A Magnetization-Chemisorption Study of Hydrogen and Sulfur Dioxide on Iron

L. M. PECORA AND P. J. FICALORA

Magnetization-pressure isotherms are measured for hydrogen and sulfur dioxide on small iron particles. The hydrogen isotherms are shown to relate directly to hydrogen uptake and obey the Temkin isotherm. The bonding of hydrogen to iron surfaces at different temperatures is determined from the data and related to other work. This conclusion is that the bond type of hydrogen on iron changes as a function of temperature. The formation of two hydrogen species on iron and at defects in the iron lattice is related to anomolous hydrogen diffusion in iron and to hydrogen embrittlement. The reactions of SO_2 and hydrogen on an iron surface are shown to explain the inhibiting effect SO_2 has an hydrogen embrittlement.

IT is well known[1-21] that hydrogen affects the mechanical properties of many steels. Changes in ductility, and crack growth rates from their values in air to lower values in the presence of hydrogen are well documented. The hydrogen may be present as a result of charging (internal hydrogen embrittlement) or as a result of hydrogen gas in the environment (external or environmental hydrogen embrittlement). Previous studies of the effect of low pressure H_2 gas (≤ 1 atm) on 4340,[1,2] 4130,[3] and 4335 V[4,5] steels demonstrate that adsorption and subsequent surface reactions are extremely crucial steps in the hydrogen embrittlement process. This becomes more obvious when the effects of the gases such as SO_2 or H_2S are considered. These gases have been shown[1,2] to inhibit or promote hydrogen embrittlement, respectively. Srikrishnan[6] has shown that H_2 adsorption on Fe foils was completely inhibited if the sample had prior exposure to SO_2 and that H_2S destroyed that inhibiting ability. These results are in complete accord with embrittlement findings[1,2] and indeed help to explain them. Therefore, a greater knowledge of the bonding of H_2 and other gases to the surface of Fe would be of great value.

One method to study bonding on surfaces of ferromagnetic substances is to measure the change of magnetization with adsorption. Under the right conditions this can shed light on the type of bonding between adsorbate and adsorbent. Selwood[7] has developed a low field a.c. method to study the effect of the adsorption of various gases on ferromagnetic materials. A collection of small diameter particles of any ferromagnetic material will act superparamagnetically and can be treated in terms of simple Langevin equations (which can often be linearized). In this way Selwood was able to treat the bonding of an adsorbate on a ferromagnetic material in a simple manner. The change measured in the magnetization experiments was taken to be due solely to the effect of bonding on the magnetic moment(s) of the atom(s). Selwood went so far as to define the bond number of an adsorbate on a particular adsorbent. This is the number of Bohr magnetons by which the magnetic moment of an adsorbent changes due to its bond formation with the adsorbate.

Most investigators have concentrated on Ni, Ni alloys and occasionally Co. However, some work has been done on Fe. Saturation magnetization changes resulting from adsorption of H_2 at temperatures in the vicinity of 373 K show that the bond number for H_2 on Fe is positive and small.[8,9] Artyukh, *et al*[10] have done a low field a.c. measurement of H_2 on Fe by simply examining abrupt changes in magnetization due to the injection of 26 to 39 kPa of H_2 over the Fe sample at different temperatures. Their findings again showed that changes in magnetization are small, the largest being +6 pct. They also found that magnetization increases occur at moderately elevated temperatures (~373 to 573 K). However, their low temperature studies showed that just below room temperature the H_2 adsorption decreased the magnetization. Slightly above room temperature no change was observable.

We report here on a similar low field a.c. magnetic study of H_2 and SO_2 on fine Fe particles supported on Al_2O_3. Our work was done at 77, 373, 448, and 498 K. Since changes could be detected on the order of ±0.05 pct of the magnetization, we report full pressure-magnetization isotherms from 65 Pa to >53 kPa for H_2 and 65 Pa to 2.6 kPa for SO_2.

EXPERIMENTAL

A. The Apparatus

Figure 1 shows a schematic of the experimental apparatus. The primary magnet consisted of a 6 cm diameter alumina tube on which were wound 3140 turns (at 710 turns/cm) of 1 mm diam enameled Cu wire. The primary was run at 1 A current at 60 Hz. This provided the a.c. magnetic field. The secondaries were placed within the primary, parallel to its axis. These were wound with 500 turns each of enameled Cu wire 0.015 cm in diam. The secondaries were wound in opposition and could be moved with respect to each other and the primary to crudely bring their total emf to zero. Further zeroing was done electronically with amplitude and phase controls. These controls consisted of a variable voltage divider and a variable RC circuit, both in parallel with one of the secondaries. The signal was further processed by a 60 cycle band-pass filter-amplifier which passed only 60 Hz signals and had a gain of 10. After filtering, the signal was monitored on an oscilloscope as well as measured with an a.c. digital millivoltmeter. The

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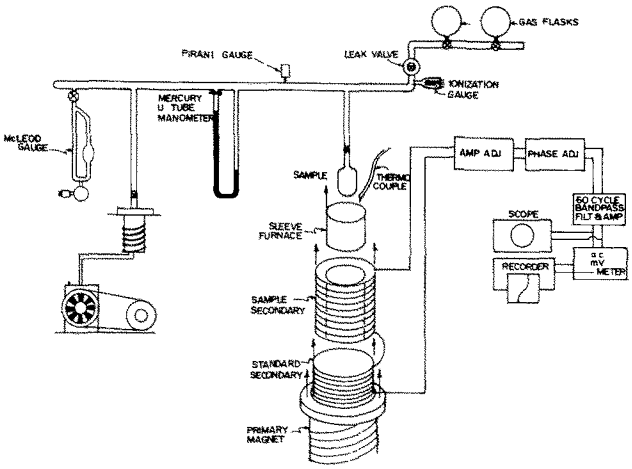

Fig. 1—Schematic of adsorption-magnetization apparatus.

results of a run were displayed permanently on a chart recorder which was driven by the analog output of the millivoltmeter.

Temperature was controlled by one of two methods. High temperatures were achieved by a sleeve furnace which fit inside the sample secondary. This was powered by a well regulated d.c. power supply so as to eliminate any induced emf in the sample secondary from the furnace windings. The sample then rested inside the sleeve furnace. Sample temperature was monitored with a chromel alumel thermocouple attached to the sample tube. Low temperatures were achieved by replacing the sleeve furnace with a small dewar which fit inside the sample secondary. The sample tube was then placed in the dewar and liquid nitrogen was added.

The sample tube was connected to a gas handling system which could be evacuated to 6.6×10^{-5} Pa by liquid nitrogen trapped oil diffusion pumps. Pirani and ionization gages permitted low and midrange pressure measurements. A mercury U-tube was used to measure pressure from 65 Pa to 1 atm. The mercury on the vacuum side had a 1 cm layer of Dupont DC 705 diffusion pump oil. This procedure was used to keep contaminating mercury vapors out of the system. The McLeod gage was used only to calibrate the other gages and was otherwise kept out of the system.

Adsorbing gases, stored in the flasks shown in Fig. 1, were admitted through a leak valve which could be adjusted to leak rates from 100 cc to 10^{-10} cc (STP) per s.

B. The Sample

The sample used was provided by Harshaw Chemical Co. This was Harshaw's Iron catalyst Fe-031 T 1/8 in. which consisted of Fe_2O_3 powder supported on porous Al_2O_3 cylindrical pellets (0.35 cm in height and 0.35 cm in diam). Pore volume was 0.31 cc/g and surface area was 41 m^2/g. The pellets were 20 pct Fe_2O_3 by weight. Typically, 50 g of pellets was used for a sample.

The sample was reduced by heating to 863 K, admitting 1 atm H_2 for 1 h evacuating the system and holding the sample at 863 K for 3 h while continually pumping on it. Typical final pressures were $\sim 10^{-2}$ Pa. This reduction was modeled after the processes which others have used.[6,10-12] The temperature of 863 K was chosen since the free energy for the reduction reaction is negative at this temperature. After a reduction cycle the magnetization of the sample was measured. The sample was continually put through reduction cycles until the magnetization no longer increased. Typically, 5 to 6 cycles were used in reducing one sample.

Electron microscopic investigation of a used sample[13] revealed an average particle diam of 15 nm. Clustering and sintering of the particles was particularly evident. Individual particle shapes were that of regular polyhedra.

C. Gases Used

The H_2 used was originally 99 pct pure as taken from the cylinder. Before storage in the system flasks it was purified by permeation through a heated palladium-silver membrane.

The SO_2 was used as obtained from Matheson Gas Products. This had a minimum purity of 99.98 pct.

D. Measurement of Magnetization-Pressure Isotherms

After reduction, the sample was brought to the desired temperature. The emf output of the secondaries was amplitude and phase adjusted to zero. The adsorbate was admitted in small pressure increments and the change in emf was recorded. After the last desired pressure increase the system was evacuated while continuously recording the emf. This last step determined whether the adsorption was reversible. The sample was cleaned between runs by raising the temperature to 773 K for 1 h to desorb any remaining gas. This high temperature cleaning procedure, however, meant that a given sample had a limited life for useful magnetization measurements. The changes in magnetization became very small after several cleaning cycles and at this point the sample was discarded. It was suspected that sintering of the particles was responsible for reduction of the surface area. The electron microscopy work previously mentioned supported this suspicion.

RESULTS

Figures 2 to 4 show the changes in sample secondary emf (Δ emf) as a function of pressure at three different temperatures; 373, 448, and 498 K. The sample was cleaned between each run. Note that the change is positive and very sensitive to temperature. The magnetization change decreases with decreasing temperature at a given pressure of hydrogen. The changes in emf were converted to percent changes in magnetization and these are shown on the right hand ordinate of the figures. The total emf of the sample (*i.e.* that value of voltage by which the secondaries change when the sample is inserted) is proportional to the total magnetization of the sample. The experimental apparatus did not allow total sample emf to be measured at temperatures other than room temperature. However, since the sample was superparamagnetic Selwood's[7] linearized equation for magnetization as a function of temperature was used to calculate the total emf at

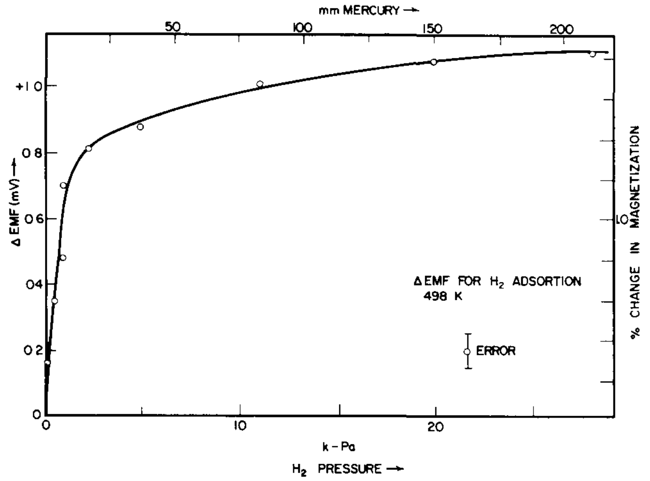

Fig. 2—Δemf for hydrogen on iron at 498 K.

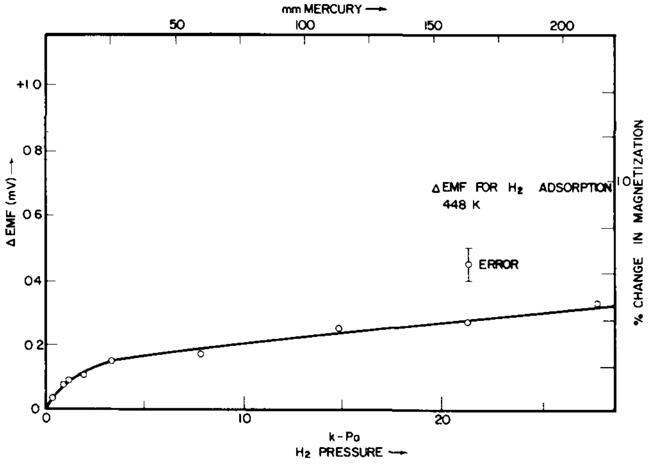

Fig. 3—Δemf for hydrogen on iron at 448 K.

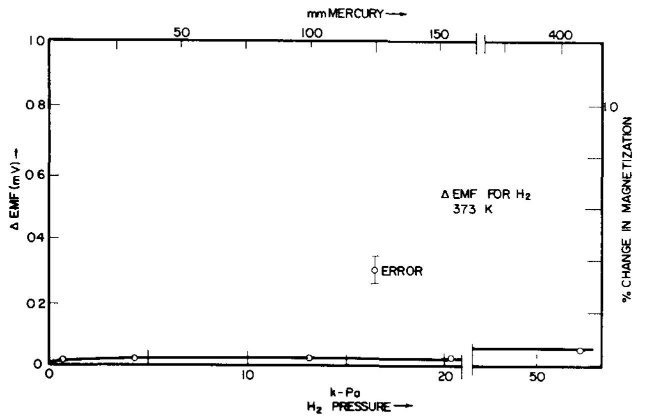

Fig. 4—Δemf for hydrogen on iron at 373 K.

temperatures other than room temperature:

$$\text{total emf} \propto M = \frac{K}{T} \qquad [1]$$

where M is the total magnetization, T, the temperature, and K a constant. At room temperature the total emf was 100 mV. Thus the emf at another temperature, T_1, is given by

$$\text{emf } (T_1) = (100 \text{ mV}) \frac{298 \text{ K}}{T_1} \qquad [2]$$

and percent changes in magnetization at temperature T_1 become

$$100 \times \frac{\Delta \text{ emf } (T_1)}{\text{emf } (T_1)} = \text{pct change in magnetization.} \qquad [3]$$

This procedure was used for all hydrogen and SO_2 runs. The experiments shown in Figs. 2 to 4 were done in the order of decreasing temperature on the same sample. In order to determine if sintering was responsible for the decrease in sample signal with decreasing temperature, a fourth run, at 498 K was carried out. An isotherm (Fig. 5) which is nearly identical to the original 498 K run (Fig. 2) resulted. Hence, the changes in isotherms can be attributed solely to the temperature dependence of the adsorption reaction. The sample saturated with respect to Δ emf near 25 kPa.

Figure 6 shows the results of H_2 adsorption at 77 K. An approach to saturation occurred at much lower pressures than for the higher temperature runs. More important, however, is the fact that the emf changes were negative at this temperature. Desorption of H_2 occurred readily at 373 K when the sample was pumped down to 1.5×10^{-3} Pa. Typical times for complete desorption were on the order of 15 min. During that time the system pressure typically dropped an order of magnitude and the sample Δ emf returned to zero. Desorption of H_2 did not occur at 77 K even after many hours of evacuation if the adsorption took place at the higher temperatures.

The adsorption of SO_2 and its effect on magnetization at 498 K is presented in Fig. 7. The changes here were positive and roughly three times larger than the corresponding changes due to H_2 adsorption at the same temperature. A typical H_2 isotherm is plotted (dotted line) on the same scale to demonstrate the differences. Note that the SO_2 isotherm saturated at about 4 kPa. The blocking effect of SO_2 on H_2 adsorption was directly tested during this run. At 3.6 kPa pressure of SO_2, hydrogen gas was injected at a partial pressure of 9.2 kPa. The magnetization increased very slightly (0.080 mV). This clearly demonstrates that H_2 did not replace SO_2 on the surface. If it did the emf would have fallen toward the H_2 isotherm at that pressure. Also if H_2 is adsorbed at all it does not interact strongly with a surface covered with SO_2.

The sample was cleaned in the usual manner and

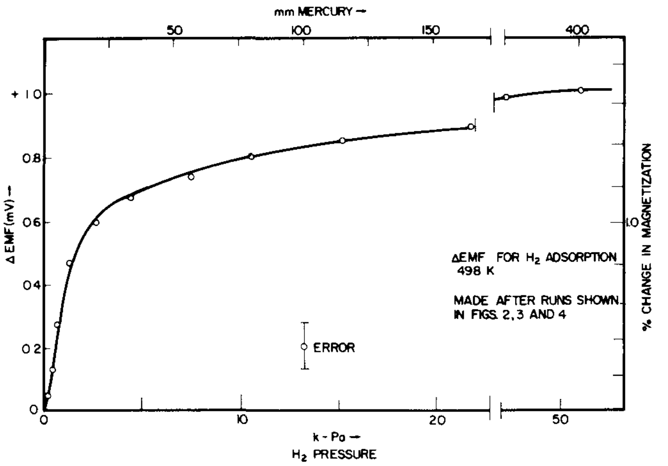

Fig. 5—Δemf for hydrogen on iron at 498 K, done after the runs shown in Figs. 2 to 4.

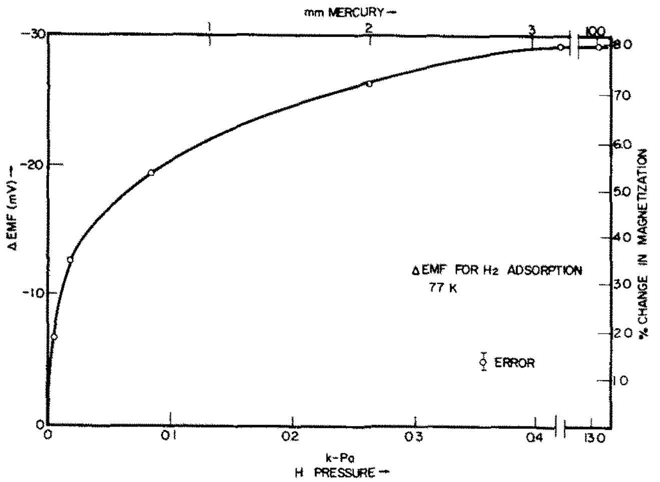

Fig. 6—Δemf for hydrogen on iron at 77 K.

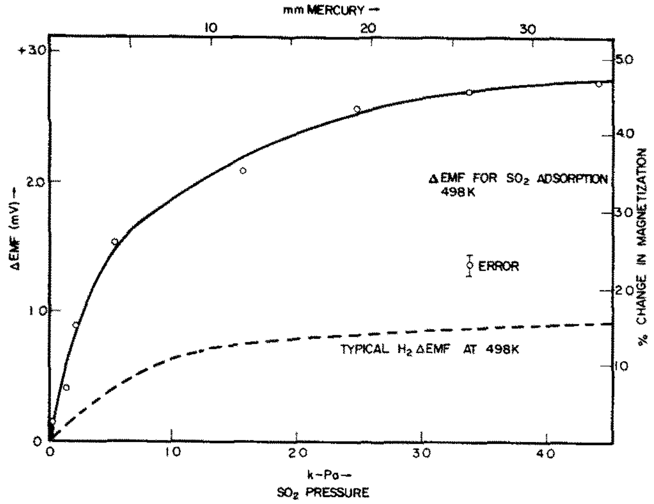

Fig. 7—Δemf for SO_2 on iron at 498 K.

another SO_2 run at 498 K was done. Figure 8 shows the results of that run. Note that while saturation took place at about the same pressure the isotherm is not the same as that of Fig. 7. The results, however, can be readily explained by examining a superposition of Figs. 7 and 8. Figure 9 shows this superposition. It can be clearly seen that the second SO_2 run simply reproduced the higher end of the first run. This means that there must have been SO_2 remaining on the Fe surface even after the 773 K vacuum cleaning. Figure 9 shows that the SO_2 adsorbed at 25 Pa during the first run remained on the surface.

Subsequent runs using SO_2 showed smaller and smaller Δ emf values. It could not be determined whether this resulted from more SO_2 permanently adsorbed or the sintering of the specimen.

Desorption of SO_2 did not take place upon evacuation at 498 K. Although pressures of 2×10^{-5} Pa were maintained at this temperature the SO_2 covered sample showed no emf changes. The SO_2 desorbed only at the extremely high cleaning temperatures and even then desorption was not complete.

Figure 10 shows a molar H_2 adsorption isotherm which was done at 498 K on the specimen before the SO_2 runs. This was performed to show that the changes in magnetization measured were parallel to the amount of H_2 adsorbed. The molar adsorption isotherms follows much the same form as the magnetization isotherm especially at lower pressures. However, there is no saturation as there is in the magnetization. This becomes clearer in Fig. 11 where the number of moles adsorbed is plotted against the Δ emf values of the same sample at 498 K. These are linearly related up to 10×10^{-5} moles adsorbed at which point the magnetization begins to saturate but adsorption continues. Hence up to ~7 kPa the magnetization change reflects the actual H_2 uptake.

DISCUSSION

A. H_2 on Fe

1. Bonding. The magnetization changes presented here are in full accord with several measurements done at single pressures of hydrogen.[8-10] In particular the change of sign of the Δ emf resulting from H_2 adsorption at different temperatures is verified. It must be noted that the change in emf detected must result from an actual change in magnetization of the particles and not from changes in anisotropy. This must be true in our case for a number of reasons. The particle shape is very nearly spherical, so that shape anisotropy cannot be a factor. The limiting factor must then be crystalline anisotropy. The Neel

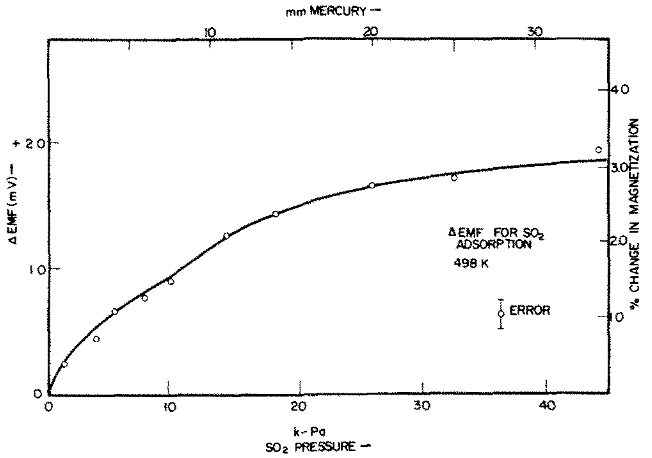

Fig. 8—Δemf for second SO_2 run at 498 K.

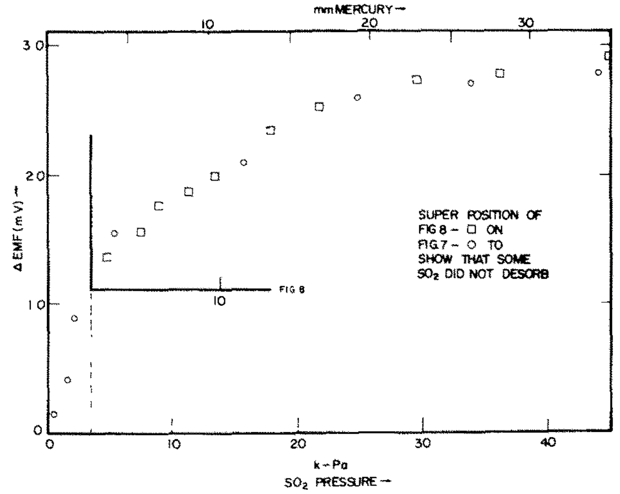

Fig. 9—Superposition of Figs. 7 and 8.

equation for the decay time of magnetization is:

$$\tau = 10^{-9}\, e^{1/4K' v/kT} \qquad [4]$$

where K' is the crystalline anisotropy, v the particle volume, k Boltzman's constant, and T the temperature. In order to completely rule out changes in anisotropy τ should be very small compared to the time, t, required in the experiment. For our experiment $t \sim 1/120$ s *i.e.* the time required for the magnetic field to go through one half a power cycle. Now at 273 K, $K' \simeq 402 \times 10^3$ erg/cm^3,[14] and

$$\tau = 3.09 \times 10^{-7} \text{ s}$$

for 7.5 nm radius particles. This value is far below the experimental times required and anisotropy effects can be ruled out for all temperatures greater than 273 K. Anisotropy can also be ruled out for other reasons at higher temperatures. As Artyukh *et al*[10] have pointed out the effect of H_2 adsorption at elevated temperatures increases as a function of temperature whereas all effects associated with anisotropy decrease as a function temperature. The conclusion shows that the effects of H_2 (and SO_2) adsorption on the magnetization of each iron particle was observed. Therefore the Δ emf values are directly proportional to ΔM, the changes in magnetization.

At liquid nitrogen temperature calculations of decay times, τ, show that we cannot rule out changes in emf resulting from changes in anisotropy upon adsorption of hydrogen. Only particles ≤6.4 nm in diam will act superparamagnetically. However, there are two reasons that the bonding at low temperature is different from that at high temperatures. One is from the observation that no magnetization change is measureable from 298 to ~370 K even though H_2 readily chemisorbs on Fe at these temperatures.[11,12,15] The relaxation time demonstrates that the sample is still superparamagnetic in this temperature region and Δ emf values must reflect the bonding. Hence, although H_2 is bonding to the surface, the Δ emf is zero. Hydrogen uptake on Fe increases with decreasing temperature[11,12] so that it is not just a matter of the effect being too small. We must therefore, conclude that the interaction of H_2 with Fe changes with temperature.

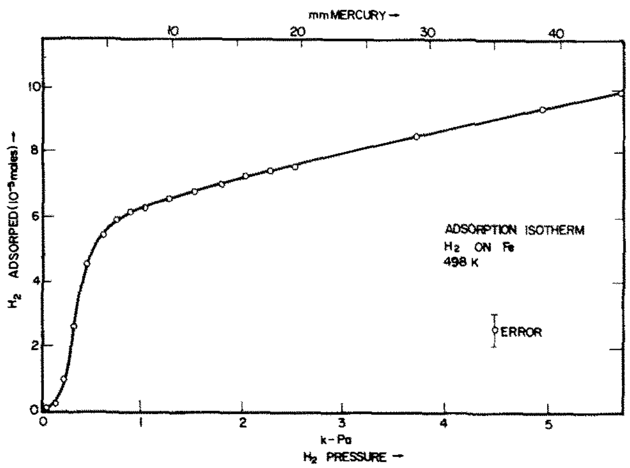

Fig. 10—Hydrogen uptake on magnetization sample at 498 K.

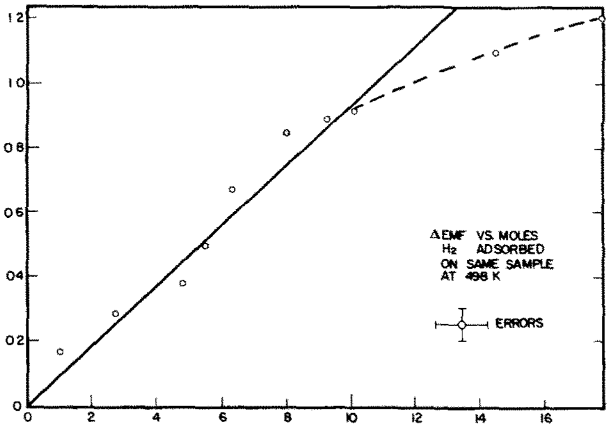

Fig. 11—Moles of hydrogen adsorbed *vs* Δemf.

The second reason stems from thermal desorption studies of H_2 adsorbed initially at different temperatures. Artyukh *et al*[10] compared the thermal desorption of H_2 on Fe resulting from an increase in temperature (77 K → 298 K) for various samples on which H_2 had initially been adsorbed at different temperatures and on which no H_2 had been adsorbed (control run). A sample which had H_2 adsorbed initially at 77 K showed both a pressure increase and a magnetization increase with respect to the control run upon warming to 298 K. Both of these increases demonstrate the thermal desorption of the H_2 adsorbed at 77 K. In a second test a sample which had H_2 adsorbed at 498 K was first pumped down at 1.31 Pa. This was done to avoid further H_2 uptake when the sample was cooled to 77 K. Since the evacuation to 1.31 Pa at 498 K did not change the magnetization, no H_2 desorption took place. The sample was then cooled to 77 K and the system was evacuated to 1.31×10^{-5} Pa. In this case no pressure increase or magnetization change (with respect to the control run) was noted. This meant that the H_2 adsorbed at 498 K did not thermally desorb, unlike the H_2 adsorbed at 77 K. We must again conclude that there are bonding differences in H_2 adsorbed at high and low temperatures and that the Δ emf values reflect this fact.

These results demonstrate unequivocally that adsorbed hydrogen interacts with the *d*-electrons of iron. It is possible to speculate on the two different bonding mechanisms found. The high temperature form of adsorbed hydrogen must increase the magnetization by reducing the total number of paired *d* electrons in Fe. This would increase the number of unpaired *d* electron spins and hence, increase the magnetization. Conversely the low temperature form of adsorbed hydrogen must reduce the number of unpaired *d* electron spins and thus reduce the magnetization. The simplest chemical manner in which these changes can be accomplished is by ionic bond formation between H and Fe. One can speculate that four possible forms of hydrogen ions might exist: H^+, H_2^+, H^- and H_2^-. However there is evidence that, even at liquid nitrogen temperatures, hydrogen dissociatively chemisorbs on Fe. Sieverts law is obeyed for H_2 uptake at low temperatures.[11,12] Hydrogen-deuterium exchange is also rapid at liquid nitrogen temperature.[15] An exchange reaction of this type does not however, rule out the existence of molecules whose atoms are loosely joined on the surface. Our own experiments were not sensitive enough in the very low pressure ranges, where adsorption might obey a Langmuir isotherm, to differentiate between a P or a $P^{1/2}$ dependence. However, based on the findings of others mentioned above we must at present rule out the possibility of H_2^+ or H_2^- formation.

Although H^+ can explain low temperature magnetization changes we cannot eliminate the possibility of covalent bonding of hydrogen atoms to Fe. This would also decrease the number of unpaired d electron spins. In the absence of any other experimental data the forms of hydrogen on Fe can only be narrowed to H^+ or covalently bonded hydrogen atoms at low temperatures and H^- at high temperatures. Both types are present from 273 → 373 K and tend to cancel each other out, hence a zero Δ emf results for H_2 adsorption.

It should be noted that in studies of adsorption[15] and rates of adsorption[12,16,17] the postulation of two types of adsorbing species was necessary to explain the data. In particular Porter and Tompkins[12] postulated an initial adsorbed species (Type C (Ref. 15)) and a final adsorbed species (Type A (Ref. 15)). They postulated that Type A resulted from an activated migration of Type C to sites which strongly adsorbed hydrogen (*i.e.* sites of lower potential energy). Since these previous studies were volumetric or gravimetric they could in no way differentiate between the bonding of Type C and Type A hydrogen on Fe. However, because of the adsorption-magnetization results we can now equate Types A and C with two different types of chemical bonding on the iron surface. On the basis of spin pairing and temperature dependence it is reasonable to equate Type A with H^- and Type C with H^+ or covalent hydrogen. The activation energy for migration now becomes the activation energy for the reaction.

$$H^+ \text{ or covalent hydrogen} + Fe \rightarrow H^- + Fe^+$$

which is a chemical reaction even though it might also involve a migration. We note here that the H^- form is an immobile species and has a much larger binding energy than the mobile Type C. The activation energy was determined to be 12 to 25 kJ/mole,[12] which is consistent with the temperature dependence of the bonding of hydrogen on Fe.

Finally Kumnick and Johnson[18] in studies of hydrogen transport through Armco iron showed that hydrogen was hindered in its diffusion through the iron by heterogeneities in the microstructure. These heterogeneities were labeled as hydrogen traps and were assumed to capture hydrogen in some manner. They found that these traps were saturable *i.e.* they could hold only a finite amount of hydrogen. Their studies on deformed Armco iron showed that some of the traps could be associated with dislocations. We must note here that any internal Fe structure which could act in any way as a surface would adsorb hydrogen in a Type C state which would be converted to an immobile Type A state at a rate dependent only on the temperature. The creation of immobile Type A (H^-) hydrogen is a trapping process which is saturable since there is a fixed amount of surface area. The trapping observed occurred in the temperature range 278 to 333 K which is the range in which the formation of the H^- begins to compete with the formation of H^+ (or covalent H) as reflected in the change of magnetization (Δ emf = 0).

2. H_2 Isotherms. The equation[7] relating changes in magnetization to surface coverage for the high temperature magnetization isotherms is:

$$\frac{\Delta M}{M} = \gamma \theta \qquad [5]$$

where $\Delta M/M$ is the fractional change in magnetization observed, γ contains the dependence on particle size distribution, bonding number, specific magnetization of the sample, surface area and particle volume; and θ is the surface coverage. Since Δ emf values are proportional to ΔM we can find the appropriate isotherm for the adsorption of H_2 on an iron surface. Langmuir isotherms for dissociated and nondissociated adsorption failed to fit the data over the entire pressure range as did the Freundlich isotherm. However, as can be seen from Fig. 12, the Temkin isotherm fits the data over the pressure range of the experiment. This isotherm is based upon the assumption that the heat of adsorption falls linearly with surface coverage. This agrees with the findings of others[15] for H_2 on Fe.

3. Hydrogen Embrittlement. There has been much speculation over the years on the mechanism of hydrogen embrittlement and on its kinetics. In light of the relationship of the two forms of hydrogen found in this study to the Types A and C speculated by Porter and Tompkins[12] and the hydrogen trap found by Johnson and Kumnick[18] it is possible to construct a model of hydrogen embrittlement which includes diffusion to embrittling sites in the Fe bulk. One must consider the total process of adsorption, diffusion and embrittling reaction.

Troiano *et al*[19,20] have shown that fracture resulting from hydrogen embrittlement of charged specimens initiates not at the crack tip but in the area in the metal just beyond the tip. The reason given for this is that fracture should occur in the region of maximum triaxial stress. The location of this region is always within the metal beyond the notch or crack tip and is a function of notch radius. The sharper the notch the closer the critical triaxial stress region is to the notch tip. We assume here that fracture resulting from low pressure (*i.e.* environmental) hydrogen also initiates in the region of maximum triaxial stress. We also assume that for a given specimen and at a given stress intensity there is a critical amount of hydrogen which must accumulate in the triaxial stress region to cause fracture. Crack growth then consists of a process of adsorption, diffusion, embrittling reaction, and fracture occurring many times as a specimen experiences low pressure hydrogen embrittlement. The crack growth rate should be inversely proportional to the amount of time required to build up the embrittling species.

Using the above assumptions and guided by the interpretation of the immobile species, H_A (H^-) in the work of Porter and Tompkins[12] and Kumnick and Johnson[18] we propose the model shown in Fig. 13. The initial Type C adsorbed species, designated as H_C, is in equilibrium with the gas phase. The Type A species, designated as H_A, is accumulating on the surface. The rate of this accumulation is temperature dependent and has the activation attributed to migration by Porter and Tompkins.[12] Porter and Tompkins[12] referred to H_A as an immobile species. This is consistent with H_A being H^- since H^- implies a local surface bond as well as a larger atom than H. Recalling that this agrees with the explanation of the trapping

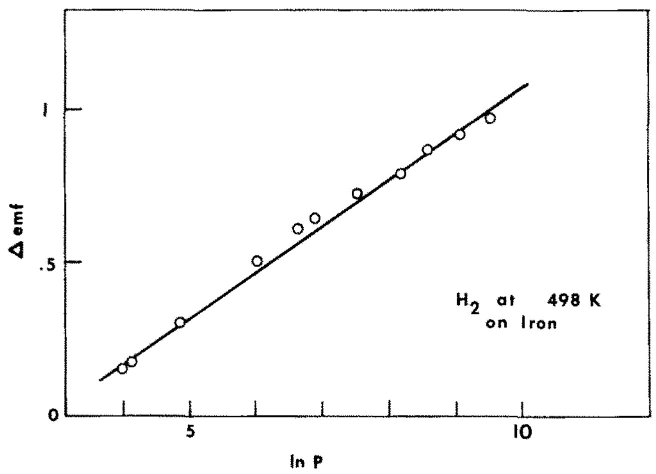

Fig. 12—Tempkin isotherm plot of Δemf *vs* ln for hydrogen on iron at 498 K.

mechanism of Kumnick and Johnson[18] we assume that H_A (H^-) does not readily diffuse into the metal. However, H_C does, as is represented by the step to H_D, a diffusing hydrogen species. H_D diffuses to the triaxial stress region and reacts at some rate determined by temperature to embrittle the metal. This is shown in the reaction as the step to H_E, the embrittling species in the triaxial stress region.

The diffusion of hydrogen from a newly formed crack surface is far from being in a steady state. As it has been shown[18] that typical times to reach steady state fluxes in membranes 0.126 cm in thickness were of the order of minutes. Most specimens for embrittlement studies have dimensions which are at least an order of magnitude larger than the membrane thickness. Since diffusion times vary as the square of the distances involved we see that many hours would be necessary to reach steady state. Typical crack growth rates are on the order of fractions of a centimeter per second so that new surfaces are created too fast to consider the diffusion being steady state.

Finally we can speculate on the embrittling species and its location in the triaxial stress region. Since the formation of H^- on internal defects is consistent with trapping, it is quite reasonable to believe that this trapped hydrogen is the embrittling species. Kumnick and Johnson[18] showed that deformation of a specimen increased the number of traps. This is in full accord with findings which show that plastic deformation is a necessary step in environmental hydrogen embrittlement.[21] It can be seen that traps correspond to internal surfaces or active sites for the adsorption of Type *A* (H^-) hydrogen. The presence of these sites is necessary for embrittlement of iron and steel by hydrogen.

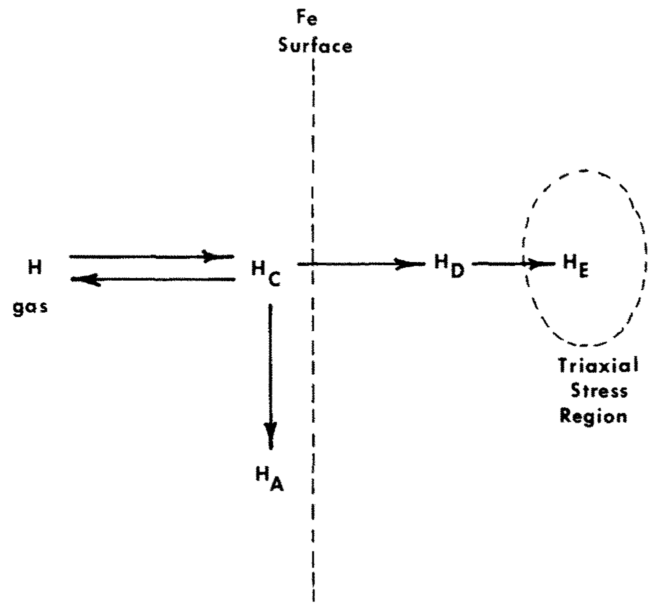

Fig. 13—Surface and subsequent bulk reactions for the environmental hydrogen embrittlement process.

B. SO_2 on Iron

We can directly compare the bonding of SO_2 and H_2 on an iron surface using the following relation:[7]

$$\Delta \text{ emf} \propto \frac{\Delta M}{M} \propto \eta\,\theta \qquad [6]$$

where θ is the surface coverage and η is the bond number. If we assume that the number of active sites is the same for SO_2 and H_2 on Fe then near saturation ($\theta \rightarrow 1$) Δemf $\propto \eta$. Thus by taking the ratio

$$\frac{\Delta \text{ emf } (SO_2 \text{ at Saturation})}{\Delta \text{ emf } (H_2 \text{ at Saturation})} \equiv \epsilon \qquad [7]$$

we can calculate the relative bond number of SO_2 to H_2 at 498 K. As can be seen from the isotherms $\epsilon \simeq +3$. This means that the SO_2-Fe surface bond is much more ionic than the H-Fe surface bond.

Transfer of paired electrons from the Fe *d* levels to SO_2 is greater than for hydrogen. The results also show that SO_2 blocks the interaction of hydrogen with the surface. Gravimetric studies have shown[6] that SO_2 does block H_2 uptake on iron foils. The reason for this result is aptly demonstrated by the magnetization measurements: SO_2 was more strongly adsorbed on iron and effectively blocked the interaction of H_2 with the iron surface. The strength of the SO_2-Fe surface bond was demonstrated both by the absence of desorption upon evacuation after a run and the inability of high temperature (~773 K) to clean the sample of all SO_2. Hydrogen on the other hand desorbed readily at relatively low temperatures (~373 K). The blocking action of SO_2 on Fe surfaces explains how SO_2 inhibits environmental hydrogen embrittlement.

CONCLUSIONS

The magnetization results conclusively demonstrate that there is an interaction between adsorbed hydrogen and the *d* electrons of iron.

In particular there are two types of interactions between hydrogen and iron surfaces: 1) a low temperature form, H^+ or covalently bonded H and 2) a high temperature form H^-. These correspond to what previously were called Type *C* (low temperature) and Type *A* (high temperature).

The immobile H^- species readily explains adsorption rates. In addition the formation of this species at internal defects explains the trapping mechanism and anomalous diffusion of hydrogen through iron.

The inhibiting ability of SO_2 on the interaction of hydrogen with an iron surface was clearly demonstrated.

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