°). This matter has been discussed at some length because of its significance in demonstrating how effective a barrier a stable oxide film can be even to the passage of hydrogen, and presumably much more of a barrier to larger molecules.

TABLE VII

DIFFUSION OF HYDROGEN THROUGH CHROMIUM OXIDE FILM ON 13 Cr 0.3 C STEEL (SAMPLE NO. 13) AT 400°

Time, minutes	Pressure of hydrogen, mm. Obs. in gas phase	Calcd. in metal	dq/dt (micromoles/ 100 g. min.)	$k = \frac{\Delta p}{dq/dt}$
	First addition of hydrogen			
16	0.182	0.001	0.0126	14
39	.154	.011	.0113	13
74	.124	.038	.0070	12
116	.113	.051	.0034	18
175	.100	.067	.0014	24
240	.094	.076	.0008	23
346	.089	.084	.0004	13
	Third addition of hydrogen			
4	1.229	0.787	0.0433	10
11	1.210	.880	.0294	11
21	1.188	.998	.0172	11
34	1.181	1.028	.0092	16
46	1.179	1.044	.0057	23
60	1.165	1.121	.0031	14
78	1.162	1.141	.0021	10

The second is the 3% silicon steel (No. 7) which showed a peculiarity deserving of mention,

---

(23) F. K. Naumann, *Tech. Krupp. Vorsch, Ber.*, **I** No. 12, 233 (1938).

(24) Sieverts, *Z. physik. Chem.*, **150**, 187 (1935).

(25) H. S. Carslaw, "Theory of Heat Conduction," 1921, p. 67; R. M. Barrer, "Diffusion in and through Solids," 1941, p. 20.

(26) The available data have recently been collated by C. G. Maier, "Sponge Chromium," U. S. Bureau of Mines, Bulletin 436, p. 17 (1942); he shows that at 500° the partial pressure of water in hydrogen must be of the order of 10^{-7} atmosphere if Cr_2O_3 is to be reduced, and less than this if CrO is to be reduced.

namely, that contact with hydrogen generated a very small quantity of something which condensed in the liquid air trap. Because of this simultaneous occurrence of a slow reaction (which, in one case, was followed over a period of many hours), the reported solubility, which was measured, as usual, after the lapse of ten to fifteen minutes, is regarded as less reliable. Doubtless the same phenomenon is responsible for the erratic variation with temperature, at temperatures below 600°, of the solubility of hydrogen at 1 atm. observed by Martin,[14] and the surface reaction, noted by Pihlstrand,[11] which prevented him from determining the effect of silicon on hydrogen solubility. Efforts to identify this condensate, by what are in effect vapor pressure measurements over a range of temperature, led to the tentative conclusion that it is a mixture, free from water, which, by elimination of the other possibilities,[27] seems to be of hydrocarbons.

Comparison of Results on Steels.—The results from the independent series of measurements, of which there were at least two, and usually more than two, at each temperature, for each steel, are in every case as concordant as the typical series given for pure iron and nickel; consequently details are omitted and the results are given in summarized form in Table VIII. In this table, the first column designates the steel; the next three columns list the values of α at 400, 500 and 600°, respectively, α being the slope of equation (1), plotted in the form of n_i/p against $1/p^{1/2}$, and also of the solubility curve, $s = \alpha p^{1/2}$. The fifth column gives the total number of measurements, which in general were almost evenly distributed over the three temperatures. The sixth column is the average deviation of the measured solubility from that calculated from the isothermal equations; although it exhibits a slight tendency to be small at the lower, and large at the higher, pressures in the range measured, it may be regarded as an estimate of the probable limit of error of α as tabulated; this value applies equally well to the three temperatures. The last column records the heat of solution derived from the data at the three temperatures, that is, from the slope of a plot of log p against $1/T$. Accordingly from Table VIII an equation can be written for each steel, analogous to equation (2) for iron and equation (3) for nickel, expressing all the data, in terms of pressure and temperature, within the precision of the measurements.

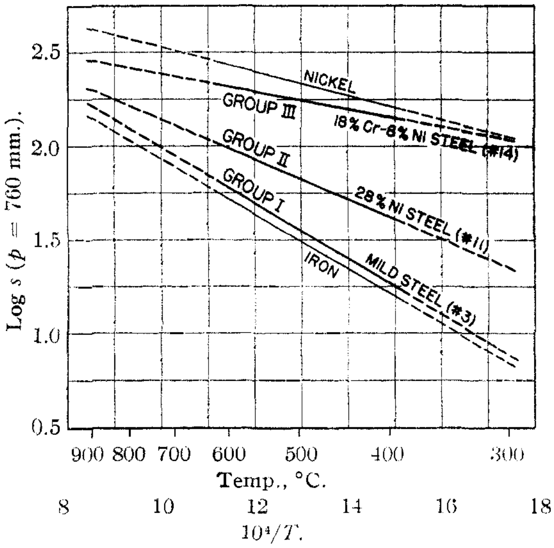

Fig. 3.—Solubility of hydrogen at 1 atmosphere in iron, nickel, and a typical steel from each of three groups, at 300 to 900°.

TABLE VIII

VALUES OF α, FROM EQUATION (1), THE SOLUBILITY OF HYDROGEN AT 1.0 MM. PRESSURE IN CERTAIN STEELS, AT 400 TO 600°

Sample number	(Micromoles/100 g. at 1.0 mm.) 400°	500°	600°	Total number of measurements	Average deviation in solubility	Heat of solution ΔH (cal./g. mole)
1	0.60	1.16	1.93	108	±0.03	13,300
2	.45	0.97	1.58	39	± .02	14,200
3	.79	1.29	2.18	74	± .03	13,600
4	.69	1.35	2.15	36	± .04	13,100
5	.45	1.00	1.79	36	± .03	16,200
6	.58	1.21	2.07	40	± .04	14,800
7	.46	1.52	2.42	43	± .05	18,600
8	.50	1.09	2.02	76	± .02	16,200
9	.33	0.73	1.46	38	± .04	16,400
10	.40	.84	1.56	47	± .03	15,900
11	1.51	2.44	3.54	48	± .03	9,700
12a (40%)	1.63	2.54	3.25	40	± .04	8,000
12b (85%)	2.45	..	..	16	± .03	
13	4.37	5.20	6.18	29	± .04	4,200
14	5.24	6.37	7.55	40	± .03	4,300
15	5.93	7.94	9.83	45	± .03	5,900

From the solubility of hydrogen at 1.0 mm. in the steels at these temperatures, which is represented by the value of α in Table VIII, and from the graphs of Fig. 3, it is apparent that the steels fall into three groups, namely: ferritic, low in alloying elements; an intermediate group, high in alloying elements; austenitic, the solubility of hydrogen in this group being several times as great as in the ferritic group, and the heat of solu-

---

(27) The conditions of formation seem to preclude the formation of silicon hydrides (silanes), on the basis of the work of Von Wartenberg [*Z. anorg. Chem.*, **79**, 71 (1912)] and of Hogness, Nelson and Johnson [THIS JOURNAL, **58**, 108 (1936)]; on the other hand Smirnov [*Metallurgy*, **12**, 48 (1937)] refers to the formation of an unstable silane complex, yet his evidence for it is quite indirect.

tion several fold less. Further, a direct plot of the experimental data, in the form of n_i/p against $1/p^{1/2}$ is in all cases a straight line within the precision of the measurements and consequently the ideal solubility law—that is, $s = \alpha p^{1/2}$—is followed precisely, both for the face-centered atomic lattice as in austenite and the body-centered as in ferrite. Let us now take up the three groups separately.

Ferritic Group.—This group comprises the steels No. 2 through 10 in Table VI, ranging in carbon from 0 to 0.4%, in manganese from 0 to 1.5%, in nickel from 0 to 3.2%, with usual small proportions of phosphorus and sulfur. Within the group there is no observable correspondence between composition and order of solubility, except for an indication of increased solubility with increase of phosphorus content. This suggests the possibility of a similar effect of nitrogen, on the one hand, and of arsenic, if it were present, on the other. It is not unlikely that chromium tends to lower the solubility in view of the statement[13] that in pure chromium hydrogen is less than half as soluble as in iron.

In general, therefore, the solubility of hydrogen in any low-alloy ferritic steel may be taken as substantially equal to that in pure iron. This conclusion is in accord with such data as are available at 1 atm. pressure; the values of the several authors for a temperature of 600° are brought together in Table IX for comparison with those for iron in Table III.

TABLE IX

COMPARISON OF MEASUREMENTS OF THE SOLUBILITY OF HYDROGEN AT 1 ATM. IN SOME LOW-ALLOY FERRITIC STEELS AT 600°

Sample	Solubility s, micromoles/ 100 g.	Investigator
0.6 Mn	60	Baukloh and Müller[16]
6.0 Mn	58	Baukloh and Müller[16]
1.1 Mn	61	Pihlstrand[11]
1.5 Mn	57	Armbruster[28]
3.0 Ni	58	Luckemeyer-Hasse and Schenck[13]
5.0 Ni and 5.0 Cr	65	
4.0 Ni	56	Armbruster[28]
3.8 Ni	183	Andrew, Lee and Quarrel[15]
3.0 Si	47	Martin[14]
3.0 Si	66	Armbruster[28]
0.4 C	60	Armbruster[28]

Intermediate Group.—The two steels in this group require little discussion. One of them contains 28% nickel and accordingly is austenitic,[29] which would lead one to expect an appreciably higher solubility; our values extrapolated to 1 atmosphere agree within 5% with those of Luckemeyer-Hasse and Schenck[13] for a 32% nickel steel at the three temperatures. The other, which contained 13% manganese, had during the process of pretreatment (120 hours at 650°) transformed to the extent of about 60% to ferrite, as gaged by microscopic examination; and the solubility is higher because, at the time of measurement, it was about 40% austenitic. This indicates that manganese has little influence on solubility of hydrogen in a ferritic steel, the position of the curve corresponding to the proportion of austenite present. This was confirmed by some measurements at 400° on a sample which, at the time of measurement, had transformed only to the extent of about 15%; comparison shows

	Solubility s at 1.0 mm. and 400°, micromoles per 100 g.
Typical ferritic steel	0.62
13% Mn steel: 40% austenite	1.61
13% Mn steel: 85% austenite	2.45
Typical austenitic steel	5.26

Austenitic Group.—In this group there are, besides pure nickel, two stainless steels, 18 chromium–8 nickel (No. 14) and 13 chromium–0.3 carbon (No. 13); in all three the relation of s to $p^{1/2}$ is again linear. As to the 18–8 nothing further need be said; the other, the stainless cutlery steel, is the identical sample on which measurements had been made while it was ferritic. When these measurements were completed, the sample was transformed to austenite by heating it in place by induction heating at 1100° for five to ten minutes in a slow stream of hydrogen, after which it was cooled rapidly to the temperature of experiment.[30] After a single austenitizing treatment, the observed solubility (a considerably longer

---

(28) These values were extrapolated by means of an equation, log $(s/p^{1/2}) = A/T + B$, which expresses data over the temperature and pressure range investigated within the precision of the measurements.

(29) Marsh, "The Alloys of Iron and Nickel," McGraw-Hill Book Company, Inc., New York, N. Y., 1938, p. 42, gives heat treatment data and phase diagrams which indicate an austenitic structure for this case. Both microscopic examination by Mr. J. R. Vilella and X-ray diffraction patterns of the strip by Mr. D. S. Miller show that this steel was initially 80% austenitic, and after measurement completely austenitic; it can be inferred from this that during the pretreatment for ninety hours at 650° the steel was completely austenitized and remained in this form during the measurements.

(30) A preliminary investigation of the behavior of this steel on isothermal transformation by Mr. R. A. Grange (to whom I am indebted for this information) indicated: that the austenitizing treatment mentioned brings about complete solution of carbon in the iron; that the region of most rapid transformation is 600 to 700°; that the quenching time from 1100 to 600° is limited to about 200 seconds; and that this steel could be held a week at 500° and many weeks at 400° without danger of appreciable reversion to austenite.

time being required for the attainment of equilibrium, as discussed earlier) was reproducible within the usual limit (±1%); after repeated austenitizing it was slightly lower. This is attributed to a loss of carbon—the total observed decrease being about 25% of that originally present—which would make it more difficult to quench in the bulb rapidly enough to keep the steel completely austenitic; and a final microscopic examination showed that a small proportion of the austenite had actually transformed.

This steel offered the possibility of following the transformation by the change in solubility of hydrogen. Accordingly, the pressure of hydrogen in contact with the austenitized sample at 600° was followed; at first it decreased to a value corresponding to the solubility in austenite (gamma), then gradually increased to a constant value corresponding to the solubility in ferrite (alpha). The results are given in Table X, together with estimates of the percentage of austenite transformed as calculated from the observed solubility by the rule of mixtures. The rate of transformation so derived is considerably slower than that inferred from microscopic examination of a series of specimens identical with the specimen as it was inserted in the bulb; namely, that, at 600°, 1% was transformed in about one hour, 25% in five hours, 50% in six hours, 100% in ten hours. This retardation may be ascribed in part to the presence of hydrogen, but is largely due to the large austenitic grain size which had developed at the time the measurements were made.

TABLE X

RATE OF TRANSFORMATION (GAMMA TO ALPHA STRUCTURE) OF AUSTENITIZED 13 Cr–0.3 C STEEL (SAMPLE 15) AT 600° DETERMINED FROM SOLUBILITY MEASUREMENTS

Time, hr.	Pressure p, mm.	Solubility (micromoles/100 g.)			gamma transformed, %
		gamma + alpha	gamma	alpha	
0	0.169	2.53	2.53	0.60	0
5.663	.214	2.06	2.84	.67	35.7
6.747	.223	1.98	2.91	.69	41.6
9.380	.232	1.89	2.97	.70	47.6
11.34	.238	1.82	3.00	.71	51.4
28.00	.289	1.24	3.31	.78	82.0
31.23	.299	1.10	3.37	.79	88.2
33.49	.304	1.01	3.40	.80	91.9
35.22	.310	0.94	3.43	.81	95.1
47.66	.320	.86	3.49	.83	98.9

Acknowledgments.—The author wishes to express her indebtedness to the Union Carbide and Carbon Research Laboratories, Inc., for the sample of stainless cutlery steel (No. 13) obtained through the kindness of Dr. A. B. Kinzel, and to the International Nickel Company for the nickel (No. 15) and the nickel steels (No. 8 and 11), obtained through the kindness of Dr. N. B. Pilling.

Summary

The solubility (s, in micromoles per 100 g.) of hydrogen was measured over a range of pressure (p, in mm.) from 0.001 to 1.5 in carefully pretreated samples of alpha-iron (initially carbonyl iron), nickel, and certain steels at 400, 500, 600° and at pressures up to 350 mm. in the iron at 600°. The results were reproducible, and in all cases were in accord at each temperature, within the precision of the measurements, with the linear relation $s = \alpha p^{1/2}$. The measurements on iron and nickel at all three temperatures are accurately reproduced by the respective equations (T is absolute temperature)

$$\log (s/p^{1/2}) = -1454/T + 1.946$$
$$\log (s/p^{1/2}) = -\ 645/T + 1.732$$

A similar equation holds for each of the several steels, which fall into three groups, according as each is (1) ferritic with low alloy content, (2) with high alloy content, (3) austenitic. The solubility in the low-alloy steels differs little from that in pure iron, but the small individual differences for different compositions are quite reproducible.

A method of calculating the amount of residual hydrogen, independent of any blank measurement to determine its effective volume (or effective pressure), from a suitable plot of the actual measurements is presented; the result, so calculated, is identical with that obtained through the use of a blank with argon in presence of the sample.

Comparison by extrapolation of the new results with data in the literature shows a general accord, particularly at temperatures of 600° and higher; at lower temperatures the values obtained in this investigation are, because of their consistency with the foregoing linear relations, believed to be of superior accuracy.

After the pretreatments (alternately with hydrogen and vacuum at temperature) reproducible equilibrium was obtained, within a few minutes, except in the case of the 13% chromium steel in which the unreducible, barely visible, oxide film slowed down the rate.

KEARNY, NEW JERSEY RECEIVED MARCH 6, 1943