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Thermodynamics of Ternary Interstitial Solid Solutions

by

Douglas Michael Coldwell

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INTRODUCTION

Despite the relatively large body of thermodynamic data available for hydrogen-metal binary systems, there is a general lack of such data for systems where hydrogen atoms are dissolved in a matrix of two metallic species. Such ternary systems afford the opportunity of studying the change in the thermodynamic properties of the dissolved hydrogen atoms on gradually changing the composition of the "binary solvent" matrix.

This investigation concerns the thermodynamic properties of the iron-chromium-hydrogen system. The iron-chromium system was chosen as the "solvent" for several reasons. In addition to iron and chromium being the major constituents of stainless steels, both end points, the iron-hydrogen system and the chromium-hydrogen system are well known. The extensive body of thermodynamic data for iron-hydrogen is largely self-consistent and the equilibrium between hydrogen gas and chromium - hydrogen solid solutions has been measured over a wide temperature range. (1)

Furthermore, the existence of the large continuous series of body centered cubic solid solutions enables the
properties of the dissolved hydrogen atoms to be measured over a wide range of iron/chromium ratios. The compositions of the binary iron-chromium solvents used this investigation are indicated by the vertical lines in the phase diagram in Figure 1. Besides this property, the iron-chromium system permits the investigation of how the thermodynamic behavior of the dissolved hydrogen atoms changes in passing from the essentially disordered $\gamma$ solid solution at high temperatures to the ordered $\alpha$-phase at lower temperatures, from face centered cubic $\gamma$-phase to body centered $\alpha$-phase, and from paramagnetic above the Curie temperature to ferromagnetic below it. Various authors have discussed these properties in relation to hydrogen solubility. Flanagan and Oates have studied the effect of ordered-disorder transformations on the solubility of hydrogen in binary metallic solvents.\(^{(2)}\)

Another advantageous feature of the iron-chromium-hydrogen system is that changes in the hydrogen-metal interaction energies as a consequence of changes in the composition of the binary solvent matrix and a concomitant volume change should be negligible. The lattice parameters of the iron-chromium body-centered cubic solid solutions show a virtually linear variation from 2.8600 kX (iron) to 2.878 kX (chromium)\(^{(3)}\) (See Figure 2). Thus the "size" of the interstitial site
occupied by the hydrogen atom is effectively independent of the composition of the binary solvent, iron-chromium.

The magnetic properties of the iron chromium system also suggest that investigation could provide useful information. Since chromium is essentially antiferromagnetic while iron is ferromagnetic, the shift from one state to the other could affect the hydrogen solubility in predictable ways. Depending on the interaction of the proton with its screening electrons, the d- or s-electrons could be determined to be the major contributors to the screening process.

In the following pages a rationale for the model of the solution chosen, the basics of the screened proton model of hydrogen diffusion in transition metals, experimental technique, results, and discussion of these results, all will be described.
Figure 1. Compositions at which the thermodynamic data have been measured.
Figure 2. Variation of lattice parameter with composition.
SOLUTION MODELS

There are several basic assumptions in deriving a model for the solid solution of the iron-chromium "binary solvent" and hydrogen solute. We can quite justifiably believe that the solute atoms are bound at interstitial sites in the solvent alloy and execute many vibrations before undergoing a diffusion jump into another interstitial site. Proof for the occupancy comes from neutron diffraction studies. The execution of many vibrations before diffusing is reasonable if we assume that the activation energy for diffusion is much greater than the mean thermal energy. Finally, due to the dilute solution of hydrogen (about 2 ppm on the average), we can say that there is no solute-solute interaction and that the distribution of the hydrogen is random among the interstitial sites.

The three models, which fulfill the above conditions, normally considered are:

1. Ideal solution
2. Regular solution
3. Quasi-regular solution.

Since the thermodynamics of the iron-chromium system are known, we may use this information to confirm or refute the
applicability of each of these three models.

In the Ideal solution model, the relative partial molar enthalpy is assumed to be zero, the configurational entropy to be that of a random solution, and nonconfigurational entropy terms to be nonexistent. If the solution is ideal, by definition, it obeys Raoult's Law. The recent measurements of Mazandarany and Pehlke\(^{(5)}\) of the activity of chromium in solid iron-chromium alloys employing the solid oxide electrolyte technique showed that, between 900 and 1200\(^{\circ}\)C, and 0 and 63 atomic percent chromium, the chromium activity exhibits positive deviation from Raoult's Law in both the \(\alpha\) and \(\gamma\) phases. The activity was referred to solid pure chromium and approached ideality with increasing temperature. These data are in substantial accord with those of Jeannin et. al.\(^{(6)}\) who used equilibration between chromium metal, chromic oxide, hydrogen, and water; and Lidster and Bell\(^{(7)}\) who used solid yttria-doped-thoria electrolytes as did Mazandarany and Pehlke above; and Kubaschewsky and Heymer\(^{(8)}\) who combined the Knudsen effusion method with tracer analysis of Cr-51. The data of McCabe et. al.\(^{(9)}\) show that the activity of chromium is very close to ideal at temperatures between 1200 and 1250\(^{\circ}\)C with very slight positive deviation and those of Reese et. al.\(^{(10)}\)
using the Knudsen effusion technique coupled with a time-of-flight mass spectrometer agree well with McCabe's\(^{(9)}\) at \(1400^\circ\)C. All these data do show deviation from ideality for the iron-chromium system. Therefore, the ideal solution model must be modified.

The next model considered is the Regular solution. This assumes that the energetics are nonideal, i.e. the relative partial molar enthalpy is not zero, and the entropy is the same as in the ideal solution model. The entropy measured is not that which is calculated using Boltzmann's equation:

\[
S^c = k \ln W \tag{1}
\]

where \(S^c\) is the configurational entropy, \(k\) is Boltzmann's constant, and \(W\) is the number of distinguishable arrangements of the solute and solvent atoms for a given energy.

If a two component system exists,

\[
W = \frac{(N_v + N_u)!}{N_v! N_u!} \tag{2}
\]

where \(N_u\) is the number of solute atoms and \(N_v\) the number of solvent atoms. Therefore,
\[ S^c = k \ln \left[ \frac{(N_v + N_u)!}{N_v! N_u!} \right] \]  \hspace{1cm} (3)

and, using Stirling's approximation:

\[ S^c = k \left( C_u \ln C_u + C_v \ln C_v \right) \]  \hspace{1cm} (4)

where \( C_u \) is the atomic concentration of the solute atoms and \( C_v \) of the solvent atoms. It is clear that the sum of these two concentrations is one.

For the maximum entropy, each of the above concentrations is equal to one-half and the resulting entropy is:

\[ S_{\text{max}}^c = -k \left( \frac{1}{2} \ln \frac{1}{2} \right) \times 2 = 1.376 \text{ cal/mole}-^\circ\text{C} \]

This is very different than the entropy measured for the iron-chromium solid solution. At the maximum, the entropy at 1600\(^\circ\)K is 2.014 cal/mole-\(^\circ\)C. (11) Again, this approach must be modified in order to get a closer approximation to reality.

The third model is the quasi-regular solution model which assumes that, as above, the energetics are nonideal, the configurational entropy ideal, but now a new quantity, the excess entropy, will be introduced and assumed to be constant.
\[ \Delta S_{u}^{xs} = \Delta S_{u}^{v} + k \ln W \]  \hspace{1cm} (5)

where \( S_{u}^{xs} \) is the relative partial molar excess entropy and \( S_{u}^{v} \) is the relative partial molar entropy due to vibration. The \( S_{u}^{xs} \) is free from dependence on both composition and temperature.

If this model is to be used, an expression for the configurational entropy must first be derived. If \( \theta \) is the ratio of solute to solvent atoms, \( \beta \) the number of interstitial sites per solvent atom, and \( N_{v}^{\beta} \) the number of interstitial sites, the number of distinguishable ways to arrange \( N_{u} \) solute atoms among \( N_{v}^{\beta} \) sites is

\[ W = \frac{(N_{v}^{\beta})!}{(N_{v}^{\beta} - N_{u})! \cdot N_{u}!} \]  \hspace{1cm} (6)

Therefore,

\[ S_{u}^{c} = k \ln W = k N_{v}^{\beta} \ln \frac{N_{v}^{\beta}}{N_{v}^{\beta} - N_{u}} - N_{u} \ln \frac{N_{u}}{N_{v}^{\beta} - N_{u}} \]  \hspace{1cm} (7)

and

\[ \frac{dS_{u}^{c}}{dN_{u}} = \left( \frac{\Delta S_{u}^{c}}{N_{v}^{\beta}} \right)_{T, P} = -k \ln \frac{N_{u}}{N_{v}^{\beta} - N_{u}} \]  \hspace{1cm} (8)
\[ S_u^c = -k \ln \frac{\theta/B}{1 - \theta/\beta} \]  

(8a)

The definition of the chemical potential \( \mu_u^s \) of the solid is

\[ \mu_u^s = \frac{\delta G}{\delta N_u} = \bar{H}_u - TS_u \]  

(9)

Substituting in this equation for \( S_u \) with the expression previously found

\[ \mu_u^s = \bar{H}_u - T(S_c + S_u^v) \] 

\[ \mu_u^s = \bar{H}_u - TS_u^v + kT \ln \frac{\theta/B}{1 - \theta/\beta} \]  

(10)

Since there is equilibrium between hydrogen in the gas and hydrogen dissolved in the solid, the chemical potential of the hydrogen gas must now be found. First, let us consider the dissociation of hydrogen gas into its atomic constituents from a statistical mechanics point of view. In order to do this, we need the total partition function of both the diatomic hydrogen gas and the hydrogen atom. The total partition function of the hydrogen gas is a combination
of the translational, rotational, vibrational, and electrical partition functions while the total atomic partition function has only translational and electronic parts.

The translational partition function is that of an assembly consisting of one structureless particle in a box with volume V and no externally applied potentials. The state sum will be derived classically first and then rederived quantum mechanically as a check on the accuracy.

The classical energy is:

$$\epsilon = \frac{1}{2m} \left( p_x^2 + p_y^2 + p_z^2 \right)$$  \hspace{1cm} (11)

where m is the mass of the particle, and \( p_x \), \( p_y \), \( p_z \) the momenta in the X, Y, and Z directions respectively. The translational state sum, \( q(V,T) \), follows:

$$q(V,T) = \frac{1}{N! \hbar^3} \sum_{a,b,c} \frac{p_x^2 + p_y^2 + p_z^2}{2m_0 kT} \; dx \; dy \; dz \; dp_x \; dp_y \; dp_z$$

$$= \frac{V^3}{3} \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2m_0 kT}\right] \; dp_x \; dp_y \; dp_z$$  \hspace{1cm} (12)

where \( N! = 1 \) for \( N = 1 \) and \( a, b, \) and \( c \) are the dimensions of the box. Thus,

$$q(V,T) = \frac{V^3}{3} \int_{0}^{\infty} e^{-p_x^2/2m_0 kT} \; dp_x \; \int_{0}^{\infty} e^{-p_y^2/2m_0 kT} \; dp_y \; \int_{0}^{\infty} e^{-p_z^2/2m_0 kT} \; dp_z$$
The solution to each of these integrals is

\[ \int_{\alpha}^{\infty} e^{-p_1^2/2mkT} \, dp_1 = 2 \int_{0}^{\infty} e^{-p_1^2/2mkT} \, dp_1 = 2 \left( \frac{\sqrt{2\pi mkT}}{2} \right) = \sqrt{2\pi mkT} \]

Therefore,

\[ q(V,T) = \frac{V(2\pi mkT)^{3/2}}{h^3} \quad (13) \]

If this result is to be believed, the relation must also be derivable from quantum mechanics. A well-known relation in quantum mechanics is the allowed energies of a translator in a box-with non-degenerate energy levels:

\[ \epsilon_{pqr} = \frac{\hbar^2}{8m} \left[ \frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2} \right] \quad (14) \]

where \( p, q, \) and \( r \) are positive integers. Therefore,

\[ q(V,T) = \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \sum_{r=1}^{\infty} \exp \left[ -\left( \frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2} \right) \frac{\hbar^2}{2mkT} \right] \]

\[ = \sum_{p=1}^{\infty} \exp \left( -\frac{p^2 \hbar^2}{a^2 8mkT} \right) \sum_{q=1}^{\infty} \exp \left( -\frac{q^2 \hbar^2}{b^2 8mkT} \right) \sum_{r=1}^{\infty} \exp \left( -\frac{r^2 \hbar^2}{c^2 8mkT} \right) \]

Since each of these factors will behave alike, we can take one of them to use as an example:

\[ \sum_{p=1}^{\infty} \exp \left( -\frac{p^2 \hbar^2}{a^2 8mkT} \right) = \sum_{p=1}^{\infty} e^{-\alpha^2 p^2} \quad (15) \]
for, \( H_2 \), \( \alpha = 10^{-16} \), therefore, we can replace the summation over such small intervals, \( \alpha \), with an integration.

\[
\sum_{p=1}^{\infty} e^{-\alpha^2 p^2} = \int_{0}^{\infty} e^{-\alpha^2 p^2} dp = \frac{\sqrt{\pi}}{2\alpha} \quad (16)
\]

Thus, for all three integrations,

\[ q(V,T) = \left( \frac{\sqrt{\pi}}{2\alpha} \right)^3 = \frac{V(2\pi mkT)^{3/2}}{h^3} \]

which was also found classically.

The second partition function needed is the rotational one. A reasonable assumption is the rigid rotor approxima-
tion. This model views the hydrogen molecule as a dumbbell
with the hydrogen atoms separated by a constant distance.
In this approximation, the quantum mechanical rotational
energies are:

\[ \epsilon_r = J(J + 1)\hbar^2/8\pi^2 I \quad (17) \]

where \( I \) is the moment of inertia of the diatomic molecule
and \( J \), the rotational quantum numbers.

Let \( \epsilon_r = J(J+1)\hbar c \) with \( B = \hbar(8\pi^2 Ic)^{-1} \). Each rota-
tional level has a degeneracy of \( 2J+1 \) because for each value
of \( J \), there are \( 2J+1 \) eigenstates. Thus,

\[ q_r(V,T) = \sum_{J=0}^{\infty} (2J + 1) e^{-J(J + 1)\hbar^2/8\pi kT} \]
\[ q_r(V, T) = \sum_{J=0}^{\infty} (2J + 1)e^{-J(J + 1)\rho} \]  
\hspace{1cm} (18)\]

with \( \rho = \frac{2\hbar c}{kT} = \frac{\hbar^2}{8\pi^2 I kT} \)

This sum can be expanded in an Euler–Maclaurin series as

\[ q_r(V, T) = \frac{1}{\rho} \left( 1 + \frac{\rho}{3} + \frac{\rho^2}{15} + \frac{4\rho^3}{315} + \cdots \right) \]

Since \( \rho \) is always small (0.005),

\[ q_r(V, T) = \frac{1}{\rho} = \frac{8\pi^2 I kT}{\hbar^2} \]  
\hspace{1cm} (19)\]

This result can be obtained using classical mechanics in a four dimensional phase space. The Hamiltonian for a rigid rotor with a free axis is:

\[ H(p, q) = \frac{1}{2I} \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) \]  
\hspace{1cm} (20)\]

Hence,

\[ q_r(V, T) = \frac{1}{\hbar^2} \iiint_0^\infty \frac{d\theta d\phi}{\sin^2 \theta} \int \int \int e^{-\left( \frac{p_\theta^2 + p_\phi^2}{2IkT} \right) / \hbar^2} \frac{d\theta d\phi}{\sin^2 \theta} \]

\[ = \frac{8\pi^2 I kT}{\hbar^2} \]

A symmetry number is usually included in this equation to account for any orientation dependence of the molecule.
involved. Since we are dealing exclusively with hydrogen which is homonuclear, we will neglect entering it into the equation because any one orientation is equivalent to any other.

The total partition function for non-localized indistinguishable elements is

$$Q_{H_2} = q_T \cdot q_r \cdot q_v \cdot q_{el}$$

$$= \frac{V(2\pi mkT)^{3/2}}{h^3} \cdot \frac{8\pi^2 qT}{h^2} \cdot q_v \cdot q_{el} \quad (21)$$

$$Q_H = q_T \cdot q_{el}$$

$$= \frac{V(2\pi mkT)^{3/2}}{h^3} \cdot q_{el} \quad (22)$$

Using these total partition functions, the equilibrium state of the assembly is given by

$$C_H^2 = \frac{(Q_H)^2}{-Q_{H_2}^{Q_H}} \cdot e^{-2E_0/kT}$$

$$C_{H_2} = \frac{V(2\pi mkT)^{3/2} \cdot h^2 \cdot \frac{1}{8\pi^2 qT}}{(2\pi mkT)^{3/2} \cdot h^3 \cdot q_{H_2} q_{H_2}^{q_{H_2}}} \cdot \frac{(q_{el})^2}{q_{el}} \cdot e^{2E_0/kT} \quad (23)$$

where $q_{H_2}^{q_{H_2}}$ is the vibrational partition function of the hydrogen molecule, $q_{H_2}^{q_{el}}$ the electronic partition function of the molecule, $q_{H}^{q_{el}}$ the electronic partition function of the hydrogen atom, and $-2E_0^{D}$ the dissociation energy of the
hydrogen molecule at $0^\circ$K.

The chemical potential of a gas of non-interacting particles, in terms of their concentration, is given by

$$
\mu^e_u = kT \ln \left( \frac{h^3}{(2\pi mkT)^{3/2}} \right) \frac{1}{q_H^e} + kT \ln (C_H)
$$

Setting equation 23 for $C_u$ and substituting in the above

$$
\mu^e_u = E^D_0 + kT \ln \left( \frac{h^3}{(2\pi mkT)^{3/2}} \right) \frac{h^2}{8\pi^2 kT} \frac{1}{q_{H_2}^e} \frac{1}{q_{H_2}^v} \frac{1}{\sqrt{kT}} + kT \ln (P_{H_2})^{1/2}
$$

where $C_{u_2}$ has been replaced by $P_{u_2}/kT$. $P_{u_2}$ is the pressure of the diatomic solute molecule. Equation 25 expresses the chemical potential of the hydrogen atoms in terms of the diatomic hydrogen molecule. Therefore, the electronic partition function of the hydrogen atoms does not appear in this expression.

The electronic partition function, $q_{H_2}^{el}$, is given by

$$
q_{H_2}^{el} = \sum_{e} g_e \exp\left(-\frac{e_e}{kT}\right)
$$

$$
= (2i_1 + 1)\exp\left(-\frac{e_1}{kT}\right) + (2i_2 + 1)\exp\left(-\frac{e_2}{kT}\right) + \cdots
$$

where $g_e$ is the electronic degeneracy and is equal to $2i+1$ with $i$ the number of the energy level $e$, and $e_e$ the energy of level $e_i$. The difference between the first and second
energy levels is very large. Thus, the electron will
normally stay in its ground state because of the great
amount of energy required to excite it. This means that
we can ignore all but the first term of the series above.
So

\[ q_{H_2}^{e_1} = 21 + 1 = 2 \]

where the degeneracy of the ground state of hydrogen is two.

The moment of inertia of the hydrogen molecule, the
vibrational partition function of the molecule, and the
dissociation energy can all be found by spectroscopic means.
This data\(^{(12)}\) shows that the vibrational partition function
given by

\[ q_{H_2}^{v} = \frac{1}{[1 - \exp(-h\nu/kT)]} \]

is approximately equal to one at all reasonable temperatures.

Now that we have an expression for the chemical
potential of hydrogen in the gas phase and in the solid, we
may set them equal and, simplifying, obtain

\[ \theta = \frac{\beta_{E_{H_2}}^{1/2}}{\lambda} \exp(- \frac{H_{u} - \beta_{E_{o}}}{kT}) \exp(\frac{\bar{s}_{x}}{k}) \]

(28)
where

\[
\lambda = \left[ \frac{h^3}{(2\pi m k)^{3/2}} \cdot \frac{2h^2}{8\pi^2 k} \cdot \frac{1}{k} \right]^{1/2}
\]  \hspace{1cm} (29)

and

\[
\ln(\theta T^{7/4}) = \ln(\beta P_{H_2}^{1/2}) + (- \frac{H_u - \frac{2E_D}{k}}{kT} \frac{\tilde{s}_u}{k}) + \frac{\tilde{s}_{xs}}{k}
\]  \hspace{1cm} (30)

Therefore, by measuring the solubility, \( \theta \), of hydrogen in our "binary solvent" matrix at various temperatures and plotting the data of \( \ln(\theta T^{7/4}) \) versus \( 1/T \), we can obtain

\[- \frac{H_u - 1/2E_D}{k} \]

as the slope of the line and as the intercept.

This method has been used on various elements in previous investigations and found to give good and consistent results. (13)(14) Because of the quality of results, it is indirect evidence that the quasi-regular solution model is the correct choice.
SCREENED PROTON MODEL

When discussing the effect of hydrogen on the thermodynamic properties of transition metals and their alloys, the fundamental problems are to describe how the hydrogen is dissolved and in what form the hydrogen exists within the material. The hydrogen could exist as a proton and a separate electron, a hydride ion, or in its atomic form. Nuclear magnetic resonance experiments \((15)(16)\) have shown that Knight proton shifts are observed. These shifts are consistent with the theory of the existence of hydrogen as a proton with its electron donated to the electron gas of the metal. But, to get a complete picture, another question must be answered: How is the proton bound to an interstitial site and what is its environment?

The best answer for transition metals lies in the tight binding approximation. The atoms are relatively far away from each other so that the behavior of an electron in the neighborhood of one atom is not influenced by any other. Forbidden energy bands are the result of this assumption.

The crystal orbitals are obtained by a method of linear combination of individual atomic orbitals of the
lattice atoms. The atomic bands overlap and broaden into crystal bands. The energy states at the lower part of the band are lower than the corresponding lowest atomic energy states and are due to the constructive overlap of the orbitals. Overlap increases electron densities between neighboring atoms. On the other hand, levels near the top of the band fall into antibonding orbitals which decrease the density of electrons between neighbors. This topic will be discussed in detail later.

A slight variation of the tight binding approximation is the rigid band model which states that the only differences among transition metals is the extent to which their bands are filled with electrons available from the crystal lattice members. The basic assumption here is that the structure and lattice constants are close to equivalent among the members of the transition metals. Let us consider that the only prerequisite is the common lattice constant and that common structure can be dropped. If this is assumed, we can apply the rigid band model to the entire series of transition metals. The filling of the d-band according to the Pauli Principle accounts for the variation of the cohesive energy as measured by the variation of the heat of sublimation.
The rigid band model when applied to transition metal-hydrogen systems suggests that the best treatment of the solubility data is to assume that the metallic matrix can act as an electron acceptor and the hydrogen atom as an electron donor. If this were the case, in the later transition metals, the electron would have to go into an antibonding orbital thereby decreasing the solubility. Conversely, in early transition metals, the electron would sit in a bonding orbital and increase the heat of solution with respect to the elements later in the series. This approach is consistent with the data of Gallagher and Oates. (17)

However, doubts have been cast upon the applicability of the rigid band model by the energy band calculations by Switendick. (18)(19)(20)(21) He has performed these for metallic hydrides of varying compositions and structural configurations utilizing the augmented plane wave (APW) method to solve the one-electron energy band problem.

The APW calculations are based on the assumption of a "muffin tin" potential. This potential is spherically symmetrical within some radius of the atomic position and constant in the interstitial regions. The Schroedinger equation then can be solved exactly, in spherical harmonics,
for the spheres around the atomic positions. Solutions can also be found for the interstices. The form of the interstitial solution is that of a plane wave. The APW method matches these two solutions at the surface of the sphere and, therefore, the solution for the Schrödinger equation for the entire crystal is now found. Because the energies derived by this method are dependent on the wave vector, the band structure of the metal can be computed.

The density of states at the Fermi level obtained by the APW computation is not identical to those in the pure metal plus a higher Fermi level in the hydride as predicted by the rigid band model. Instead, the density of states is modified by the introduction of hydrogen. The modification consists of the lowering of some of the energy states which were initially above the Fermi level to a point below the top of the d-bands. Observations have been made for the palladium-hydrogen system (18) and were sufficiently general to be applied to other transition metal-hydrogen systems. In fact, the Pd-H system is probably the most extensively studied metal-hydrogen system.

Since the low-lying states in palladium hydride already existed and were occupied in the palladium metal, the additional electrons associated with the hydrogen must
fill previously unoccupied states. These states are of three classes. The first is the normally expected holes or unfilled orbitals in the unmodified d-band of the pure metal. The second is a group of states located around the L point of the Brillouin Zone. The L point is in the center of one of the faces of the surface of the Brillouin Zone. These states were associated with the unoccupied top of the lowest sp-band of the pure metal. Upon addition of hydrogen these states take on the s-character of the hydrogen and fall below the top of the d-band. The final class are those sp-states above the d-band which are not filled due to the substantial energy increase associated with them.

The band gap was calculated using APW methods and verified by using a linear combination of atomic orbitals (LCAO) scheme. The atomic orbitals included one s-, three p-, and five d-orbitals for the metal and one s-orbital for the hydrogen atom.

The symmetry of the second class of modified states allows the s-like character around the hydrogen site. The zone boundary state L2 allows only odd angular momentum components (not s-components) at the lattice positions but even components at the octahedral site. Calculations for PdH$_{32}$ show that, in the absence of hydrogen-hydrogen interactions,
the states around the octahedral site are modified so that the total amount of s-character is one s-band per cell or one "s-orbital" on the interstitial site. This orbital hybridizes with the lattice s-, p-, and d-states to give the final state of the hydrogen in the metal. Switendick points out that any calculations using the total average density of states should be invalid. This average has a large d-character due to the metal d-bands. Instead, one should realize that the s-character of the electrons about the interstitials is the important effect in the screening of the dissolved proton. (21)

The description of the hydrogen atom in solution is the next problem. Let us consider the transition metal solvent, not as a lattice of discreet points with their associated electrons, but as a background of uniform positive charges exactly balanced by a superimposed electron gas so that the entire system is electrically neutral. This is a reasonable model since, as Switendick pointed out, (21) the s-character of the electrons at the interstitial provides a relatively uniform cloud of negative charge. This quantum mechanical electron gas is in its ground state. Into this "jelly" we insert a single positive charge. The Coulomb interactions cause a shield of electrons to form around this
proton. The shield screens out the entire positive charge so as to cause the electrostatic charge to diminish faster than $1/R$, where $R$ is the distance from the charge. By applying Gauss's Law, we can see that this is accomplished by displacing an electron charge equal in intensity to the positive perturbation.

Call this perturbation $\delta \phi$. A charge gradient or potential is formed, so $\delta \phi$ must satisfy Poisson's equation:

$$\nabla^2 (\delta \phi) = -4\pi e^2 \delta n(r)$$

(31)

where $e$ is the unit charge and $\delta n(r)$ is the change in the local electron density. Since the electron gas is in its lowest energy state and the volume of the solid effected by the perturbation is very small, the Thomas-Fermi approximation (20) is the logical simplifying assumption.

The local disturbance causes the Fermi level in the neighborhood of the positive charge to be raised above that for the remainder of the solid. This means that the chemical potential of the disturbance is different from that of the bulk material. However, by losing a layer off the top of the Fermi level at the point of the perturbation and distributing it over the bulk, the chemical potential is, once again, a property of the entire material. The "layer"
that is lost corresponds to the $\delta n(r)$ found in equation 31.

\[ \delta n(r) = -N(E_F)\delta \phi(r) \]  \hspace{1cm} (32)

where $N(E_F)$ is the density of states at the Fermi level. Using the expression in equation 32:

\[ \nabla^2 (\delta \phi) = 4\pi e^2 N(E_F) \delta \phi(r) \]  \hspace{1cm} (33)

\[ = \lambda^2 \delta \phi(r) \]

which has a solution of

\[ \delta \phi(r) = \frac{e^2}{r} \exp(-\lambda r) \]  \hspace{1cm} (34)

where $1/\lambda$ is the screening length. We know that the $N(E_F)$ is between 0.05 and 0.3 cal$^{-1}$ cm$^{-3}$ so the screening length varies from 0.14 to 0.67 Å. Beyond a few multiples of this distance the Coulomb effect of the proton will not be noticeable. This is the basis for the screened proton model.

To apply this model, the hydrogen must dissolve in the metal as a proton and an electron. The electron is donated to the electron gas in the metal while the proton is viewed, as above, as a small local perturbation of the Fermi level of the system. We may write the steps of this solution
and the associated enthalpies as:

\[
\frac{1}{2} \text{H}^+_2 \rightarrow \text{H}^+_M + e^-_M \quad \Delta H = H_T \\
\frac{1}{2} \text{H}^+_2 \rightarrow \text{H}^+_g + e^-_g \quad \Delta H = 15.9 \text{ ev} \\
\text{H}^+_g \rightarrow \text{H}^+_M \\
e^-_g \rightarrow e^-_M \quad \Delta H = -\phi
\]

where \( \text{H}^+_g \) and \( e^-_g \) are the hydrogen ion and its electron in the gas phase and \( \text{H}^+_M \) and \( e^-_M \) the proton and electron dissolved in the metal. \( h \) and \( \phi \) are the enthalpy of solution of the proton and the work function of the metal solvent, respectively. The total enthalpy of solution of the hydrogen in the metal is the sum of the above enthalpies so

\[
h = \Delta H_T + \phi - 15.9 \text{ ev} \quad (35)
\]

If we take the work function to be 3-5 ev,\(^{(23)}\) this means that \( h \) is a very large -11 ev. Since the perturbation of the "jellium" causes only a very small disturbance in the material, no pressure or volume changes are detectable. Therefore, the enthalpy in the previous equations may be replaced by the energy. Schnabl\(^{(24)}\) has written this energy as
\[ h = E_0 + E_{REP} + E_{POL} \]  

(36)

where \( E_0 \) is a zero point energy, \( E_{REP} \) the repulsive energy due to the Coulomb effects of the electrons surrounding the proton, and \( E_{POL} \) the polarization energy from the alignment of spins of the electrons in the screening cloud. The zero point energy is typically about 0.05 eV. The repulsive term, \( E_{REP} \), has also been shown to be small.\(^{(25)}\) Therefore, the major contribution to \( h \) will be from the polarization of the electrons.

According to Corless and March,\(^{(26)}\) the energy of the free electron gas is not changed locally due to the introduction of a perturbing potential. The potential energy of a small region immediately surrounding the perturbation will decrease to keep energy conserved, the kinetic energy of the screening electrons will increase by an equal amount. The polarization energy is identical to this increase in kinetic energy which can be calculated by taking the drop in potential, multiplying it by the increase in electron density and integrating over all space, i.e.

\[ E_{POL} = \frac{e^2}{2} \int_0^\infty \nabla V(r) \delta n(r) \cdot 4\pi r^2 dr \]  

(37)
Substituting equations 32 and 34,

\[ E_{\text{POL}} = -\frac{\lambda a^2}{4} \]  

For \( \lambda = 3 \, \text{Å}^{-1} \), \( E_{\text{POL}} \) is \(-12 \, \text{eV}\), very close to the \(-11 \, \text{eV}\) observed.

We have seen that this screened proton model predicts

\[ \Delta H_T = 15.9 - \phi + E_{\text{REP}} + E_{\text{POL}} + E_0 \]

\[ = 15.9 - \phi + E_{\text{POL}} \]  

Therefore, the total observed heat of solution will be dependent on the form \( E_{\text{POL}} \) takes. This energy will decrease upon increasing the density of states at the Fermi level. For all the transition metals, if we plot the heat of solution of hydrogen at zero solubility versus the density of states, there are two distinct lines formed. One, with negative slope, consists of points that represent the metals that have high hydrogen solubilities. The second, with a positive slope, represents metals with low absorption characteristics. There exist problems with this theory with respect to the hydride forming metals. A purely electronic theory cannot explain all their thermodynamic properties.\(^{(23)}(27)\)

However, the iron-chromium system seems to closely follow
the predictions of the simple screened proton model and a linear relationship between the heat of solution and the density of states at the Fermi level can be assumed.

\( N(E_F) \) is not an easy quantity to measure. The Fermi level itself may be approximately determined using cyclotron resonance and the deHaas-van Alphen effect. For a free electron gas,

\[
N(E_F) = \frac{3}{2} \frac{n}{E_F}
\]  

(40)

where \( E_F \) is the Fermi level energy and \( n \) is the density of electrons with energy \( E_F \). However, for the narrow d-bands with their high density of electrons, the free electron gas model is not applicable. Therefore, the density of states must be measured directly or a relation found to connect it with a measurable quantity.

Ziman\(^{(28)}\) has shown that the mean energy of a highly degenerate electron gas is

\[
\overline{E} = \int_{-\infty}^{\infty} E N(E) dE + \frac{n^2}{6} (kT)^2 \left[ \frac{\partial}{\partial E} (E N(E)) \right]_{E=\mu}
\]

(41)

where \( \mu \) is the chemical potential of the gas.

The specific heat, \( C \), is defined as the derivative of the mean energy of the system with respect to temperature.
For an electron gas, the specific heat, $C_{el}$, is

$$C_{el} = \frac{\partial E}{\partial T} = E_F N(E_F) \frac{dE_F}{dT} + \frac{\pi^2}{3} k^2 T [N(E) + E_F \frac{dN(E)}{dE}]_{E = E_F}$$

$$= \frac{\pi^2}{3} k^2 T N(E_F) + E_F N(E_F) \left[ \frac{dE_F}{dT} + \frac{\pi^2}{3} k^2 T \frac{dN(E)}{dE} \right]_{E = E_F}$$

$$= k^2 T \frac{\pi^2}{3} N(E_F)$$

(42)

where second and higher order terms have been ignored.

Thus, measuring $C_{el}$ is equivalent to measuring the density of states.

In normal metals, at normal temperatures, $C_{el}$ is very small; in fact, it makes up less than one percent of the classical specific heat of a material. At low temperatures, $C_{el}$ may be written as

$$C_{el} = \gamma T$$

(43)

where $\gamma$ is the electronic specific heat coefficient. This linear term can be easily separated from the lattice term which is proportional to $T^3$. Therefore, measurement of $\gamma$ provides information on the density of states at the Fermi level.

$$N(E_F) = \frac{3\gamma}{k^2 \pi^2}$$
The important consequence is that the electrons at the top of the Fermi distribution, i.e. those within kT of the Fermi level, are the ones that react and account for many of the properties of the material. This is valid for reasonable temperatures until the entire Fermi statistical skeleton breaks down at very high temperatures.

In applying this model to some transition metal alloys, we should be aware of some characteristic properties of transition metals. Their uniqueness is due, in part, to the incomplete 3d-shell beneath a 4s-state. This d-state is fairly compact and forms a narrow d-band when an assembly of atoms is brought together. Progressing across the row, the extra electrons are placed in the 3d-shell according to the Pauli Principle until copper is reached where the 3d-subshell is filled. Being early members of the transition elements, iron and chromium have the d-band only about half-filled with outer shell structures of $3d^64s^2$ and $3d^54s^1$, respectively. This d-band is only 1.5 eV lower in energy than the exterior s-band and, consequently, may hybridize with it to form an sd-hybrid. These hybrids are extremely important in understanding the attendant magnetic properties. The states at the bottom and top of the hybrid are predominately s-derived while those in the center are of d-character. (29)
As stated earlier, Switendick believes that the s-electrons are the primary source of screening at the interstitial site due to their high probability of existence there \(^{(19)}\) and their velocity; the s-electrons are faster than the d-electrons and, therefore, better at screening. On the other hand, the d-electrons are of high density and low velocity. The contribution to the density of states at the Fermi level is roughly proportional to the inverse of the electron velocity; the s-contribution will be low while the d- will be much greater. This contribution to the density of states has led Friedel\(^{(30)}\) to believe that the d-electrons are the major contributors to the screening in transition metals.

This alternative viewpoint to the uniform s-electrons is derived from a perturbation calculation. Perturbation theory rests on the premise that at a position \(R_i\) the interstitial ion attracts valence electrons to screen out the added charge. Thus, each Fourier component of the perturbation due to the bare proton, \(V_b(\vec{R})\), is related to the corresponding Fourier component of the screened perturbation, \(V_s(\vec{R})\), by

\[
v_s(\vec{R}) = v_b(\vec{R})/\varepsilon(\vec{R})
\]

\[(44)\]
where \( \epsilon(\mathbf{K}) \) is the Fourier component of the dielectric function and \( \mathbf{K} \) is the wave number. For lighter metals, the electrons in the intersticies act as though they were free, so a Bloch formulation would not significantly increase the reliability.

If we write the total screening charge as the sum of the contributions of the s- and d-electrons as

\[
1 = Z_d + Z_s
\]

where \( Z_d \) is the charge displaced in the d-band and, similarly, \( Z_s \) for the s-band. The density of states contribution from these bands is \( N_d \) and \( N_s \) with Bloch states \( k_d \) and \( k_s \), respectively. Therefore, \( N_d \) and \( N_s \) are the number of states per unit volume in the bands and \( k_d \) and \( k_s \) are the wave vectors.

\[
Z_d \approx N_d(E_F) \langle k_d | V_s | k_d \rangle
\]

\[
Z_s \approx N_s(E_F) \langle k_s | V_s | k_s \rangle
\]

where \( V_s \) is the total screened perturbation. Since the tight binding approximation is used, the atomic orbitals are considered to be localized on a particular atom and may be linearly combined to obtain the orbitals of the crystal. Therefore, \( \langle k_d | V_s | k_d \rangle \) may be written as a summation:
\[ \langle k_s | V_s | k_s \rangle = \frac{1}{n} \sum \langle \text{id} | V_s | \text{id} \rangle \]  

where there are \( n \) atoms in the crystal. And

\[ \langle k_s | V_s | k_s \rangle \geq \overline{V}_s \]  

(49)

There is probably little overlap of the \( d \)-functions in the interstitial regions because of their high degree of directionality. The \( s \)-band has spherical symmetry and will be a much more efficient screen in the interstitial region, therefore

\[ \langle k_d | V_s | k_d \rangle \leq \langle k_s | V_s | k_s \rangle \]  

(50)

The effect of the density of states in each band will make \( Z_s \) not as large as \( Z_d \) because of the large difference in \( N_s(E_F) \) and \( N_d(E_F) \).

There is also experimental evidence to indicate that the \( d \)-band screening is predominant:

1. The energies of solution are more negative for some transition metals than for light "normal" metals. This indicates the greater role of the \( d \)-bands.

2. At high hydrogen concentrations, the \( d \)-bands fill.

3. Other interstitial solutes seem to donate their electrons to the \( d \)-band. Genin\(^{(31)}\) has measured the hyperfine
magnetic coupling of iron and interstitial solutes by Mossbauer spectroscopy. The magnetic moment of the iron atoms decreases in the neighborhood of a carbon or nitrogen atom.

There seems to be justifiable evidence for both theories, either s- or d-electron screening. Using hydrogen solubility measurements, this conflict could be resolved. By measuring this solubility on either side of the Curie temperature, any shift could be detected. If there is no shift in solubility upon crossing this transition temperature, the s electrons must be predominant in screening the proton. Since magnetism is due to the exchange interaction of the d-electrons, if the d-electrons screen the proton, the magnetic interaction must influence the hydrogen solubility.

Serious problems occur when the simple screened proton model is applied to metals which form hydrides and are poor adsorbers. Neither exchange nor correlation forces are considered in the derivation. Exchange forces are those associated with the anti-symmetry of the wave function. The electrons are always magnetically polarized, either spin "up" or spin "down" and are governed by Hund's rule. Exchange forces come into play when the impurity, in this case the
hydrogen atom, is dissolved and forms either excess up or down states. The correlation forces are those due to the Coulomb interaction among the screening electrons around the impurities. If very dilute solutions are considered, correlation effects would be minimized. Both effects are long range and quite strong and must, in any rigorous theory, be taken into account.

The consideration of correlation and exchange effects necessitates approaching the problem from a new angle, the many-body calculation. Pines\(^{(32)}\) and Nozieres\(^{(33)}\) were the initiators of this route. The basic premise is that a bare ion lies in a sea of electrons where it is effected by the potential of all other ions in the lattice. This total self-consistent potential (a Hartree-Fock potential) is simply a superposition of the individual self-consistent potentials of the separate ions. The form of the potential within the ion-core (the rare gas configuration) need not be considered since the electrons in the gas will not be present there.

Each ion carries with it a screening charge so that the pair may be treated as a unit. When several are brought together, they interact as if they were in free space. This concept is the foundation of the pseudo-potential theory of metals. Using this theory, Ziman\(^{(34)}\) obtains
\[ U_s(r) = -\frac{Ze^2}{r}\exp(-\lambda r) \]

where \( U_s(r) \) is the self-consistent Hartree-Fock potential of an individual ion, \( Ze \) the charge of the impurity atom, \( \lambda \) the screening length, and \( r \) the distance from the origin atom. \( U_s(r) \) is exactly the result found earlier using the much simpler Thomas-Fermi approximation of the screened proton model. This is confirmation of the validity of our original model.

With the perturbation approach, Bardeen\(^{(35)}\) has calculated the dielectric function to a good approximation, ignoring exchange effects,

\[ \epsilon(K) = 1 + \frac{4\pi e^2 N(E_F)}{K^2} \left[ \frac{3}{2} + \frac{4k_F^2 - K^2}{8k_F^2 \ln \frac{2k_F + K}{2k_F - K}} \right] \quad (51) \]

where \( K \) is the wave number of the perturbation, \( N(E_F) \) the density of states at the Fermi level, \( E_F \), and \( k_F \) the Fermi radius. When \( K \) is twice the Fermi radius, there is a singularity in the logarithmic term in the derivative of \( \epsilon(K) \). This condition should be enough to produce oscillations in \( U_s(r) \) at very long distances. These oscillations do, in fact, exist and were studied by Friedel,\(^{(36)}\) Kohn and Vosko,\(^{(37)}\) Blandin \textit{et. al.},\(^{(38)}\) and March and Murray.\(^{(39)(40)}\)
Friedel\(^{(36)}\) has found that, at large distances from the ion, there is a periodic variation in the charge density, \(\delta n(r)\), as

\[
\delta n(r) \propto \frac{1}{r^3} \cos(2k_r r)
\]  

(52)

This function does not decrease as rapidly as the screening function with the result that these effects are "felt" over a longer distance than would be expected. This approach helps to explain the interaction of impurities over some distance within the crystal, another reason for the importance of maintaining dilute solutions of hydrogen in the "binary solvent."

As pointed out in the previous section, the partial enthalpy of solution of the hydrogen atom may be determined. If this curve is linearly proportional to the electronic specific heat coefficient curve, the comparison may be viewed as direct experimental evidence for the validity of the screened proton model. Fortunately, the specific heat coefficient versus composition curve of the iron chromium system shows a sharp peak that may be used as a convenient reference point.

The screened proton model gives a very good picture of the dissolution of hydrogen in transition metals and
greater validity is ascribed to it since two different derivations from two different formulations are possible. Finally, long range effects can be accounted for by assuming exchange effects.
EXPERIMENTAL PROCEDURE

Solid solutions of chromium and iron were made by melting Marz grade material with an arc melter under argon. The starting materials were first etched in a hydrochloric acid - nitric acid solution to remove exterior contaminants and oxide layer. The purity of these materials is shown in Table I. Due to the weight loss of the materials in etching and the high vapor pressure of chromium at its melting point, the combined weight of iron and chromium was greater than the final sample weight by approximately one-tenth of a gram. The final weight of the samples was between seven and ten grams. Since there was some uncertainty as to the composition of the samples, all compositions were determined by wet chemical analyses. See Table 2 for exact sample compositions and weights.

The solubility of hydrogen in these binary solid solutions was measured by equilibrating the samples with high purity hydrogen (nominal purity 99.9995 volume % and less than 1 ppm by volume of hydrocarbons) at one atmosphere pressure, quenching the equilibrated samples and analyzing them for hydrogen. A schematic diagram of the system is
shown in Figure 3. Thermocouple wires of Pt-10% Pt-Rh were used to monitor the temperature and also to serve as support wires. Small holes (1/16 inch) were drilled in each sample and the thermocouple wires threaded through and attached the alligator clips on the break seal.

The specimens were heated to the desired equilibration temperature using a Lepel high frequency generator. The control of the generator was able to maintain the desired temperature within two degrees over an extended period. The break seal mechanism enabled the samples to be quenched without breaking the gas tight seal. The quenchant used was cooled methanol. Any additional hydrogen dissolved in the sample during quenching was undetectable. Previous investigations (13) showed that the hydrogen solubilities were consistent using this quenchant.

Hydrogen analyses were performed using a modified Leco apparatus in which the pressure of the H₂ evolved from the specimen by hot vacuum extraction is measured in a known constant volume. Conversion of the hydrogen to H₂O vapor by rare earth base copper oxide enables an inert gas correction to be made. The analytical system was calibrated volumetrically by expanding a known amount of pure dry hydrogen into the measuring volume and these measurements were confirmed
using National Bureau of Standards unalloyed titanium samples. With the specimens used, each weighing between three and eight grams, hydrogen levels of between 0.1 and 15 ppm by weight could be determined. Since no diffusivity data for hydrogen in iron-chromium alloys was available, approximate diffusivities were estimated by measuring the outgassing times at low temperatures during the analysis phase. These approximate diffusivities along with that of pure iron were used to estimate the times necessary to ensure that equilibrium had been achieved. Solubilities were also compared for differing equilibration times. Those solubilities that were consistent determined the times used. Each hydrogen solubility of the solid solution samples was measured between $500^\circ C$ and $1250^\circ C$.

In the composition range 30% to 65% chromium, the sigma phase of the iron-chromium system occurs. The optimum annealing treatment has been described in the literature. For 99% sigma phase in a 46% chromium-iron alloy sample (the center of the sigma phase region), a heat treatment of three hours at $700^\circ C$ is prescribed. Samples of composition 45.26% and 49.55% were annealed at $750^\circ C$ for three and one half hours in order to produce this phase. The presence of the ordered phase was checked metallographically. Using standard
metallographic techniques, a sample of the sigma phase alloy was mounted, polished and etched with Emmanuel's reagent \((K_3Fe(CN)_6, KOH, H_2O)\). This phase is identified in Figure 4. The hydrogen solubility in the ordered material was measured in the same manner as was used for the other samples.

The usual experimental procedure for determining the hydrogen solubility of a specific alloy at a particular temperature is as follows:

1. Place the sample in the vertical tube and support it by the thermocouple wires that are attached to the detachable alligator clips on the break seal assembly.

2. Flow the hydrogen by the sample for five to ten minutes to flush most of the air from the column.

3. Turn on the radio frequency generator and heat the sample to the desired temperature as indicated on the potentiometer.

4. After reaching equilibration temperature, maintain the sample at that temperature for thirty minutes if above 700°C and forty-five if below. Sigma phase samples should be maintained for 210 minutes at 750°C and then sixty minutes at the desired equilibration temperature.

5. When the desired time has passed, use the break
seal assembly to drop the sample into chilled methanol.

6. Dry and clean sample with acetone then place in Leco vacuum apparatus.

7. Let the vacuum pumps lower the pressure in the analysis system until it is unmeasurable by tilting the McLeod gauge.

8. Close off the system from the pumps and allow to sit for five minutes then check pressure again. If pressure appears, there is a leak in the system which needs repair.

9. If there is no leak, heat sample and measure pressure that appears. Take readings at five minute intervals until pressure levels off. This is the total pressure of the gas given off by the sample.

10. Close the valve to isolate the sample, cut off the radio frequency generator, allow the gas to circulate through the copper oxide catalyst and anhydrome for ten minutes. Measure this pressure. This is the pressure of the gases other than hydrogen which are dissolved in the sample.

11. Subtract the second pressure from the first and use this value in the following equation for the solubility $\theta$:
\[ \theta = \frac{V_c P}{W} \times MW \quad (53) \]

where \( V_c \) is the volume of the Leco system, \( P \) the difference in the pressures, \( W \) the weight of the sample, and \( MW \) the molecular weight of the alloy used.
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### TABLE II

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*After etching

All weights are in grams
Figure 3. Schematic diagram of hydrogenation and analysis equipment.
Figure 4. Micrograph of 45.26% Cr sample. 80X. Dark areas are sigma phase.
RESULTS

Previous analyses of experimental data have extracted the relative partial quantities $\Delta \overline{H}_u = \overline{H}_u - \frac{1}{2} \overline{H}_2^0$ and $\Delta \overline{S}_u = \overline{S}_u - \frac{1}{2} \overline{S}_2^0$. Unfortunately, since both $\overline{H}_2^0$ and $\overline{S}_2^0$ vary with temperature, especially at low temperature, the values of $\Delta \overline{H}_u$ and $\Delta \overline{S}_u$, presumably obtained at some mean temperature, do not give unambiguous information on the temperature and composition dependence of $\overline{H}_u$ and $\overline{S}_u$. Consequently, the decision was made to measure $\overline{H}_u$ and $\overline{S}_u^{xs}$ directly where

$$\overline{S}_u^{xs} = \overline{S}_u^{\text{observed}} - \overline{S}_u^{\text{ideal}}$$

The solubility measurements made by the method outlined earlier are depicted in Figure 5 and Figure 6. These figures are plots of $\ln \Theta T^{7/4}$ versus $1/T$ where $\Theta$, the concentration unit, is given by equation 53. The partial molar enthalpy of the solute atoms with respect to an atom at rest in a vacuum and the partial excess entropy is $\overline{S}_u^{xs}$. These two quantities are found by measuring the slope of the above plots for $\overline{H}_u$ and the intercept for $\overline{S}_u^{xs}$. The exact expressions are
\[ \bar{H}_u = -km + \frac{1}{2} \bar{E}_o^D \]

\[ \bar{S}^xs_u = k(b - \beta \bar{P}^{1/2}_H) \]

where \( m \) is the slope of the plot and \( b \) its intercept. The other terms are defined in the section on solution models.

The constant \( \beta \) above is the number of interstitial sites per solvent atom. \( \beta \) is not known for all metals but the bulk of evidence accrued from neutron scattering experiments indicates that the tetrahedral sites, for which \( \beta = 6 \), in body centered cubic metals are occupied by hydrogen atoms. For face centered cubic and hexagonal closest packed metals, the hydrogen atoms are located in the octahedral sites for which \( \beta = 1 \).

Gallagher and Oates\(^{(44)}\) have shown that there are two linear correlations between \( \bar{S}^xs_u \) and \( \bar{H}_u \) for hydrogen-metal solutions. One correlation is valid for B.C.C. metals and the other for closest packed metals although a lattice effect is also apparent. The experimental values of \( \bar{H}_u \) and \( \bar{S}^xs_u \) for hydrogen in \( \alpha \)-phase (B.C.C.) iron agree well with the correlation of Gallagher and Oates for B.C.C. metals, but those for the Cr-H system\(^{(1)}\) are close to the correlation for close-packed metals. Furthermore, some preliminary data from
ion-channeling using hydrogen-implanted chromium indicates that hydrogen atoms may indeed occupy the octahedral sites in chromium.\(^{(45)}\) In this investigation, no solubility shifts of the kind that would result from a change in the occupancy of a given type of interstitial site were observed. Since we are dealing with data obtained in the \(\alpha\)-phase region of the iron-chromium phase diagram, the site occupied by the hydrogen atom is assumed to be tetrahedral and, therefore, \(\beta = 6\). It is possible for the hydrogen to occupy the octahedral sites in both chromium and iron; however, the use of a different value for \(\beta\) only affects the extraction of the excess entropy and not the values of the partial enthalpy. Figures 5 and 6 show that the plots of \(\ln \theta T^{7/4}\) versus \(1/T\) are linear. A linear least squares regression of the data yields the values of \(\overline{H}_u\) and \(\overline{S}_u^{xs}\) shown in Table III.

The intercepts and slopes of the straight lines representing the data were found using a standard linear least squares analysis. The error of the data was calculated by determining the 90% confidence interval of this t-distribution with \(n-2\) degrees of freedom where \(n\) is the number of observations.\(^{(46)}\)
<table>
<thead>
<tr>
<th>Atomic % Cr</th>
<th>Phase Field</th>
<th>$-\bar{H}_u$ kcal/mole</th>
<th>$\bar{S}^{\text{xs}}_u/k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.12</td>
<td></td>
<td>42.09 ± 0.25</td>
<td>1.56 ± 0.56</td>
</tr>
<tr>
<td>13.53</td>
<td></td>
<td>38.91 ± 0.22</td>
<td>3.41 ± 0.52</td>
</tr>
<tr>
<td>17.43</td>
<td></td>
<td>38.71 ± 0.13</td>
<td>3.43 ± 0.45</td>
</tr>
<tr>
<td>45.26</td>
<td></td>
<td>36.92 ± 0.18</td>
<td>4.16 ± 0.49</td>
</tr>
<tr>
<td>47.50</td>
<td>$\alpha$</td>
<td>38.12 ± 0.32</td>
<td>3.66 ± 0.56</td>
</tr>
<tr>
<td>49.44</td>
<td></td>
<td>38.31 ± 0.19</td>
<td>3.64 ± 0.50</td>
</tr>
<tr>
<td>61.02</td>
<td></td>
<td>39.90 ± 0.15</td>
<td>2.74 ± 0.48</td>
</tr>
<tr>
<td>69.04</td>
<td></td>
<td>37.32 ± 0.14</td>
<td>3.82 ± 0.46</td>
</tr>
<tr>
<td>84.54</td>
<td></td>
<td>36.92 ± 0.21</td>
<td>3.84 ± 0.52</td>
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<tr>
<td>5.12</td>
<td>$\gamma$</td>
<td>41.69 ± 0.20</td>
<td>2.25 ± 0.51</td>
</tr>
<tr>
<td>45.26</td>
<td>$\sigma$</td>
<td>37.12 ± 0.18</td>
<td>4.09 ± 0.49</td>
</tr>
<tr>
<td>49.44</td>
<td></td>
<td>37.92 ± 0.19</td>
<td>3.75 ± 0.50</td>
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</tbody>
</table>
Figure 5. Variation of $\ln T^{7/4}$ with $1/T$. 
Figure 6. Variation of $\ln T^{\frac{7}{4}}$ with $\frac{1}{T}$
DISCUSSION OF RESULTS

We have assumed in this investigation that hydrogen dissolves as atomic hydrogen and then dissociates into an electron and a proton. Sievert's Law is the basis for this prediction. A simple derivation of this law shows how reasonable this assumption really is. (47)

If we have a diatomic gas $X_2$ ($X_2$ may be $H_2$, $O_2$, $N_2$, etc.) in equilibrium with a metal, $M$, $X_2$ can dissolve either as $X_2$ or $X$. We can have for the equilibrium

$$X_2(g) = X_2(M)$$

or

$$1/2X_2(g) = X(M)$$

where $g$ signifies solution in the gas phase and $M$ the metal phase. For the first, the equilibrium constant $K$ is

$$K_1 = \frac{h_{X_2}(g)}{p_{X_2}(g)}$$

and for the second

$$K_2 = \frac{h_{X(M)}}{p_{X_2}^{1/2}(g)}$$ (54)
where $h_x$ is the activity of the atomic gas, $h_{X_2}$ the activity of the diatomic gas, and $P_{X_2}(g)$ the pressure of the diatomic gas.

Whether the gas dissolves atomically or molecularly can be ascertained experimentally by determining which equilibrium constant, $K_1$ or $K_2$, is actually constant. It is invariably found that $K_2$ is observed, indicating that atomic solution occurs and equation 54 is the correct expression for equilibrium and Sievert's Law.

It is clear from the discussion presented earlier that there is a departure from Raoultian behavior in the Fe-Cr binary system. At least a proportion of the positive deviation from Raoult's Law can be ascribed to deviations from the ideal distribution. The fact that the H-atoms in the ternary solution obey Henry's Law is due to the low solute concentrations and the energetics of solution formation. The term in the chemical potential of the solute atoms resulting from the partial configurational entropy is $-k\ln \theta$, so that at the low concentrations observed in these solutions, the entropy exerts a large force to render the H distribution random. If the pairwise interaction energy between H and Fe were large compared to that between H and Cr, the possibility of non-random solute distributions due to a preference of the H-atoms to be located nearest to a given
kind of solvent neighbor would arise. The difference between these energies is given by

\[ \Delta \varepsilon = \frac{\bar{H}_u(\text{Fe}) - \bar{H}_u(\text{Cr})}{Z} \]  

(55)

where \( Z \) is the coordination number of the solvent lattice. The value of using the data for the \( H_u \)'s in the literature is \( = 0.7 \) kcal./mole. Thus, at \( 700^\circ \text{C} \), \( \Delta \varepsilon/kT \) 0.35 so that a random distribution is to be expected.

The fact that the plots of \( \ln \theta T^{7/4} \) versus \( 1/T \) shown in Figures 4 and 5 are linear can be taken as a consequence of the adherence to Sievert's Law and the fact that the \( H \)-atom distribution in the ternary solution is random. Thus, the assumptions implicit in the derivation of the quasi-regular solution model are validated through these experiments.

It is interesting to note that on equilibrating with the \( \sigma \)-phase material there is no solubility discontinuity with respect to the substantially disordered \( \sigma \) solid solution. Flanagan, Majchrzak, and Baranowski (48) have studied \( H \) solubility in the ordered \( \text{FePd}_3 \) phase. This solid absorbs approximately ten times the amount of \( H \) at 200 atmospheres and \( 25^\circ \text{C} \), than does the disordered solution. However, at such low temperatures the solute distribution is determined principally by the energetics of solution
formation and not by the entropy changes. Even if $\Delta\varepsilon$ is small, $\Delta\varepsilon/kT$ can be greater than unity and it is not surprising that the $H$-atoms preferentially locate in the site in the FePd$_3$ structure in which it has only Pd nearest neighbors.

Also of interest is the possible solubility discontinuity due to magnetic interaction between the solvent lattice and the hydrogen. This discontinuity should occur at the Curie point. In this investigation, three samples were measured through the Curie point and no discernable effect was produced by the magnetic change. This seems to indicate that magnetic properties of the solvent lattice, at least in the iron-chromium system, have little, if any, effect on the solubility of hydrogen.

Using the data from the slopes and intercepts of Figures 5 and 6 and the predictions by Ebisuzaki and O'Keefe (23) as summarized in the screened proton model section, we can correlate the partial enthalpy and the electronic specific heat to obtain information on the behavior of the density of states at the Fermi level.

The low temperature specific heat of Fe-Cr solid solutions has been investigated extensively by Cheng, Wei, and Beck (49). Their data for the variation of $\gamma$ with
composition are illustrated in Figure 7 together with the \( \bar{H}_u \) values obtained in the present investigation. Cheng, Wei, and Beck concluded that the peak found in \( \gamma \) for Fe-Cr (and also Mn-Cr and Fe-V) solutions is a true electronic specific heat coefficient and not an anomaly connected with a phase transformation, or a contribution to the specific heat due to spin waves as explained by Ebisuzaki and O'Keefe. (23)

A comparison of the \( N(E_F) \) versus Fermi energy curve calculated from the experimental \( \gamma \)-data bears a close resemblance to that calculated using the tight binding approximation (28) so that Cheng et al. conclude that the density of states interpretation of the measured specific heat coefficients is not inconsistent with theory. It is interesting to note that there is also a peak in the \( \bar{H}_u \) values in the chromium rich solutions in the vicinity of the \( \gamma \)-peak. It is tempting to think of the two peaks as representing a confirmation of the screened proton model. However, it is not easy to explain why they are not coincident if this were indeed the case.

The electronic specific heat coefficient is measured at extremely low temperatures in order to separate the effect of the electron gas from the lattice effects. The solubility
measurements, on the other hand, were made at room temperature and above. It is difficult to assume that the electronic specific heat coefficient is constant over such a large temperature range. Thus, the shift in peaks may be due to the temperature dependence of $\gamma$. Additional work needs to be done on measuring this phenomenon in order to correlate partial enthalpy of solution of the hydrogen atom data with these possible shifts.

The lack of a solubility shift upon crossing the Curie temperature seems to verify Switendick's proposed screening of the proton by the s-electrons. However, the similarity of the $\gamma$ and $\bar{H}_u$ curves in Figure 7 gives added credence to Friedel's model of d-electron screening since the electronic specific heat coefficient is directly proportional to the density of states at the Fermi level. $N(E_F)$ has its major contribution in the d-electrons so this similarity in curve shapes might be due to proton d-electron interaction.

The results obtained in this investigation show that more data of this nature, especially for other transition element binary solvent matrices, are desirable. The chromium-manganese system also shows a peak in the electronic specific heat, as does the iron-vanadium system, and it would be very
instructive if hydrogen solubility measurements were made on these systems. To obtain more data on stainless steels, the chromium-nickel system should be studied and those results, coupled with Stafford and McLellan's\(^{(50)}\) and these, would give a more complete picture as to how stainless steels react to hydrogen.

To fully determine which electrons screen the proton, electrical conductivity measurements should be made. The s-electrons exist in the interstices and contribute to the conductance of the metal. The d-electrons occur primarily between nearest neighbor solvent atoms and do not contribute significantly to the conductance. Consequently, resistance changes upon the solution of hydrogen in a series of alloys could measure the change from s- to d-electron screening and its relation to the structure of the alloy.

Finally, mention must be made of possible improvements to the experimental technique. The heat capacity of methanol at 0°C is lower than that of water cooled to the same temperature. The possible contamination of the samples due to the carbon in methanol is an everpresent probability. Thus, a change in quenchant to water should be made in order to preserve the cleanliness of the sample and prevent the introduction of extraneous hydrogen. Similarly, when hot
samples are removed from the extraction phase, they should be quenched in water rather than methanol or acetone. Consideration should also be given to the possibility of cleaning the sample with something other than acetone.
Figure 7. Comparison of the composition variation of $\bar{H}_u$ and $\gamma$, the electronic specific heat coefficient.
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