Diffusion of Hydrogen in Titanium Alloys Due to Composition, Temperature, and Stress Gradients

J. L. WAISMAN, GEORGE SINES, AND L. B. ROBINSON

A theoretical and experimental study was conducted to determine the combined effects on interstitial diffusion in metals of gradients in interstitial concentration, in solvent composition, in stress, and in temperature. The theory consolidates relationships, some of which have been previously published. It is based on macroscopic irreversible thermodynamics, and is applicable to anisotropic or isotropic materials. Experiments were conducted and literature analyzed to determine the numerical quantities required to predict the change in hydrogen distribution with time for pure and alloy titanium, where the solvent gradient, stress gradient, and temperature gradient are constant with time. The diffusion driving forces for solute gradient, solvent gradient, and stress gradient are related to the effect of each factor on hydrogen activity. In addition, the material property which determines the diffusion driving force of a stress gradient for anisotropic material is a matter tensor analogous to the scalar partial molal volume used for isotropic material. The experiments, conducted with commercially pure titanium and titanium alloy, 6Al-4V, consist of measuring the effect of alloy additions and stress on the hydrogen activity in solid solution and the dilatation effect of hydrogen. Stress states tested were tension, compression, and torsion. The measurements were made by exposing titanium and the alloy to hydrogen at temperatures from 600° to 800° C, and measuring the equilibrium hydrogen gas pressure at various solid solution hydrogen contents. Both materials were tested with and without stress. Tension decreased the activity, compression increased it, and torsion had no effect. This is consistent with the stress effect theory of Li, Oriani, and Darken. The stress effect corresponds to an apparent partial molal volume of 1.7 to 2.2 cm^3/mol, depending on the alloy and hydrogen content.

THIS study was motivated by the need to predict quantitatively the mass movement of hydrogen in titanium where such movement is caused by gradients other than the solute concentration gradient. This need arose when catastrophic failure of an important pressure vessel occurred. Subsequent investigation of the failure indicated that, during storage of the pressure vessel at temperatures near room temperature for $1\frac{1}{2}$ years, an initially uniform hydrogen distribution became highly segregated. The segregation took the form of an almost continuous line of brittle titanium hydride near a weld fusion line where the failure initiated. The pressure vessel was constructed from 6Al-4V-Ti alloy and welded with commercially pure filler rod.

Fig. 1 is a photomicrograph of the offending microstructure. During the course of manufacture, the zone in which the failure originated had been subjected to a temperature gradient during welding, a solvent (or alloy) concentration gradient at the fusion line, residual stresses due to the welding, and stresses applied during test and operation. The complete explanation of the failure requires an explanation of the hydrogen diffusion, the subsequent precipitation of titanium hydride and finally crack propagation under stress. This study is concerned only with the hydrogen diffusion.

It is known[1,2] that such diffusion can be caused not only by solute concentration gradients, but by other gradients such as solvent concentration,[1] stress,[2] and temperature.[3] However, the theory for these driving forces has not been consolidated, and the experimental data required for its use are not available for specific cases.

This study will present the equation for the hydrogen flux and change in distribution induced by the four factors listed above and experimental data applicable to hydrogen in titanium and in a titanium alloy. Part I will develop the consolidated equation and Part II will present the experimental data of this study together with other data extracted from the literature.

PART I. THE FLUX EQUATION

General

It was desirable to develop a differential equation for diffusion which contains quantities that can be determined experimentally. A theory based on Thermodynamics of Irreversible Processes (T.I.P.) is used which gives a clear picture of the assumptions and qualifications inherent in the equations.

T.I.P. is applicable to spontaneous processes,[4] except those which occur at high rates and with high gradients, such as in a flame front or in an explosive reaction. It applies to fluxes of mass or heat caused by appropriate spatial gradients, and to rates of a chemical reaction caused by deviations from equilibrium. Although T.I.P. can include the effect of any field, electric, magnetic, and gravitational fields were ignored in this work because they are assumed to be unimportant in the cases of interest.

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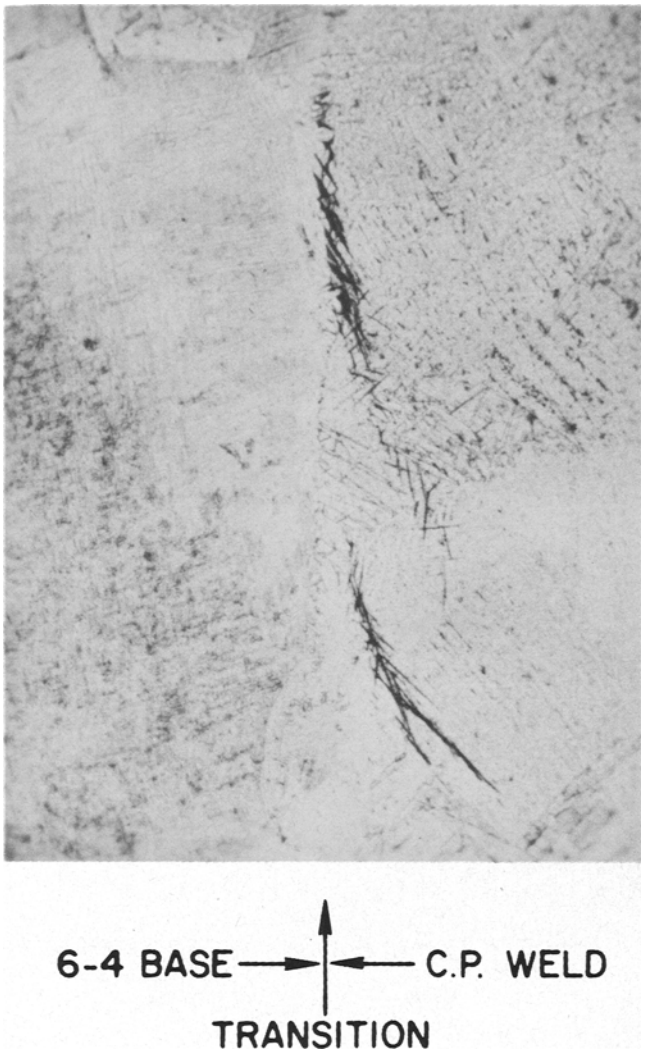

Fig. 1—Dark etching hydride needles near the edge of a weld in titanium. Magnification 100 times.

The gradients causing diffusion of matter or heat may be called forces, **X**. If j species are present, including heat as a species, if we ignore vacancy diffusion since our interest is in interstitial diffusion, and if each force can cause any flux, the flux of species i is:

$$\mathbf{J}_i = \sum_j L_{ij}\mathbf{X}_j$$

where the L_{ij} are called the phenomenological coefficients. For a system consisting of a mobile species, m, three stationary matrix species 1, 2, 3, and with heat flow Q,

$$\begin{aligned} J_m &= L_{mm}X_m + L_{m1}X_1 + L_{m2}X_2 + L_{m3}X_3 + L_{mQ}X_Q \\ J_1 &= L_{1m}X_m + L_{11}X_1 + L_{12}X_2 + L_{13}X_3 + L_{1Q}X_Q \\ &\bullet \qquad\qquad \bullet \\ &\bullet \qquad\qquad \bullet \\ J_Q &= L_{Qm}X_m + L_{Q1}X_1 + L_{Q2}X_2 + L_{Q3}X_3 + L_{QQ}X_Q \end{aligned} \qquad [1.1]$$

The mobile hydrogen flux $\mathbf{J}_m$ is the flux of interest, with the coefficients L_{m1}, L_{m2}, L_{m3} representing the interaction between $\mathbf{J}_m$ and the forces $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$. Intuitively, one would expect a negligible effect of the $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$ since species 1, 2, 3 are stationary at the temperatures of interest. This is confirmed as follows by the formalism of Eq. [1.1] and the Onsager theorem, $L_{ij} = L_{ji}$. (Application of the Onsager theorem requires use of forces and fluxes conforming to Eq. [1.3] below.)

Table I. Diffusion of Various Solutes in Titanium as Solvent

Solute	Phase of Ti	D 800°C, cm²/s	D_O, cm²/s	Q_O, cal/mole	Author	Ref
H	α	5.6×10^{-5}	1.8×10^{-2}	12,380	Wasilewski and Kehl	21
H	β	9.0×10^{-5}	1.9×10^{-3}	6,640		
O	β	2.8×10^{-10}	1.6	48,200	Wasilewski and Kehl	22
N	α	7.7×10^{-12}	1.2×10^{-2}	45,200		
N	β	4.8×10^{-8}	3.5×10^{-2}	33,800		
C	α	7.6×10^{-9}	5.06	43,500	Wagner, *et al.*	23
C	β	1.6×10^{-8}	108	48,400		
Al	α	3.8×10^{-11}	1.6×10^{-5}	23,700	Goold	24
Al	β	5.0×10^{-10}	1.4×10^{-5}	21,900		
V	β	5.0×10^{-11}	6.0×10^{-3}	39,600		

$$D = D_O \exp\left(-\frac{Q_O}{RT}\right)$$

D = Diffusivity.
D_O = Temperature independent factor of diffusivity.
Q_O = Activation energy for diffusion.

According to Table I, the diffusivities of elements other than hydrogen are negligible compared to that of hydrogen, or $\mathbf{J}_1 \cong \mathbf{J}_2 \cong \mathbf{J}_3 \cong 0$. Since $\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3 \neq 0$, therefore $L_{1m} \cong L_{11} \cong L_{12} \cong L_{13} \cong 0$, and similarly for the $\mathbf{J}_2$ and $\mathbf{J}_3$ equations. By the Onsager theorem, therefore $L_{m1} \cong L_{m2} \cong L_{m3} \cong 0$. Similarly, $L_{Q1} \cong L_{Q2} \cong L_{Q3} \cong 0$.

Therefore we use

$$\begin{aligned} \mathbf{J}_m &= L_{mm}\mathbf{X}_m + L_{mQ}\mathbf{X}_Q \\ \mathbf{J}_Q &= L_{Qm}\mathbf{X}_m + L_{QQ}\mathbf{X}_Q \end{aligned} \qquad [1.2]$$

To determine the explicit form of the thermodynamic forces $\mathbf{X}_m$ and $\mathbf{X}_Q$, we use the conjugate forces and fluxes which are identified by T.I.P.[4,5] as those which fit the relationship

$$(\Delta\dot{S})T = \sum_i \mathbf{J}_i \cdot \mathbf{X}_i \qquad [1.3]$$

where $\Delta\dot{S}$ is the rate of entropy production accompanying the irreversible processes, and T is the absolute temperature. For our choice of flux the thermodynamic forces $\mathbf{X}_m$ and $\mathbf{X}_Q$, have been shown to be[4,6]

$$\mathbf{X}_m = -T\nabla\left(\frac{\mu_m}{T}\right); \quad \mathbf{X}_Q = -\frac{\nabla T}{T} \qquad [1.4]$$

where μ_m is the chemical potential of m. Conservation of mass and energy are implicitly included in Eqs. [1.3] and [1.4]. The first portion of Eq. [1.2] thus becomes

$$\mathbf{J}_m = -L_{mm}\left[T\nabla\left(\frac{\mu_m}{T}\right) + \frac{L_{mQ}}{L_{mm}}\frac{\nabla T}{T}\right] \qquad [1.5]$$

The thermodynamic significance of L_{mQ}/L_{mm} can be seen by defining a quantity Q which is the quantity of energy transported by each mole of mobile constituent m at constant temperature,

$$Q \equiv \left(\frac{\mathbf{J}_Q}{\mathbf{J}_m}\right)_{\nabla T=0}$$

Consistent with Eq. [1.2], since $L_{ij} = L_{ji}$, and $\mathbf{X}_Q = 0$ when $\nabla T = 0$.

$$Q = \frac{L_{Qm}}{L_{mm}} = \frac{L_{mQ}}{L_{mm}} \qquad [1.6]$$

so that Eq. [1.5] becomes

$$\mathbf{J}_m = -L_{mm}\left[T\nabla\left(\frac{\mu_m}{T}\right) + Q\frac{\nabla T}{T}\right] \qquad [1.7]$$

Since by thermodynamics $\mu_m = \bar{H}_m - \bar{S}_m T$, and $d\mu_m = RT\, d \ln a_m - \bar{S}_m dT$ where $\bar{S}_m$ and $\bar{H}_m$ are partial molal entropy and partial molal enthalpy respectively and a_m is the activity of m, and since the heat of transport is defined as $\mathbf{Q}^* \equiv \mathbf{Q} - H_m$, where H_m is the molal enthalpy of m, and $(d\mu_m)_T = RT\, D \ln a_m$.

$$\mathbf{J}_m = -L_{mm}\left[RT(\nabla \ln a_m)_T + \frac{Q^*}{T}\nabla T\right] \qquad [1.8]$$

Here we have grouped all factors having a ∇T dependency in the $\mathbf{Q}^*\, \nabla T/T$ term, and those factors not dependent on the ∇T in the term $RT(\nabla \ln a_m)_T$, using the subscript T to remind us of the grouping.

Since the sensible heat added when hydrogen at temperature T is raised to $T + dT$ is $C_P\, dT = H_m$, Q^* is the excess of energy transported over that due to the sensible heat, which must be supplied by the surrounding as a mole of m moves under the influence of a temperature gradient. A Q^* of zero represents no interaction of the hydrogen and heat flows. The quantities a_m and Q^* can be determined experimentally.

Converting the L_{mm} in Eq. [1.8] into terms of the scalar diffusivity D, which is defined as $-\mathbf{J}_m/\nabla C_m$ when $\nabla T = 0$, and for an isotropic dilute solution for which $a_m \propto C_m$ and $\nabla T = 0$,

$$L_{mm} = \frac{DC_m}{RT}$$

Eq. [1.8] becomes:

$$\mathbf{J}_m = -DC_m\left[(\nabla \ln a_m)_T + \frac{Q^*}{RT^2}\nabla T\right] \qquad [1.9]$$

For the anisotropic case, one can derive similarly an expression in which the diffusivity is a matter tensor of the second rank

$$(\mathbf{J}_m)_i = -\sum_{j=1,2,3} D_{ij}C_m\left[\left(\frac{\partial \ln a_m}{\partial x_j}\right)_T + \frac{Q^*}{RT^2}\frac{\partial T}{\partial x_j}\right] \qquad [1.10]$$

where 1, 2, 3, refer to three orthogonal axes, and $(\mathbf{J}_m)_i$ is the flux of species m in the i direction.

In this treatment Q^* is assumed to be isotropic and is presented as a scalar. Since Q^* describes the interaction between two vectors, heat flow and matter flux, it is a tensor of the second rank and is anisotropic for crystals of lower symmetry than cubic. The authors know of no measurements of the degree of anisotropy of this tensor.

We shall now apply Eq. [1.10] to a solid solution of a mobile species m in stationary species 1, that contains small amounts of substitutional stationary species 2. Since $\ln a_m$ is a function of three independent variables, concentrations C_m, C_2, and a stress function ν, then by the chain rule

$$\left(\frac{d \ln a_m}{dx_j}\right)_T = \left(\frac{\partial \ln a_m}{\partial C_m}\frac{dC_m}{dx_j} + \frac{\partial \ln a_m}{\partial C_2}\frac{dC_2}{dx_j} + \frac{\partial \ln a_m}{\partial \nu}\frac{d\nu}{dx_j}\right)_T \qquad [1.11]$$

All terms are explicit except for ν which we will now evaluate.

Stress Function

Li, Oriani, and Darken[7] show that for a single or multiple-phase system containing an immobile constituent, (such as a crystal lattice) and a mobile constituent m, in an isothermal arbitrarily stressed system, with elastic constants which do not change with hydrogen content, and with an applied stress much less than the Young's modulus of a material (a stress of 50,000 psi in titanium causes a 0.15 pct error in the following equations) then

$$\mu_m = \mu_m^\circ - W_m \qquad [1.12]$$

where μ_m is the chemical potential of constituent m at a given location of a homogeneously stressed body, μ_m°, its chemical potential in the standard (unstressed) state for the same composition, and W_m is the work done on the body per mole addition of m by an arbitrary stress field.

Since, for the isothermal case, by thermodynamics $\mu_m = \mu_m^\circ + RT \ln a_m$,

$$W_m = -RT \ln a_m \qquad [1.13]$$

Li, Oriani, and Darken also show that

$$W_m = V\sum_{i,j=1,2,3} \tau_{ij}\left(\frac{\partial \epsilon_{ij}}{\partial n_m}\right)_{n'} \qquad [1.14]$$

where V is the volume of the body, τ_{ij} is a component of a stress tensor, ϵ_{ij} is the corresponding component of the strain tensor, n_m is the number of moles of species m, and the subscript n' denotes constancy of moles of all the other species. The right side of Eq. [1.14] is equivalent to $P\, dV$ for gas systems.[8]

In distinguishing the portion of Eq. [1.14] which is a material property, and in understanding the symmetry of this property, it is useful to realize that the quantity $V(\partial \epsilon_{ij}/\partial n_m)_{n'}$, in Eq. [1.14] is a component of a matter tensor which we will denote by $(\bar{V}_m)_{ij}$. This is illustrated as follows: A common way of expressing the expansion of a solvent accompanying the introduction of a solute, for isotropic and cubic material is in terms of the partial molal volume,[9] $\bar{V}_m \equiv \partial V/\partial n_m$, a scalar quantity. The partial molal volume is a material property and is approximately independent of solute concentration for dilute solutions as will be shown in Table III. To identify the analogous property in Eq. [1.14], one notes that when expansion is isotropic $\epsilon_{ij} = 0$ when $i \neq j$ (no shear distortions) and $\epsilon_{11} = \epsilon_{22} = \epsilon_{33}$, and

$$W_m = V\sum_{i=1}^{3}\tau_{ii}\left(\frac{\partial \epsilon_{ii}}{\partial n_m}\right)_{n'} = \tau_{ii}\left(3V\frac{\partial \epsilon_{ii}}{\partial n_m}\right)_{n'} \simeq \tau_{ii}\left(\frac{\partial V}{\partial n_m}\right)_{n'} \qquad [1.15]$$

We therefore identify the quantity $V(\partial\epsilon_{ij}/\partial n_m)_{n'}$ as the material property analogous to the partial molal volume. This quantity is a tensor since it is obtained from the tensor ϵ_{ij} by differentiating relative to a scalar n_m, and multiplying by a scalar V. We define the partial molal volume (P.M.V.) tensor,

$$(\bar{V}_m)_{ij} \equiv V \frac{\partial \epsilon_{ij}}{\partial n_m} \qquad [1.17]$$

The physical meaning of components of this tensor when $i = j$ can be seen by noting that if the initial volume V is a parallelepiped with a length and cross-sectional area in the i direction of l_i, A_i, then

$$(\bar{V}_m)_{ii} = A_i \frac{\partial l_i}{\partial n_m} \qquad [1.18]$$

The component of the tensor $(\bar{V}_m)_{ii}$ is therefore the volume traversed in the i-direction by the cross-section A_i during the hydrogen induced expansion.

Since the matter tensor $(\bar{V}_m)_{ij}$ is a physical property, it must have its principal axes coincident with axes of high symmetry of the crystal (Neumann's Principle, see Nye[10]). If the solution of hydrogen does not destroy the crystal symmetry, there will be no shear strains in all systems having orthogonal axes of symmetry and $(\bar{V}_m)_{ij} = 0$ when $i \neq j$.

The symmetry of the second rank matter tensor tells us the following about the number of values needed to describe it:[10]

1) In cubic crystals $\bar{V}_m$ is isotropic.

2) In hexagonal, tetragonal, or trigonal crystals, it has one value in the direction of the six, four, or threefold axis and another value in any direction perpendicular to it (cylindrical symmetry).

3) In orthorhombic, monoclinic, and triclinic symmetries it has 3, 4, and 6 values respectively.

When the tensor is isotropic, a component of the tensor is identical to $\frac{1}{3}$ the scalar partial molal volume $\bar{V}_m$.

Combining the definition of the P.M.V. tensor, Eq. [1.17] with [1.13] and [1.14],

$$RT \ln a_m = -\sum_{i=1}^{3} \tau_{ii}(\bar{V}_m)_{ii} \qquad [1.19]$$

Inspection of this equation indicates that uniaxial tension or compression would affect the hydrogen activity the same amount but with opposite sign. For isotropic material, the stress function is proportional to the hydrostatic stress ($\frac{1}{3}$ the sum of the principal stresses) which causes a pure dilatation of the lattice. On the other hand a pure shear or torsional stress should have no effect since the hydrostatic stress is zero.

Consolidated Equation

Identifying the quantity $-\sum_{i=1}^{3} \tau_{ii}(\bar{V}_m)_{ii}$ with ν in Eq. [1.11] and using Eq. [1.19], Eq. [1.10] becomes

$$(J_m)_i = -\sum_{j=1}^{3} D_{ij} C_m \left[\left(\frac{\partial \ln a_m}{\partial C_m} \frac{dC_m}{dx_j} \right)_T + \left(\frac{\partial \ln a_m}{\partial C_2} \frac{dC_2}{dx_j} \right)_T - \frac{1}{RT} \left(\frac{d\left[\sum_{i=1}^{3} \tau_{ii}(\bar{V}_m)_{ii}\right]}{dx_j} \right)_T + \frac{Q^*}{RT^2} \frac{dT}{dx_j} \right] \qquad [1.20]$$

If one has a problem in which C_m and the spatial gradients of the four factors are known, and if the partials $\frac{\partial \ln a_m}{\partial C_m}$, $\frac{\partial \ln a_m}{\partial N_2}$, $\frac{\partial \ln a_m}{\partial \nu}$ and the quantity Q^* can be determined experimentally as will be shown in Part II, Eq. [1.20] can be solved numerically.

Finally, to determine the change of hydrogen concentration at any location with time, note that the combined statements of continuity and conservation of mass can be expressed as[11]

$$\frac{\partial C_m}{\partial t} = -\text{div } \mathbf{J}_m \equiv -\left[\frac{\partial (J_m)_1}{\partial x_1} + \frac{\partial (J_m)_2}{\partial x_2} + \frac{\partial (J_m)_3}{\partial x_3} \right] \qquad [1.21]$$

where t is the time. Combining Eq. [1.21] with Eq. [1.20], and integrating,

$$(C_m)_t = (C_m)_{t_0} + \int_{t_0}^{t} \left[\sum_{i=1}^{3} \sum_{j=1}^{3} \frac{\partial}{\partial x_i} (D_{ij} C_m) \times \left(\frac{\partial \ln a_m}{\partial C_m} \frac{dC_m}{dx_j} + \frac{\partial \ln a_m}{\partial C_2} \frac{dC_2}{dx_j} - \frac{1}{RT} \frac{d\left[\sum_{i=1}^{3} \tau_{ii}(\bar{V}_m)_{ii}\right]}{dx_j} + \frac{Q^*}{RT^2} \frac{dT}{dx_j} \right) \right] dt \qquad [1.22]$$

This is the desired equation from initial time t_0 to time t.

For one-dimensional diffusion in isotropic material, or one-dimensional diffusion along an axis of symmetry with the D appropriately chosen,

$$(C_m)_t = (C_m)_{t_0} + \int_{t_0}^{t} \left[\frac{d}{dx} (D C_m) \left(\frac{\partial \ln a_m}{\partial C_m} \frac{dC_m}{dx} + \frac{\partial \ln a_m}{\partial C_2} \frac{dC_2}{dx} - \frac{(\bar{V}_m)_{xx}}{RT} \frac{d\tau_{xx}}{dx} + \frac{Q^*}{RT^2} \frac{dT}{dx} \right) \right] dt \qquad [1.23]$$

This equation is a hypothesis that is subject to experimental verification since the equation $\mathbf{J}_i = \Sigma L_{ij} \mathbf{X}_j$ in the introductory paragraphs was presented as an assumption. However, one notes that in the absence of all gradients except the solute, species m, and in the dilute range of concentration where $a_m \propto C_m$, Eq. [1.23] becomes a form of the experimentally verified Fick's second law:

$$(C_m)_t = (C_m)_{t_0} + \frac{d}{dx} \left(D \frac{dC_m}{dx} \right) dt \qquad [1.24]$$

Similarly, in the absence of all gradients but a solute gradient and a temperature gradient, in the dilute range of solute concentration, Eq. [1.23] becomes

$$(C_m)_t = (C_m)_{t_0} + D C_m \int_{t_0}^{t} \frac{d}{dx} \left(\frac{d \ln C_m}{dx} + \frac{Q^*}{RT^2} \frac{dT}{dx} \right) dt \qquad [1.25]$$

which in differential form was proposed by Shewmon.[3]

For long times, the validity of this equation for hydrogen in titanium at temperatures between 400° and 500°C has been verified by Marshall.[12] Validation of the combined Eqs. [1.22] and [1.23] will require additional experiments.

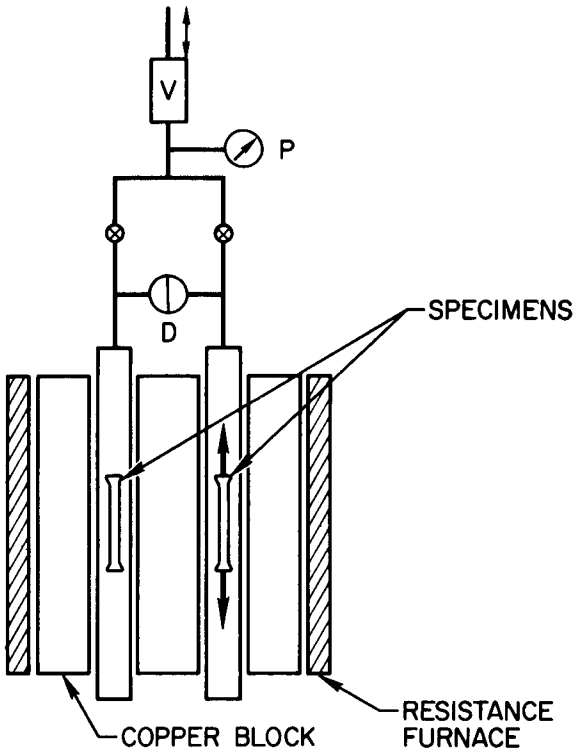

Fig. 2—Schematic of apparatus for the determination of the effect of stress on equilibrium hydrogen pressure. ⟷ Line for evacuating or adding H_2, D Differential pressure gage, P pressure gage, V Calibrated volume.

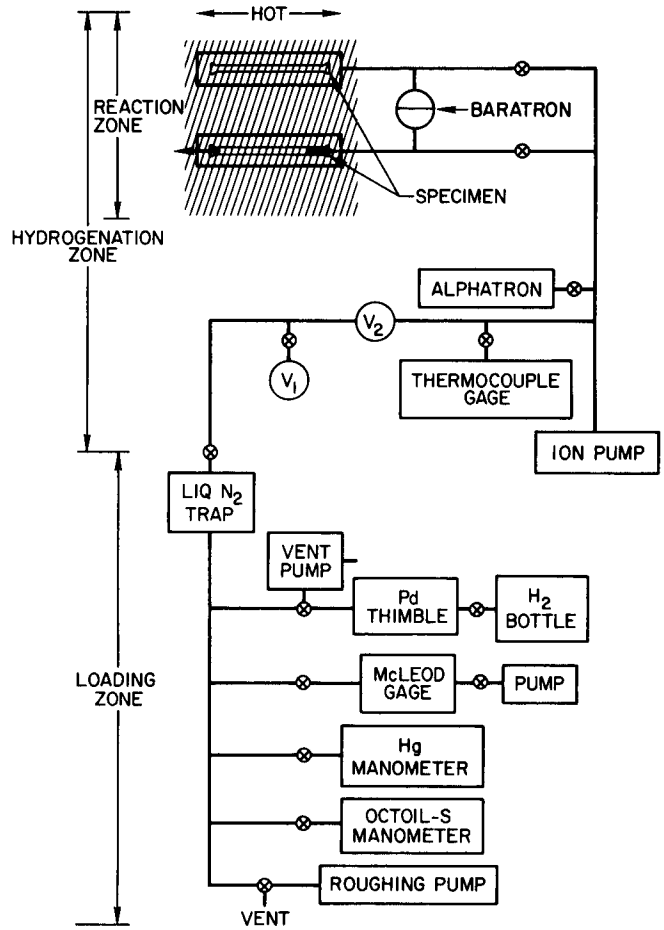

Fig. 3—Schematic of gas system.

PART II. EXPERIMENTAL

Experiments and Equipment

We now proceed to determine all the quantities necessary to make numerical calculations for cases of interest using Eq. [1.22] or [1.23]. For one-dimensional diffusion the problem to be handled is of the type where for a series of spatial points the quantities dC_2/dx, $d\tau_{xx}/dx$, dT/dx are known and are stationary, and the diffusivity D and $(C_m)_{t_0}$ are known. The quantities $\partial \ln a_m/\partial C_m$, $\partial \ln a_m/\partial C_2$, $(\bar{V}_m)_{11}$, Q^* are determined experimentally in the manner to be described, permitting one to solve these equations.

The factors $\partial \ln a_m/\partial C_m$, $\partial \ln a_m/\partial C_2$, and $(\bar{V}_m)_{11}$ can be calculated from the functional relationship between a_m, the activity of hydrogen, and C_m, N_2, and τ. We need only to measure the variation of a_m as we vary each of the quantities. If an equilibrium is established between hydrogen gas and hydrogen in solid solution, then for the reaction

$$(H_2)_{gas} \longleftrightarrow 2(H)_{solid\ solution}$$

the equilibrium constant K is

$$K \equiv \frac{(a_H)^2}{a_{H_2}}$$

where a_H and a_{H_2} are the activities of atomic hydrogen in solid solution and gaseous hydrogen respectively.

Over the range of pressures where hydrogen gas is an ideal gas, and employing as a standard state hydrogen gas at 1 torr,

$$a_{H_2} = P_{H_2} \text{ and } a_H = \sqrt{P_{H_2}} \qquad [2.1]$$

Thus by observing the pressure of hydrogen gas in equilibrium with a hydrogen solid solution of known composition and stress state, and by observing the change in equilibrium hydrogen gas pressure as the sample composition or stress state is changed, the desired quantities can be measured.

Except for the elements to apply and measure stress, many of the elements of the equipment to be described are similar to those developed by McQuillan[13,14] for determination of equilibrium diagrams. A simplified schematic of the equipment is shown in Fig. 2, and a more complete one in Fig. 3. There are provisions for evacuation of the retort and dehydrogenation of the specimen, for adding known amounts of pure hydrogen gas to the retort, and for measuring the hot-zone temperature and the retort pressure at any time. Devices are also included for stressing the right hand specimen. A screw jack applies tension and compression to the specimen train, and a calibrated load cell reads these loads. A torque wrench applies torsion to a shaft passing through a gland at the top of the load train.

There were two predominant needs which formed the basis of the equipment design. The first need was to measure a pressure change of 0.1 pct, a resolution not possible with conventional pressure measuring equipment. The second need was to avoid the significant pressure changes caused by small temperature variations. (If one operates at a temperature and concentration which corresponds to a 300 mtorr equilibrium pressure, a 1°C temperature variation will cause a 4 mtorr pressure variation or 1.3 pct.)

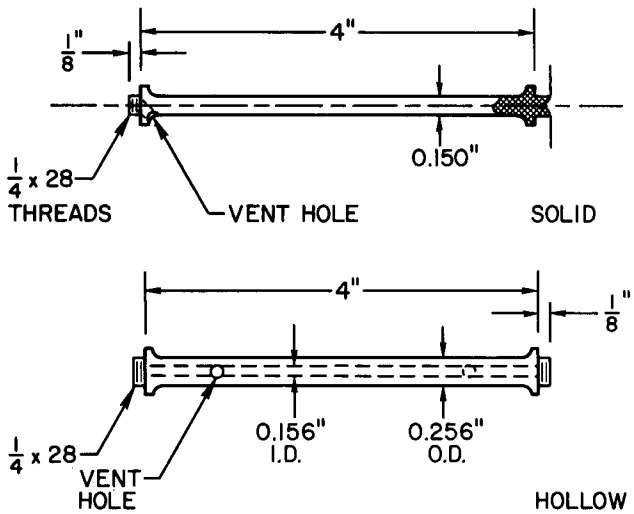

Fig. 4—Specimen: solid one used for C.P. titanium, hollow one for 6-4 alloy.

Both needs were met by the "reference specimen" technique shown in Fig. 2. In an experiment, a specimen was inserted into each of two parallel retorts. In each retort, the specimens and all features of the specimen train which affect heat flow were identical. In addition, the retorts were immersed in a massive copper block, and all elements of the furnace were made symmetrical to a center line midway between the specimens. The temperature of the copper block was a automatically controlled to ±1°C, but the difference in temperature between the specimens was a fraction of this value as judged by observations of the insignificant change in pressure difference between the two specimen chambers with time. For determining the effect of stress on the equilibrium pressure, each retort was isolated from the system, one specimen was stressed, and the difference in the pressure of the two was read with the differential pressure gage (D). The differential gage, (Baratron 77, H-3 head), measures the deflection of a very thin diaphragm. By this technique differential pressure drift due to temperature drift was insignificant. A pressure resolution of less than 0.01 pct of average pressure was achieved. Uncertainty of specific readings and averages was satisfactory.

Fig. 4 gives the specimen dimensions. The solid specimens were stressed in tension and torsion; the hollow specimens in tension and compression. Specimens were first heated at 800°C and a pressure of 10^{-5} torr or less to remove the hydrogen and activate the surface for subsequent hydrogenation. All materials other than the specimens were selected so as not to absorb hydrogen at the test temperatures. The amounts of hydrogen present in the specimen at any time and in the retort space were calculated from the known mass introduced by a calibrated volume, the equilibrium pressure of the retort, and its volume. These calculations were checked by the gain-in-weight and by quantitative analysis of several hydrogenated specimens.

For determining the effect of solid solution hydrogen concentrations on the equilibrium gas pressures, equilibrium was established with various known masses of hydrogen dissolved in the unstressed specimens. To determine the effect of different alloy compositions at a given hydrogen solute concentration, specimens of

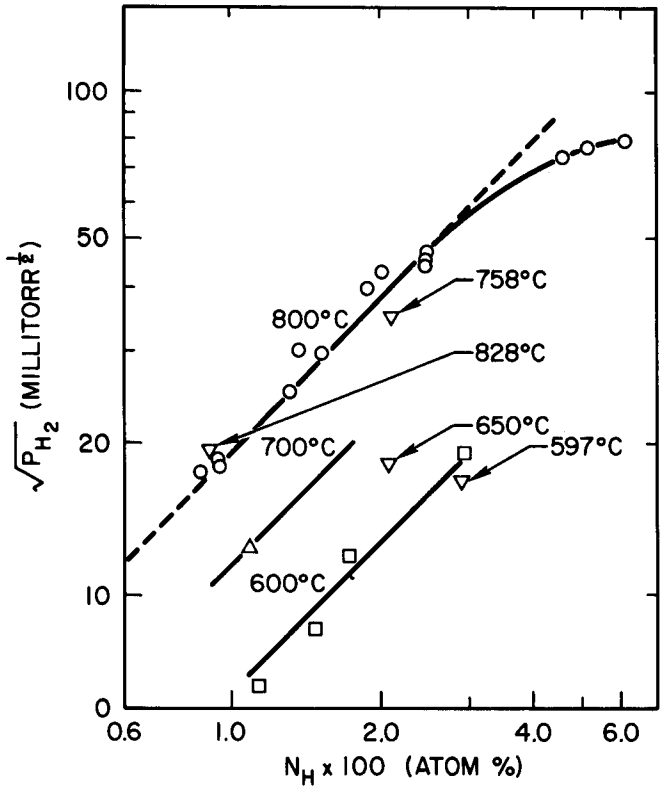

Fig. 5—Effect of temperature and hydrogen concentration on the activity of hydrogen in C.P. titanium.

varying composition were introduced. Two materials, 6Al-4V alloy, and commercially pure titanium were used, with their mill analyses and strengths described in the Appendix. The 6-4 alloy is mostly α phase with some β, with the β increasing somewhat at the higher hydrogen contents and higher temperatures. The commercially pure material is α phase at all the times and temperature of the stress tests, but with increasing amounts of β at the higher temperatures and concentrations used for other tests. The results of short time tensile tests and creep tests at 600°C included in the Appendix indicate little permanent set at the stresses and short stressing times employed for the tests.

The systematic experimental errors, the calibrations, and the accuracy of all observed quantities are discussed in the Appendix.

EFFECT OF HYDROGEN

The change in pressure with increasing amounts of hydrogen in solid solution is shown for the two materials in Figs. 5 and 6. The $\sqrt{P_{H_2}}$ can be seen to be proportional to the H concentration up to 2 at. pct. The atom percent, N_H, rather than the concentration, C, is used in these plots to emphasize the linear portion which corresponds to Sievert's law and Henry's law. Both laws of linearity are in terms of atom percent. This linearity is, of course expected, as was discussed in connection with [1.24] for the case of the absence of all gradients except the solute gradient. For simple diffusion in this hydrogen range, Fick's laws are obeyed, and these data define the limits of this law. For concentrations higher than 2 pct the data from Figs. 5 and 6 can be used to determine the activity

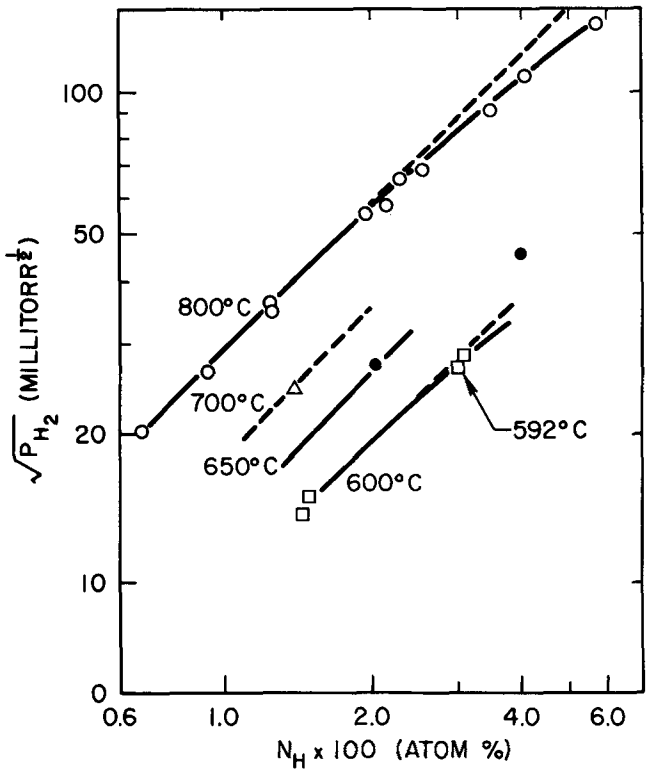

Fig. 6—Effect of temperature and concentration on the activity of hydrogen in 6-4 titanium alloy.

corresponding to various hydrogen concentrations, and these values inserted in Eq. [1.23].

EFFECT OF ALLOY CONTENT

Inspection of Figs. 5 and 6 shows that for the range of hydrogen contents and temperatures studied, at a given hydrogen level and temperature the 6-4 alloy has an equilibrium pressure 2.31 times that for the C.P. titanium. This is equivalent to $\sqrt{2.31}$ or 1.52 times the activity.

Besel[15] studied the equilibrium diagram of binary Ti-Al alloys using the hydrogen equilibrium pressure technique similar to that employed here for unstressed specimens. Fig. 7 is a replot of his results. The upper two triangles in this figure are the result of the present study. Note that 6-4 alloy has 10.7 at. pct Al.

At all hydrogen concentrations, Besel's data fit the equation

$$\ln P = \ln P_0 + 7.10 N_{AL} \qquad [2.2]$$

where P is the pressure for a given hydrogen content with N_{AL} atomic fraction aluminum, and P_0 is the pressure of the same hydrogen content with $N_{AL} = 0$. Other data in Besel's paper show that this relationship is valid over the entire range studied, 600° to 800°C. For the triangular points, the pressure ratios for the 6-4 and the C.P. correspond exactly to the ratio for the binary alloys at the same aluminum content. Apparently the vanadium has no effect on the activity. For use in Eqs. [1.22] or [1.23], from Eq. [2.2] we obtain

$$\frac{\partial \ln a_m}{\partial N_{Al}} = \frac{1}{2}\frac{\partial \ln P}{\partial N_{AL}} = 3.55 \qquad [2.3]$$

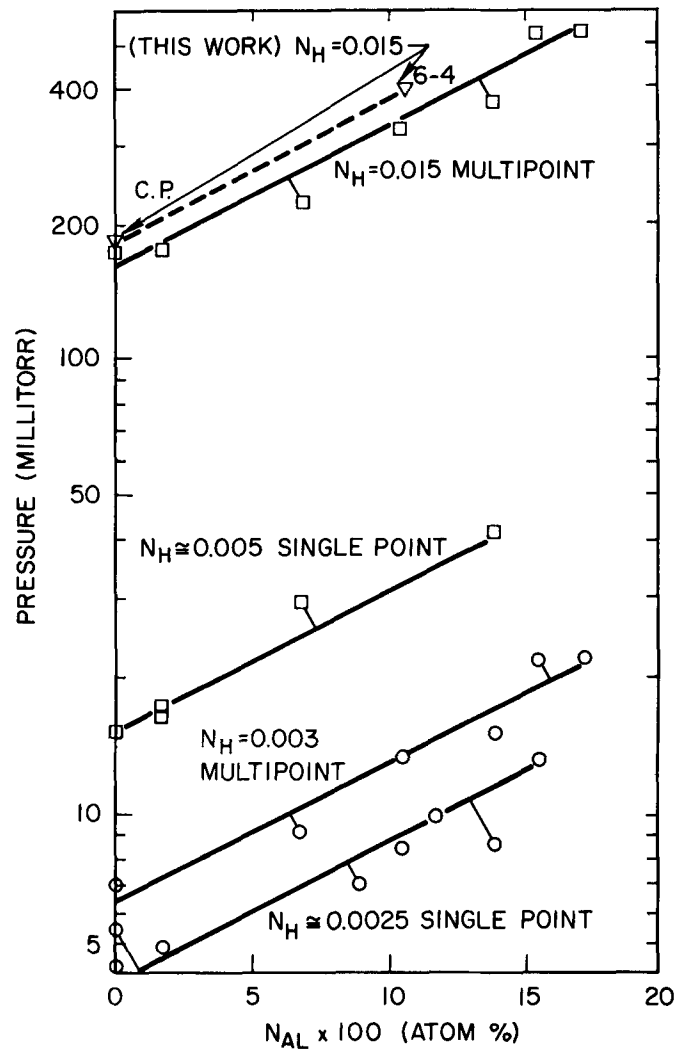

Fig. 7—Effect of aluminum on the equilibrium pressure of hydrogen in titanium. Ti-Al binary alloys except for the 6-4.

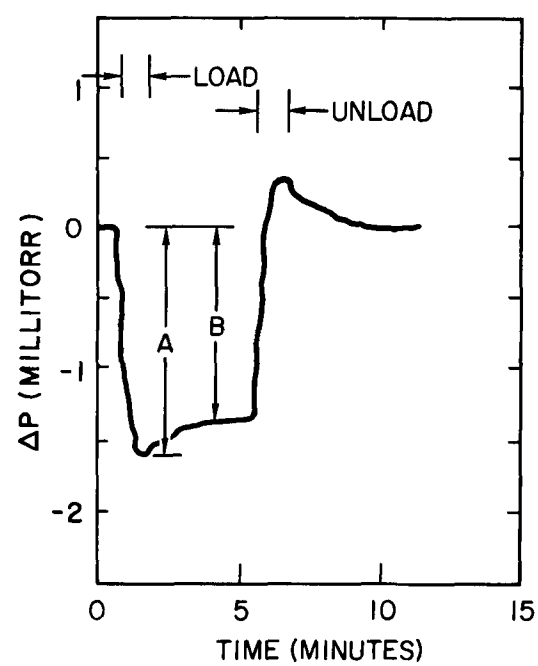

Fig. 8—Typical hydrogen pressure change upon application of a tensile stress of 4 ksi to C.P. titanium with 2.95 at. pct H.

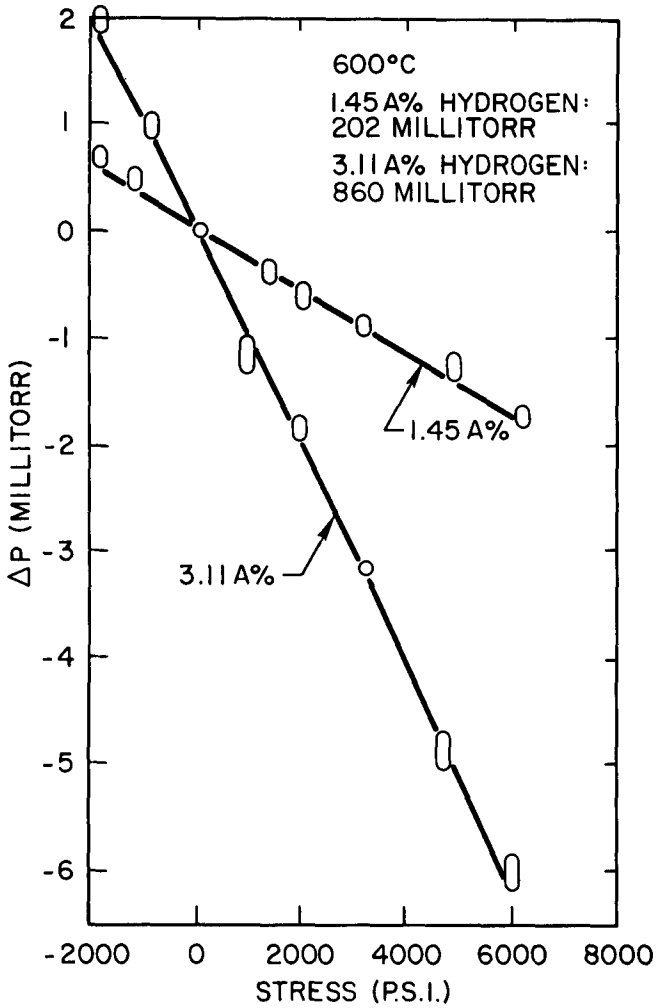

Fig. 9—Equilibrium pressure of hydrogen with 6-4 titanium alloy as a function of normal stress.

EFFECT OF STRESS

A typical pressure vs. time curve for tension or compression is shown in Fig. 8. As the load is changed, an almost simultaneous pressure change occurs. In Ref. 16 a discussion of the possible reasons for the pressure relaxation leads to the conclusion that the pressure A of Fig. 8 is the correct equilibrium pressure in the hot zone, and that the drop to B is an artifact associated with thermal transpiration and other features of the experimental technique.

Fig. 9 presents the relationship of applied stress to pressure for the 6-4 alloy, at 600°C, for two hydrogen contents. The relationships are linear, with the effects of tension and compression represented by the same straight line.

Modifying Eq. [1.19] for uniaxial tension, and assuming that the value of the P.M.V. tensor is not a function of stress,

$$d \ln a_m = -\frac{(\bar{V}_m)_{11} d\tau}{RT} \qquad [2.4]$$

where τ is the applied stress. Since $2d \ln a_m = d \ln P \cong \Delta P/P$, for $\Delta P/P \ll 1, (\Delta P/P)/(\Delta\tau/T)$ is proportional to the value of $\bar{V}_m)_{11}$.

In Figs. 10 and 11 are plotted the data for $\Delta P/P$ vs $\Delta\tau/T$. Note that all except four points in Fig. 10 are for 600°C tests. The four points for 700°C fall on the same line. In Fig. 10 there is a slight increase in slope for lower hydrogen concentrations in the alloy, but in Fig. 11 no such increase is apparent for the C.P. material.

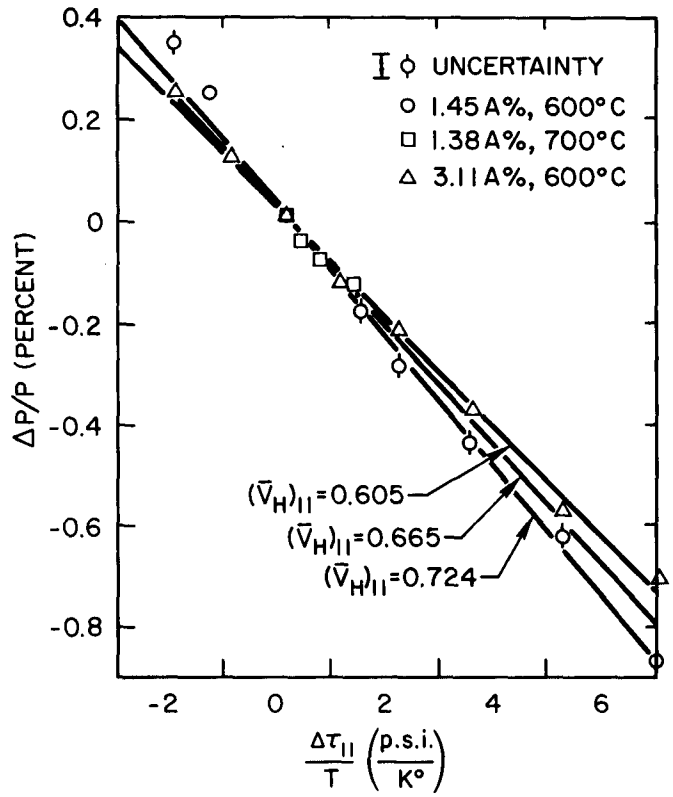

Fig. 10—Data for 6-4 alloy reduced to check validity of P.M.V. tensor.

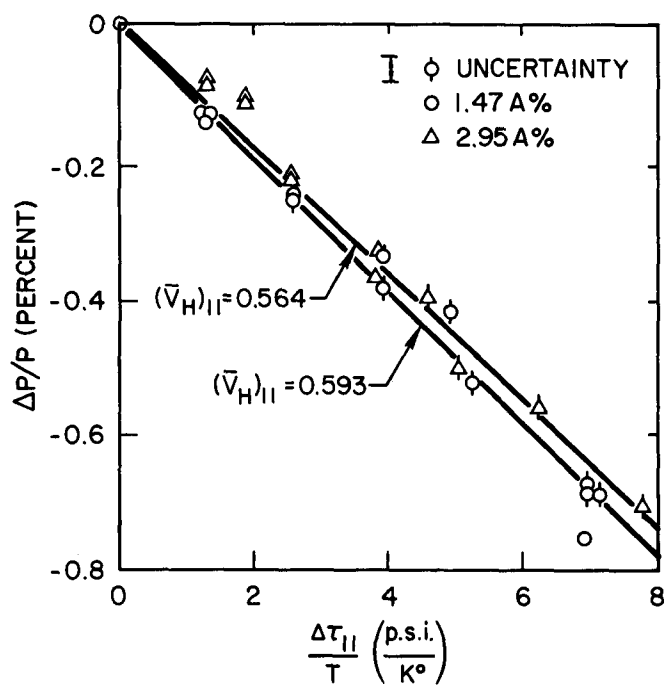

Fig. 11—Data for C.P. titanium reduced to check validity of P.M.V. tensor.

Table II shows the results of calculations of the component of the P.M.V. matter tensor, $(\bar{V}_H)_{11}$, for the tests at 600°C using Eq. [2.4]. The subscript H is used to indicate that the mobile component is hydrogen. Sta-

Table II. P. M. V. Calculations From Stress Test Results

Titanium	Hydrogen Concentration, At. Pct	$(\bar{V}_H)_{11}$ Averages*, cm^3/mole	Apparent $\bar{V}_H$ Averages†, cm^3/mole
6-4	$1\frac{1}{2}$	0.731 (±5 pct)	2.19
6-4	3	0.610 (+$2\frac{1}{2}$ pct)	1.83
C. P.	$1\frac{1}{2}$	0.593 (±$4\frac{1}{2}$ pct)	1.78
C. P.	3	0.564 (±$6\frac{1}{2}$ pct)	1.69

*The ± values include 80 pct of the population based on a regression analysis for the relationships between $R/2$, $\Delta P/P$ and $\Delta\tau/T$. The statistical techniques and calculations are given in Ref. 16.

†Apparent $\bar{V}_H = 3 \times (\bar{V}_H)_{11}$.

tistical calculations referred to in the Appendix indicate that there is a high probability that there is a real difference in the $(\bar{V}_H)_{11}$ for the two alloys at a given hydrogen concentration, and for the two hydrogen concentrations in each alloy. Changes due to temperature (Fig. 10 data) show no statistical significance.

A series of pure torques was applied to a cylindrical C.P. specimen. A torsional load corresponding to a shear stress of 5810 psi was applied three times, for durations of $\frac{1}{4}$, $\frac{1}{2}$, and 1 min. No pressure change was detected. In contrast, the pressure changes accompanying tension and compression occur almost simultaneously with the loading, indicating a response time of several seconds or less. A torque corresponding to a maximum shear stress of 7550 psi was then applied for durations of $\frac{1}{2}$ and $\frac{3}{4}$ min. During the first application, creep of approximately 15 deg occurred. After

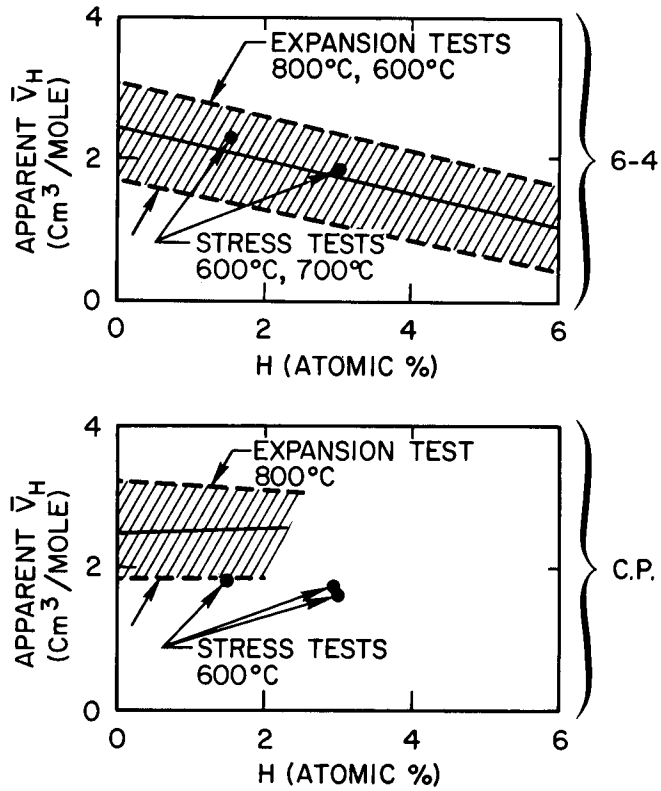

Fig. 12—Comparison of the P.M.V. determination from the effect of stress on hydrogen equilibrium pressure with that from expansion caused by hydrogen concentration. (top curve 6-4 alloy, bottom curve C.P. titanium).

Table III. Hydrogen Partial Molal Volume Comparisons

	Ref.	Method	Material	P. M. V. Sym.	Temp., °C	H Conc., Atom Fraction	P. M. V., cm^3/mole
This work		Effect of tension, compression and torsion on H_2 gas-H solution equilibrium	6-4 Ti, α	Cyl.	600	0.015 0.030	2.2* 1.8*
			C P Ti, α	Cyl.	600	0.015 0.030	1.8* 1.7*
McQuillan	25	Expansion, macroscopic	Pure Ti, β	Iso.	600 to	0 to 0.09	1.6
Calc. by Oriani	17		Pure Zr, β	Iso.	900	→ 0	1.6
Beck	26	Effect of stress	Iron and		20		1.8
de Kazinczy	27	on permeability	Steels, α	Iso.	to	?	
Calc. by Oriani	17				80		2.0
Lindsay quoted by Wriedt and Oriani	20	Expansion, macroscopic	Pd + Ag	Iso.	150 to 350	0 to 0.24	1.90
Margolin and Portisch	28	Lattice exp., X-ray diffraction	Pure Ti, α	Hex	250	0.03	1.1
Margolin	29					0.05	1.4
Lindsay	19	Expansion,	Pd	Iso.	350	?	1.7
Elliott	30	macroscopic					0.43
Calc. by Oriani	17						
Wriedt and Oriani	20	Uniaxial tension Uniaxial compression	Pd + Ag	Iso.	75	0.24	1.97 1.94

*In this work $(\bar{V}_H)_{11}$ was measured and an apparent P. M. V. calculated from $\bar{V}_H = 3 \times (\bar{V}_H)_{11}$. The 1-direction is the cylindrical axis of the specimen and also an axis of cylindrical symmetry of properties. For comparison with other investigators, uncertainty is 10 pct. For comparison within this investigation, uncertainty is less than 10 pct, as shown in other parts.

the second application cumulative creep of approximately 45 deg was observed. A torque corresponding to a shear stress of 5650 psi was then applied three times for $\frac{1}{2}$ min resulting in additional creep. In no case could any pressure change be detected. Background fluctuation during this test was 0.05 mtorr, with the retort pressure at 285 mtorr, so that the value of $\Delta P/P$ due to the shear stresses is less than 2×10^{-4} (or less than 0.02 pct).

The results confirm the remarks after Eq. [1.19] predicting the equal and opposite effects of tension and compression, and no effect of torsion. This test is proof that shear strain has no effect, and that only the stresses causing dilatation affect the hydrogen activity.

During most of the hydrogenations for activity measurements, dial indicators were positioned to measure the expansion of a flexible bellows forming the room temperature portion of the retort. They were used primarily for determining the strain on a specimen while procedures were established for minimizing unintended loads. They also give approximate readings of the strains caused by adding or removing solid solution hydrogen.

The data for strain vs H concentration can be used to calculate $(\bar{V}_H)_{11}$ giving an independent determination of the partial molal volume by the equation

$$(\bar{V}_H)_{11} = V_s(1 - N_H)\frac{\Delta e_{11}}{\Delta N_H} \qquad [2.5]$$

which is similar to an equation used by Oriani[17]. V_s is the molal volume of the solution at the composition in question (not the partial molal volume, and not the molal volume of the pure titanium). Since for the isotropic case, $\bar{V}_H = 3(\bar{V}_H)_{11}$ Eq. [2.5] can also be used for calculating the isotropic $\bar{V}_H$ by multiplying by three. The molal volume of pure titanium at 800°C was assumed to be 10.50 cm^3 which corresponds to a room temperature density of 4.55 g/cm^3 and a linear coefficient of thermal expansion of $11 \times 10^{-6}/°C$.[18]

In Fig. 12 the cross-hatched area shows the "apparent" molal volume vs atomic percent hydrogen as determined from the strain data. The term "apparent" denotes the value obtained by assuming the material is isotropic and is three times the value of $(\bar{V}_H)_{11}$. In this figure we superimpose the values of $\bar{V}_H$ obtained from the stress tests. The agreement is good, further validating the Li, Oriani, and Darken theory.

Table III compares the partial molal volume results of this investigation with results obtained by others on other materials and using other experimental techniques. This investigation contributes the only measurements on the effect of torsion on any material and on the effect of stress on titanium and 6-4 alloy. Note that Lindsay[19] obtained a value 1.90 g/cm^3 by expansion measurements using palladium alloys having from 0 to 25 pct Ag. Wriedt and Oriani,[20] using uniaxial tension and compression tests on Pd-25 pct Ag specimens in equilibrium with hydrogen gas, measured the change in solid solution concentration with applied stress. Their values of 1.97 and 1.94 for compression and tension, are within experimental error of the value of Lindsay obtained by expansion. The values obtained in this study are in the range of values obtained by a variety of techniques and materials.

EFFECT OF TEMPERATURE GRADIENT

We have shown in Eq. [1.20] that the diffusion induced by the temperature gradient is represented by the term $(Q^*/RT^2)\ \partial T/\partial x$; only the Q^*, the heat of transport, is required for numerical calculations. In the absence of a theory to determine Q^* we rely on the following values obtained experimentally by Marshall.[12]

Material	Average H Content P. P. M.	Q* Calories/Mole	Temperature Range
C. P. Titanium	35	5300	390° to 500°C
6Al-4V Titanium	56	1800	320° to 530°C

The experiment consisted of heating a specimen of the material, initially at a constant hydrogen content, in a temperature gradient for 18 days and measuring the hydrogen redistribution. Q^* is calculated using Eq. [2.7] derived below. If only a thermal gradient is present, then Eq. [1.20] in one-dimensional form becomes

$$J_m = -D\left[\frac{dN_m}{dx} + \frac{N_m Q^*}{RT^2}\frac{dT}{dx}\right] \qquad [2.6]$$

For steady state, $J_m = 0$, and

$$Q^* = \left[\frac{d \ln N_m}{d(1/T)}\right] R \qquad [2.7]$$

so that a plot of $\ln N_m$ vs $1/T$ suffices to determine Q^*. In numerical work the Q^* for a composition intermediate between the C.P. and 6-4 will be determined by linear interpolation.

FINAL EQUATION

As an example, for dilute hydrogen concentrations, for commercially pure titanium, binary Ti-Al alloys, or 6-4 alloy, for uniaxial stressing, and for bodies with isotropic or cubic symmetry, Eq. [1.20] becomes

$$J_m = -D\left[\frac{dC_m}{dx} + 3.55C_m\frac{dN_{AL}}{dx} - \frac{2.0C_m}{RT}\frac{d\tau}{dx} + \frac{(5300 - 583N_{AL})}{RT^2}C_m\frac{dT}{dx}\right] \qquad [2.8]$$

In this equation the 2.0 represents the average partial molal volume in cm^3/mol for 6-4 alloy, the τ is the uniaxial stress, and the expression $(5300 - 583N_{AL})$ is the expression for interpolating the Q^* for the aluminum content between the values previously quoted for C.P. and 6-4 material. The use of a single partial molal volume, obtained from the bar experiment without qualification as to direction, contains the implicit assumption that the polycrystalline bar is isotropic. This may be slightly in error if the bar stock had some preferred orientation, since the stress tests were conducted at temperatures where the C.P. material is hexagonal and the 6-4 alloy mostly hexagonal.

ACKNOWLEDGMENTS

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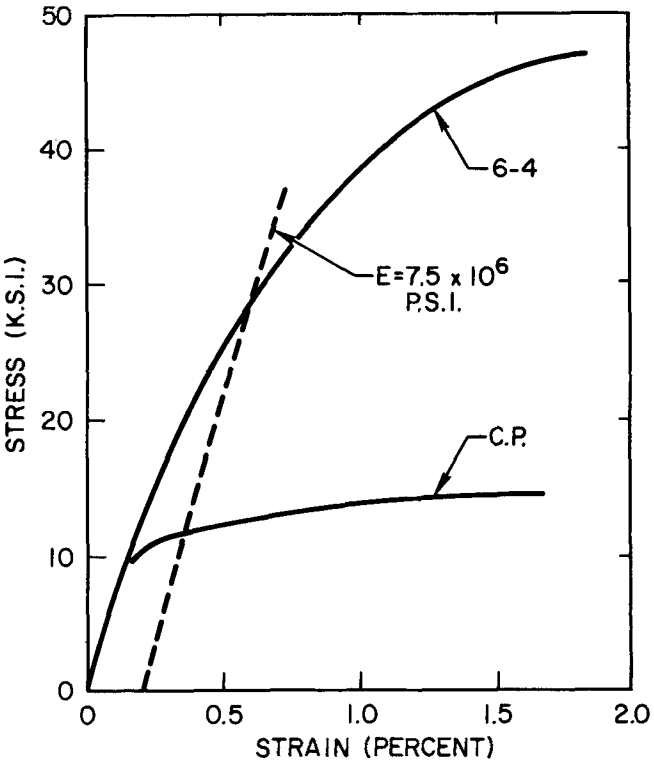
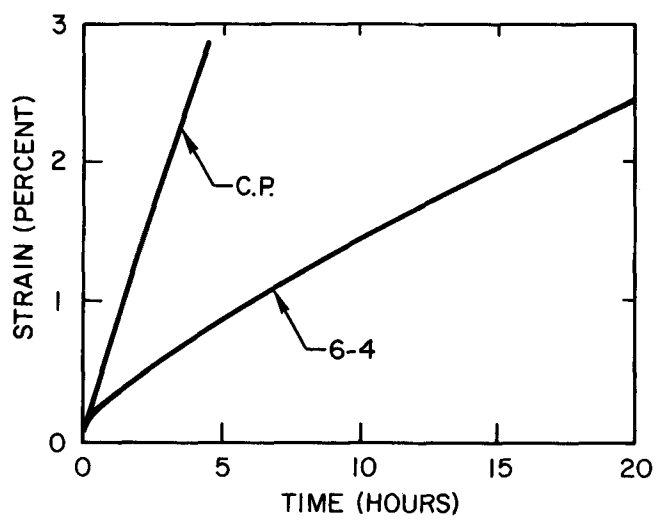


Fig. 13—Stress-strain curves at 600°C. Strain rates: 6-4 alloy at 0.006/min, C.P. titanium 0.005/min.



MATERIAL	C.P.	6-4
APPLIED STRESS	2,500 p.s.i.	5,000 p.s.i.
STRAIN AT 0.1 HOUR	0.13%	0.08%

Fig. 14—Creep tests at 600°C.

APPENDIX

The following systematic errors are small for the experimental conditions employed or are compensated for in the equipment.

1) Error in pressure reading due to thermal transpiration.

2) Error in McLeod gage when used with a liquid nitrogen trap.

3) Deviation in hydrogen solid solution concentration during the stress test.

4) Hydrogen cooling effects on the expansion measurements.

5) End load in the retort due to ambient pressure.

They are discussed in detail in Ref. 16.

All instruments used were calibrated against standards. Based on such calibration, and employing the square root of the sum of the squares for the error of quantities calculated from products or quotients of measured quantities (Kline and McClintock, 31), absolute accuracies with an 80 pct probability are as follows:

$\Delta P/P$ for stress tests:	± = 10 pct
τ_{11}:	± 1 pct
T:	± 1 pct
$\dfrac{\Delta P/P}{\tau_{11}/T}$ for stress tests:	± 10 pct
P for any test:	± 10 pct
Torque:	± 5 pct
H concentration in solution:	± 1 pct

The scatter band for the expansion test results in Fig. 12 are calculated to include 80 pct of the population using Student's distribution for small samples. The mean line is a least squares fit for all the dependable data, with its slope established by regression analysis. The detail calculations can be found in Ref. 16.

The material used in this investigation was hot rolled, and annealed bar, purchased from the Titanium Metals Corporation.

Material	Commercially Pure	Titanium, 6 Aluminum, 4 Vanadium
H	0.0052 pct	0.005 pct
O		0.19
N	0.011	0.009
C	0.023	0.025
Fe		0.16
Al		6.3
V		4.2
Bar Diameter	$\frac{3}{4}$ in.	$\frac{1}{2}$ in.
Heat Number	G2717	G-8580
Yield Strength	49,500 psi	154,000 psi
Tensile Strength	69,000	166,000
Elongation	34 pct	15 pct
Reduction in Area	60 pct	40 pct

The results of short time tensile tests and creep tests conducted for both materials at 600°C are shown in Figs. 13 and 14.

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