Equilibrium and Kinetics Studies of Hydrogen Isotope Exchange on Vanadium Hydride

Y. W. WONG
and
F. B. HILL
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Chromatography experiments and pressure-composition isotherm measurements were carried out on the vanadium-hydrogen system in order to obtain an understanding of the equilibrium and kinetic factors affecting hydrogen isotope exchange. Analysis of the results yielded values of the hydrogen equilibrium distribution coefficient, the tritium-protium separation factor, the rate of the gas-solid exchange reaction, and the axial dispersion coefficient.

SCOPE

Hydrogen isotope separations of current technical interest include deuterium enrichment for heavy water production and removal of tritium from nuclear industry effluents. Insofar as isotopic composition is concerned, feed streams for these processes consist mainly of the light isotope, protium, with a trace amount of a heavy isotope, deuterium, or tritium. A solid sorbent useful for concentrating the heavy isotope should preferentially take up that isotope.

A gas-solid system having this property is the vanadium-hydrogen system. In contrast to most metal hydride systems, the deuteride and tritide are more stable than the protide in the vanadium system.

This paper presents a study of the equilibrium and kinetic properties of isotope exchange in the HT-H_2-vanadium hydride system. The object of the investigation was to obtain an understanding of the factors affecting isotope exchange which are useful in isotope separation process design and analysis. Equilibrium and rate data were obtained from chromatography experiments conducted on the HT-H_2-vanadium hydride system and from measurements of hydrogen-vanadium pressure-composition isotherms.

CONCLUSIONS AND SIGNIFICANCE

Pressure-composition isotherms for the hydrogen-vanadium system were determined over the composition range $VH_{\sim 0.6}$ to $VH_{\sim 1.8}$. The data in the $VH_{\sim 0.6}$ region at high temperatures were in good agreement with a correlation of Veleckis and Edwards (1969) which was based on the assumption that hydrogen was in simple interstitial solution in the metal lattice.

Chromatography experiments on the HT-H_2-V system were conducted in the $VH_{\sim 0.6}$ region and were interpreted in terms of a model of mass transfer and reaction. Data from these experiments were used in combination with the pressure-composition data to derive the tritium-protium separation factor, the magnitude as well as the temperature and pressure dependence of the gas-solid interfacial exchange rate, and the axial dispersion coefficient. The separation factor decreased approximately linearly with temperature from a value of 1.20 at 40°C to 1.06 at 300°C. No discontinuity was found at the α-β phase boundary. As expected, the separation factor did not vary with pressure. The interfacial exchange reaction was found to be the rate limiting step in the overall exchange process, being slow compared to mass transfer external to the hydride particles and to diffusion within the particles. The pressure and temperature dependence of the exchange rate was characteristic of mechanisms involving activated chemisorption of hydrogen. Values of the axial dispersion coefficient were somewhat larger than expectations based on transport by molecular diffusion alone.

The results of the study are of value in understanding the mechanisms and rates of isotope exchange in the vanadium-hydrogen system and thus in the design and analysis of separation processes based upon this system.

Isotope effects are commonly observed in metal hydrides. The usual finding is that stability increases in the order tritide, deuteride, protide. Vanadium hydride, one of the few exceptions, exhibits an inverse isotope effect with stability increasing in the reverse order. An inverse isotope effect may serve as the basis for a hydrogen isotope separation process in which trace levels of a heavy isotope are removed from a mixture consisting

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predominantly of a light isotope. This is the situation normally encountered in tritium removal from nuclear industry effluents and in deuterium enrichment for heavy water production.

Information required for understanding the factors affecting isotope exchange in the hydrogen-vanadium system includes the equilibrium interphase distribution coefficient for hydrogen, the equilibrium isotope separation factor, and information on rates of attainment of equilibrium between phases. Previously obtained data of this kind on the vanadium-hydrogen system in the range of compositions of present interest are essentially those of Wiswall, Reilly, and co-workers. Reilly and Wiswall (1970) measured pressure-composition isotherms from which equilibrium distribution coefficients may be obtained. They measured these isotherms over the composition range $VH_{\sim 1}$ to $VH_{\sim 2}$ using hydrides derived from zone refined vanadium. They later noted the strong influence of impurities in vanadium on the equilibrium dissociation pressures and the rates of decomposition of VH_2 (Reilly and Wiswall, 1972). In a study of hydrogen isotope separation factors, Wiswall and Reilly (1972) noted the inverse isotope effect and reported tritium-protium separation factors principally for the dihydride and principally for the material derived from zone refined vanadium. Finally, in a study of the potential of the vanadium-hydrogen system as the basis for an isotope separation process, Wiswall et al. (1977) conducted a series of survey experiments on the kinetics of isotope exchange on columns of vanadium hydride derived from vanadium of commercial grade. The results of chromatographic experiments employing tritium as a tracer were interpreted in terms of heights of equivalent theoretical stages. A few experiments on a temperature cycling process similar to cycling zone adsorption (Baker and Pigford, 1971) were conducted.

The purposes of the present work were to obtain a comprehensive set of equilibrium and rate data on isotope exchange using hydrides made from a single batch of commercial grade vanadium, to interpret the rate data in terms of a reasonable model of mass transfer and reaction, and to obtain thereby an understanding of the factors affecting isotope exchange which would be useful in process design and in analysis of process performance. The information obtained in this study will be used to guide the design of single stage separation processes using the same batch of vanadium. The performance of these processes will be discussed in a future paper.

In the present work, chromatographic experiments were conducted on columns of vanadium hydride. Pulses of tritiated hydrogen were eluted with pure hydrogen. Equilibrium tritium-protium separation factors, rates of HT-H_2 exchange, and axial dispersion coefficients were derived from the elution curves. Pressure-composition isotherms required for distribution coefficient calculation were determined in separate batch contacting experiments. A few separation factor experiments were also carried out in batch contacting experiments for purposes of comparison with those obtained from the chromatography experiments.

THEORY

A chromatography experiment had the following features. A square pulse of hydrogen containing a trace amount of HT was introduced into a stream of pure hydrogen flowing into a column of vanadium hydride particles. The shape of the delayed and broadened pulse was determined as it emerged from the column by means of a proportional counter.

Interpretation of the data from such an experiment was based on a model of the overall gas-solid exchange process which occurred as the pulse passed through the column. The overall exchange process may be written as

$$\mathrm{HT}(g) + \mathrm{H}(\beta\text{-VH}) \rightleftarrows \mathrm{H_2}(g) + T(\beta\text{-VH}) \qquad (1)$$

In this equation, (g) denotes a species in the bulk gas phase, and (β-VH) signifies a species in the β-hydride phase used experimentally. The overall exchange process is made up of a number of steps in series, including mass transfer across a resistance external to a particle, gas-solid surface exchange, and diffusion in the solid phase. Axial dispersion occurs in the flowing gas phase.

Mathematical representation of the overall process is contained in the following equations. A total mass balance for tritium assuming plug flow is

$$E_z \frac{\partial^2 C_{\mathrm{HT}}}{\partial z^2} - u \frac{\partial C_{\mathrm{HT}}}{\partial z} - \frac{\partial C_{\mathrm{HT}}}{\partial t} - \frac{1-\epsilon}{\epsilon} \frac{\partial \overline{C}_T}{\partial t} = 0 \qquad (2)$$

Mass transfer of HT across a fictitious laminar gas film adjacent to a particle is described by

$$\frac{\partial \overline{C}_T}{\partial t} = \frac{3k_g}{r_p}\left(C_{\mathrm{HT}} - C^*_{\mathrm{HT}}\right) \qquad (3)$$

In the laminar flow region used experimentally, the Frössling equation for mass transfer (Bird, Stewart, and Lightfoot, 1960) reduces to

$$\frac{k_g r_p}{D_{\mathrm{HT-H_2}}} = 1 \qquad (4)$$

and Equation (3) may be written as

$$\frac{\partial \overline{C}_T}{\partial t} = \frac{3D_{\mathrm{HT-H_2}}}{r_p^2}\left(C_{\mathrm{HT}} - C^*_{\mathrm{HT}}\right) \qquad (5)$$

The isotopic exchange reaction represented by Equation (1) occurs at the gas-solid interface. Thus, the exchanging species in their respective phases are those at the interface rather than in the bulk phases. The rate of this reaction is given by

$$\frac{\partial \overline{C}_T}{\partial t} = k_f{}^T C^*{}_{\mathrm{HT}} C^*{}_{\mathrm{H}} - k_r{}^T C^*{}_{\mathrm{H_2}} C^*{}_T \qquad (6)$$

Diffusion of T in the solid phase is described by

$$\frac{\partial C_T}{\partial t} = D_s\left(\frac{\partial^2 C_T}{\partial r^2} + \frac{2}{r}\frac{\partial C_T}{\partial r}\right) \qquad (7)$$

By definition

$$\overline{C}_T = \frac{3}{r_p{}^3}\int_0^{r_p} C_T r^2 dr \qquad (8)$$

Boundary conditions for these equations are

$$\begin{aligned} z = 0 \quad & C_{\mathrm{HT}} = C^0{}_{\mathrm{HT}}, \quad 0 \leqq t \leqq t_0 \\ & C_{\mathrm{HT}} = 0, \quad t > t_0 \\ r = 0 \quad & \frac{\partial C_T}{\partial r} = 0 \\ r = r_p \quad & C_T = C^*{}_T \end{aligned} \qquad (9)$$

Initial conditions are

$$t = 0 \quad C_{\mathrm{HT}} = C_T = 0, \quad z > 0$$

$$
\begin{aligned}
C_T &= 0, \quad 0 \leq r < r_p \\
C^*_T &= 0, \quad r = r_p
\end{aligned}
\tag{10}
$$

From Equations (2) to (10), following Kubin (1965), one can derive expressions for the moments of the HT peak at any value of z in the bed. Expressions for the first absolute moment μ_1' and the second central moment μ_2 at the bed exit ($z = L$) are as follows:

$$
\mu_1'(L) = \left(1 + \frac{1-\epsilon}{\epsilon}\frac{\alpha}{2}K_{H_2}\right)\frac{L}{u} + \frac{t_0}{2} \tag{11}
$$

$$
\mu_2(L) = \left\{ \frac{1-\epsilon}{\epsilon}\frac{\alpha}{2}K_{H_2} \left[\left[\frac{\frac{\alpha}{2}K_{H_2}}{3D_{HT-H_2}} + \frac{1}{15D_s} \right] r_p^2 + \frac{\frac{\alpha}{2}K_{H_2}}{k_f^T C^*_H} \right] + E_z \left(1 + \frac{1-\epsilon}{\epsilon}\frac{\alpha}{2}K_{H_2}\right)^2 \frac{1}{u^2} \right\} \times \frac{2L}{u} + \frac{t_0^2}{12} \tag{12}
$$

where

$$
\alpha = \frac{2k_f^T}{k_r^T} \tag{13}
$$

$$
K_{H_2} = \frac{C^*_H}{C^*_{H_2}} \tag{14}
$$

Equations (11) and (12) are used to interpret chromatography experiments in the following way. The first and second moments are evaluated for a series of experiments which are conducted at constant temperature, pressure, and particle size and in which gas velocity u is the independent variable. Then, if $\mu_1'(L) - t_0/2$ is plotted vs. residence time $\theta = L/u$, according to Equation (11), a straight line should be obtained with slope

$$
S_1 = 1 + \frac{1-\epsilon}{\epsilon}\frac{\alpha}{2}K_{H_2} \tag{15}
$$

and zero intercept. If, say, the values of ϵ and K_{H_2} are known, then α may be evaluated from a knowledge of the slope and Equation (15).

In accordance with Equation (12), a plot of $[\mu_2(L) - t_0^2/12]\cdot u/2L$ vs. θ^2 should yield a straight line with slope

$$
S_2 = E_z \left(1 + \frac{1-\epsilon}{\epsilon}\frac{\alpha}{2}K_{H_2}\right)^2 \Big/ L^2 \tag{16}
$$

and intercept

$$
I_2 = \frac{1-\epsilon}{\epsilon}\frac{\alpha}{2}K_{H_2} \left[\left[\frac{\frac{\alpha}{2}K_{H_2}}{3D_{HT-H_2}} + \frac{1}{15D_s} \right] r_p^2 + \frac{\frac{\alpha}{2}K_{H_2}}{k_f^T C^*_H} \right] \tag{17}
$$

From the slope and values of ϵ, K_{H_2}, L, and α, the value of E_z can be obtained. The intercept can be used with these same data to obtain values of the rate constants for the steps in the overall isotope exchange process. The details of this latter evaluation will be presented later.

The above development is similar in some respects to that of Suzuki and Smith (1971) who used elution of deuterium pulses to study hydrogen exchange on columns of nickel/kieselguhr catalyst. It differs importantly in that pore diffusion is absent and solid phase diffusion following surface exchange is present.

EXPERIMENTAL

Materials

Hydrogen was obtained from the Matheson Gas Company, Rutherford, New Jersey, with a purity of 99.999%. Gaseous tritium was obtained from the New England Nuclear Corporation, Boston, Massachusetts, in the form of a 1-curie ampoule, carrier free. A master batch of tritiated hydrogen (approximately 4 × 10^{-9} mole fraction HT in hydrogen) was prepared by diluting the tritium with ~3 m^3 of the Matheson hydrogen. Ingots of vanadium were obtained from the Gallard-Schlesinger Chemical Manufacturing Corporation, Carle Place, New York. The vanadium purity was 99.5% vanadium minimum with major impurities in percent, 0.15 silicon, 0.05 iron,

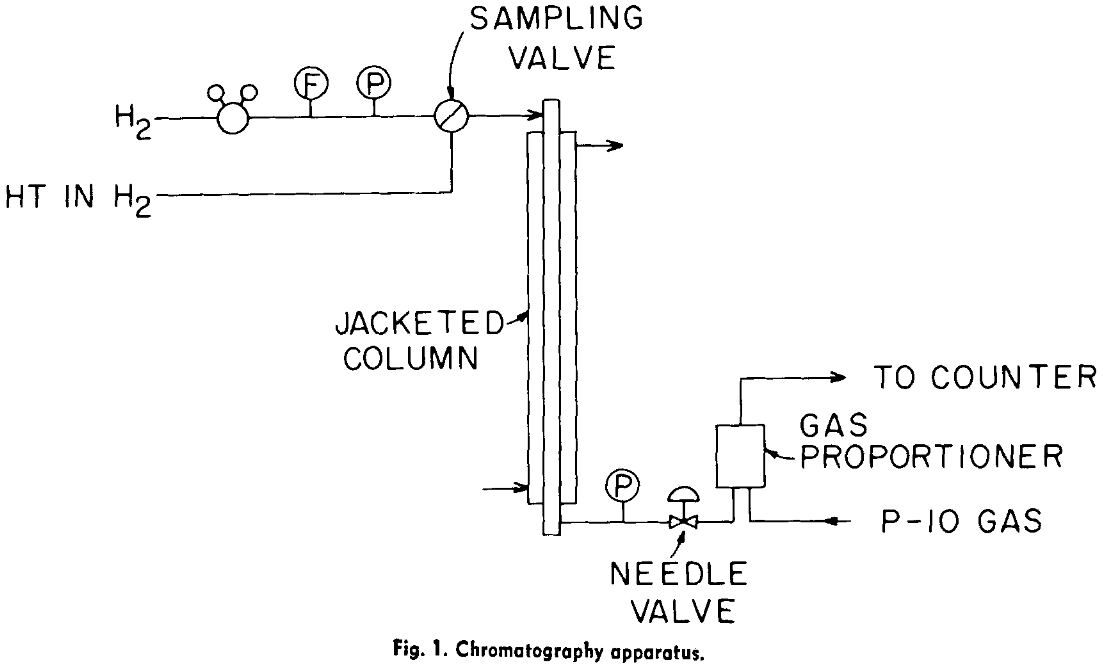

Fig. 1. Chromatography apparatus.

0.04 nitrogen, 0.02 oxygen, 0.03 carbon, 0.01 all other metals. Upon receipt, the ingots were partially hydrided to facilitate crushing and sizing with standard sieves.

Pressure-Composition Isotherms and Separation Factors

These measurements were made using the techniques and apparatus of Reilly and Wiswall (1967) and Tanaka, Wiswall, and Reilly (1978). Batch contacting techniques were used. Briefly, pressure-composition isotherms were measured by first applying sufficient hydrogen pressure at the temperature of interest to a weighed quantity of activated vanadium to obtain the most hydrogen rich composition desired. Measured amounts of hydrogen were then successively withdrawn until the hydride was completely decomposed to metal and hydrogen. Equilibrium hydrogen pressure was measured after each withdrawal. Knowledge of pressures and amount of hydrogen permitted isotherm calculation. Tritium-protium separation factors were measured by contacting a measured volume of tritiated hydrogen with a hydride sample prepared from a weighed quantity of activated vanadium. The hydride sample had previously been equilibrated with pure hydrogen at the temperature and pressure conditions required to produce a desired composition. The count rate of the tritiated hydrogen was determined prior to contacting. After equilibration, the volume and count rate of the gas phase were determined. Then the hydride was decomposed, and the volume and count rate of the evolved gas were determined. From these data, the separation factor and solid phase composition could be calculated.

Chromatography Experiments

The apparatus is depicted schematically in Figure 1. It consisted of a vanadium hydride column into which a pure hydrogen stream was fed. The effluent stream flowed through an internal proportional counter before venting. Pulses of the master batch of tritiated hydrogen were introduced into the hydrogen stream by the switching of a Carle Model 2018 Micro-Volume gas sampling valve. Pulse volume was 1 cm^3. The column was made of stainless steel and had a 0.77 cm I.D. and contained a 45.7 cm packed length of vanadium hydride particles. The temperature of the column was maintained constant to within ±1°C by means of a water jacket and constant temperature bath. Resistance heating wires wrapped around the outside of the jacket were used to raise the column temperature to levels as high as 450°C for vanadium activation.

A flow through proportional counter of the kind described by Bernstein and Ballantine (1950) was used. The gas flowing through the counter was a mixture of the column effluent and P-10 counting gas. The column effluent and the counting gas were combined and mixed in a Matheson Model 7342 gas proportioner.

Hydrogen flow rate was regulated by a Precision Gas Products Model 350-1900-G004 two-stage regulator and needle valve. Flow rates were measured by a Hastings Model ALL-1KG-H-1 KM mass flowmeter.

The vanadium particles were activated in the following way. After the vanadium particles were charged to the column, the bed was outgassed at 450°C until a vacuum better than 7×10^{-4} Pa (5×10^{-6} torr) was attained. The bed was then cooled to room temperature and pressurized with hydrogen to 1 030 kPa (150 lb/in.^{2}). Hydrogen absorption was very rapid and was accompanied by rapid heat release. After this procedure was carried out twice, the bed was considered to be fully activated. It was necessary to reactivate a bed frequently in order to obtain reproducible chromatography experiments. No significant particle attrition was found after repeated activation procedures.

An experiment consisted of measuring the count rate in the column effluent from the time of pulse injection to the time at which the count rate returned to background following pulse emergence. Experiments were conducted as a function of hydrogen flow rate, temperature, pressure, and particle size.

The dead volume in the hydrogen flow path was determined to be 15.8 cm^3. At the flow rates used in the main chromatographic study, the dead volume residence time was less than 0.1% of the shortest elution time. Also, the second moments of peaks eluted from inactivated beds were negligible compared to the second moments of peaks eluted from activated beds. Thus no corrections to the moments for active beds on account of the presence of dead volume were necessary.

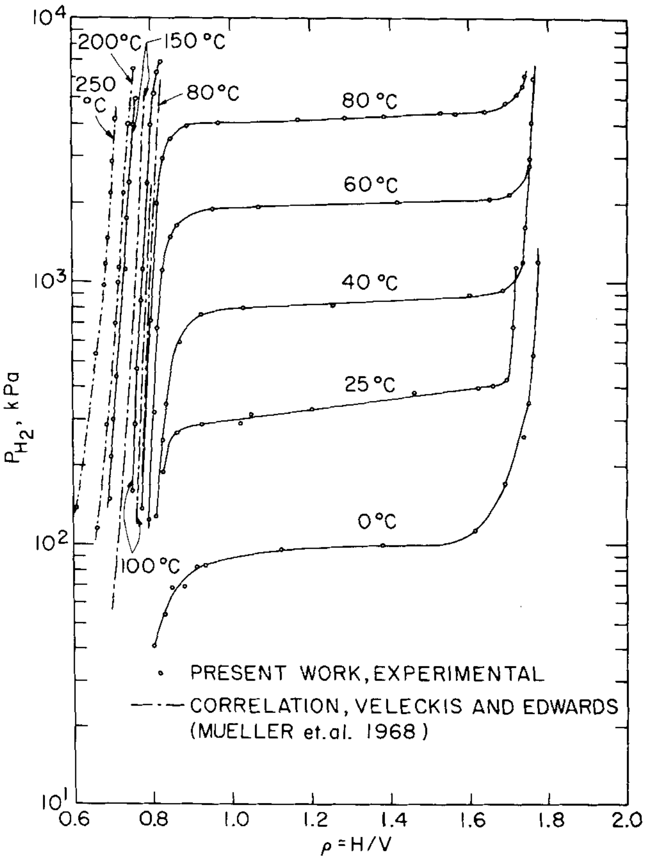

Fig. 2. Pressure-composition isotherms for the vanadium-hydrogen system. Vanadium was of commercial grade, 99.5% vanadium. See text for major impurities.

Experiments performed to determine whether the HT in the tritiated hydrogen pulse injected into a bed was quantitatively contained in the pulse leaving the bed disclosed no appreciable long term retention of HT.

Electron microscope photographs were made of a number of batches of vanadium monohydride particles. Hydrogen pressure applied during the activation process was a variable in the preparation of these batches. For some batches, this pressure was only high enough to produce the monohydride, while for others it was increased to a value sufficient to produce the dihydride. In all cases, nonporous structures were found with numerous cracks. However, for those particles activated at the higher pressure, more deeply penetrating finer cracks were observed. For all chromatographic runs, particles were used which had been activated at the higher pressure.

A BET surface area measurement using nitrogen gas was made on a sample of vanadium hydride particles having a geometrically averaged particle diameter of 0.027 cm. The specific surface area found was 0.0375 m^2/g. The specific geometrical area of the particles, assumed to be spherical, was 0.004 m^2/g. When particle shape and internal cracks are taken into account, the BET surface area measurement may well be in agreement with the actual geometrical area. The fact that the BET area was not orders of magnitude larger as for porous solids lends support to the notion that the particles were essentially nonporous.

RESULTS AND DISCUSSION

Pressure-Composition Isotherms

Measurements were made in the $VH_{\sim 0.6}$ – $VH_{\sim 1.8}$ region at temperatures from 0° to 250°C and pressures from approximately atmospheric to 7 000 kPa. The results

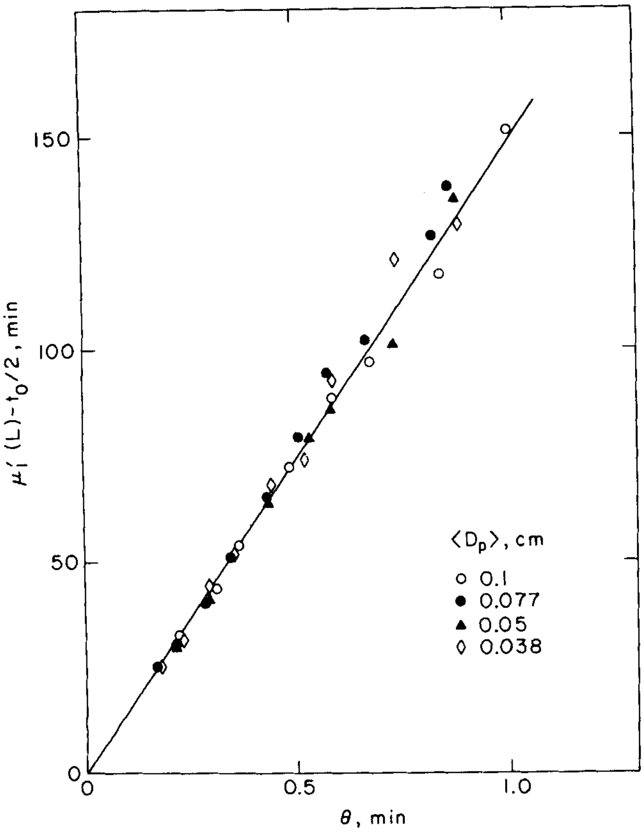

Fig. 3. Typical first moment data for chromatographic experiments. $T = 98.5°C$, $P = 1\,030$ kPa(150 lb/in.^{2}).

are shown in Figure 2. The plateau pressures, corresponding to dihydride dissociation, were approximately twice those reported by Reilly and Wiswall (1970) for hydride made from zone refined vanadium, thus reflecting the strong influence of impurities. Hydrogen content of hydrides made from commercial grade vanadium was lower than that for hydrides from zone refined vanadium. Impurities were found to exert no significant influence on the temperature dependence of the plateau pressures, confirming the earlier findings of Reilly and Wiswall (1972).

Also shown in Figure 2 is a comparison of the present data with the predictions of a semiempirical formula due to Veleckis and Edwards (Mueller, Blackledge, and Libowitz, 1968):

$$\ln p_{\mathrm{mm}}^{1/2} = 10.283 + 1.0598 \ln \frac{\rho}{0.89-\rho} + \frac{1}{T}(-3\,489.2 - 3\,269.0\,\rho + 2\,563.0\,\rho^2 - 762.39\,\rho^3 + 4\,818.3\,\rho^4) \quad (18)$$

Agreement with this relation is good at high temperature and at pressures below the dihydride dissociation pressure. Equation (18) was developed by fitting pressure-composition data for the α phase to a model based on simple interstitial solution of hydrogen atoms in a perfect crystalline lattice. Thus, this model appears to apply also to the β phase at higher temperatures.

The distribution coefficient K_{H_2}, as defined in Equation (14), was calculated from the isotherm data as follows. From the perfect gas law

$$C^*_{H_2} = \frac{P}{RT} \quad (19)$$

The equilibrium concentration of hydrogen atoms in the solid phase is given by

$$C^*_H = \rho \left(\frac{5.55}{50.95 + 1.008\,\rho} \right) \quad (20)$$

where ρ is the hydrogen to vanadium ratio corresponding to the pressure P on the isotherm, 50.95 and 1.008 are the atomic weights of vanadium and hydrogen, and 5.55 is the density of vanadium hydride in grams per cubic centimeter estimated from a knowledge of the unit cell structure and lattice parameters of vanadium monohydride (Trzeciak et al., 1956; Maeland, 1964).

It should be noted that while the pressure-composition isotherm measurements were made over both the monohydride (β) and dihydride (γ) regions, interest is centered in the chromatography experiments in the β region only. Rates of isotope exchange (Wiswall and Reilly, 1972) and hydrogen absorption-desorption rates (Reilly and Wiswall, 1970) had earlier been shown to be much greater in this region.

Chromatography Experiments

These experiments were conducted over the temperature range 40° to 307°C and over the pressure range 210 to 1 030 kPa (30 to 150 lb/in.^{2}). Hydrogen flow rates were varied from 80 to 400 standard cm^3/min. Four particle sizes were used: 40/45 mesh (380 μm geometric average diameter), 30/40 (500), 20/25 (770), and 16/20 (1 000).

Preliminary experiments disclosed that first moments could be determined with considerably less scatter than second moments. Hence, when it was solely of interest to determine separation factors from first moment plots of the type described previously and shown in Figure 3, fewer experiments were required than when determination of rate information from second moments was of interest as well. Determination of rate information was restricted to the temperature range 60° to 98.5°C. Within this range at pressures below the dihydride dissociation plateau pressure, reasonably short experiments could be conducted and restricted to the β phase. In this temperature range for each set of temperature, pressure, and particle size values, ten to twelve experiments were carried out with hydrogen velocity being the independent variable. At temperatures above 98.5°C and below 60°C where the separation factor alone was of interest, just three experiments were necessary for reasonably precise determination of first moment data.

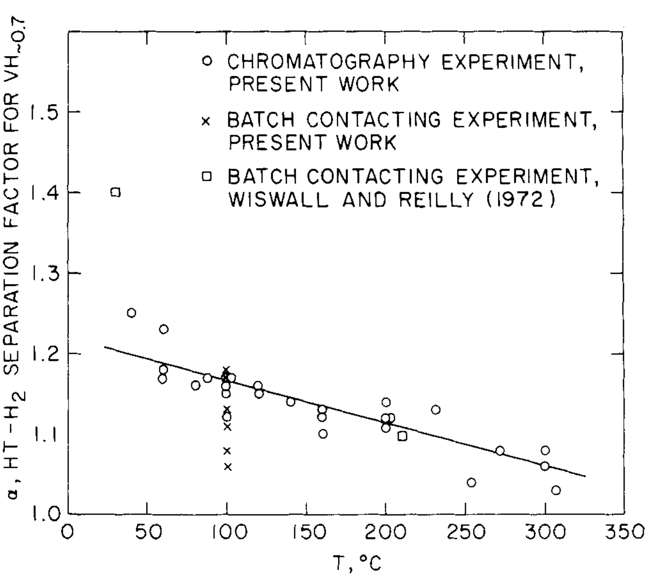

Fig. 4. Tritium-protium separation factor as a function of temperature.

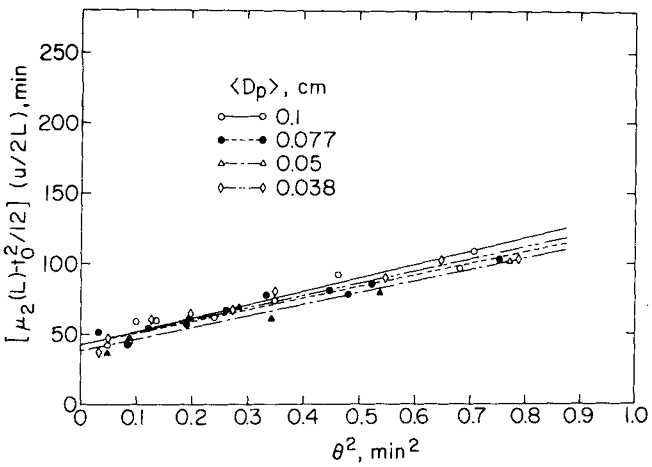

Fig. 5. Typical second moment data from chromatographic experiments. $T = 98.5°C$, $P = 1\,030$ kPa(150 lb/in.^{2}).

Elution curves for these experiments were very nearly Gaussian. First and second moments at the column outlet $\mu_1'(L)$ and $\mu_2(L)$ were derived by numerical integration of the resulting elution curves.

A typical plot of $\mu_1'(L) - t_0/2$ vs. θ is shown in Figure 3. The data in the figure are for a pressure of 1 030 kPa (150 lb/in.^{2}) and 98.5°C, and for all particle sizes. The line through the data is a least-squares straight line through the origin fitted to the data for all particle sizes. According to Equation (11), a straight line with zero intercept should be obtained if ϵ, α, and K_{H_2}, the quantities determining the slope, are constants independent of velocity and particle size. The quantities α and K_{H_2} are equilibrium properties which are indeed independent of these variables. The void fraction ϵ is independent of velocity and was found to be 0.5, independent of particle size.

The slope of the line in Figure 3 and the slopes of all other such lines corresponding to the combinations of temperature and pressure used were determined. Those slopes in combination with the independently measured void fraction and the appropriate distribution coefficient derived from the pressure composition isotherm data were used to obtain values of the separation factor α. (Distribution coefficients for temperatures above 250°C, the maximum temperature for which pressure-composition data were obtained, were derived from the Veleckis and Edwards correlation.)

The values of α so determined are plotted vs. temperature in Figure 4. It was found that α is not a function of pressure. This behavior is expected, since α is held to be related to the Einstein vibration frequencies of the isotopes in the metal lattice (Ebisuzake and O'Keeffe, 1967) and hence should be a function of lattice structure and temperature only. It is generally true that isotope effects disappear, that is, $\alpha \rightarrow 1$, at high temperature (Melander, 1960). As a result, the magnitude of the measured α was expected to decrease with temperature. This was found to be so experimentally. It is interesting that there is no discontinuity in the variation of α with temperature in the range 160° to 180°C, where a transition from the β to the α phase occurs (Schober and Wenzl, 1978).

Also shown in Figure 4 are separation factors obtained by Wiswall and Reilly (1972) and in this work using the batch contacting technique. Those obtained in the present work were derived from measurements made at 100°C and pressures ranging from 690 to 1 240 kPa. Activity balances were good to excellent. The separation factors obtained did not vary significantly with pressure. The average value at 100°C was 1.12. Good agreement exists between the data for the batch contacting and chromatography experiments. Also, agreement is good between data for hydrides derived from pure and commercial grade vanadium (Wiswall and Reilly's data are for zone refined vanadium). The presence or absence of impurities seemed to have no influence on separation factor.

A typical plot of second moment data in a straight line form suggested by Equation (12) is presented in Figure 5. Each line is a least-squares fit and represents the data for a particular particle size. A general conclusion found for all such plots was that within experimental error neither the intercepts nor the slopes of these lines varied with particle size. According to Equation (17), the intercept is a function of the sum of two terms, one of which is particle size dependent through the factor r_p^2. The other is independent of particle size. Particle size was varied by a factor of 2.6 in the experiments, and therefore r_p^2 was varied by a factor of 6.9. A lack of dependence of the intercept on particle size in spite of a sevenfold variation in r_p^2 implies that the first term in brackets in Equation (17) was always small compared to the second. The first term represents the sum of the resistances due to external mass transfer and to diffusion of tritium atoms within a particle, whereas the second term expresses the resistance due to the interfacial gas-solid exchange reaction. The implication is that the latter resistance is controlling.

With knowledge that the first term in brackets in Equation (17) is small compared with the second, this equation was used in combination with values of ϵ, α, and K_{H_2} to determine values of $k_f^T C^*_H$ for each set of temperature and pressure conditions. For purposes which will become

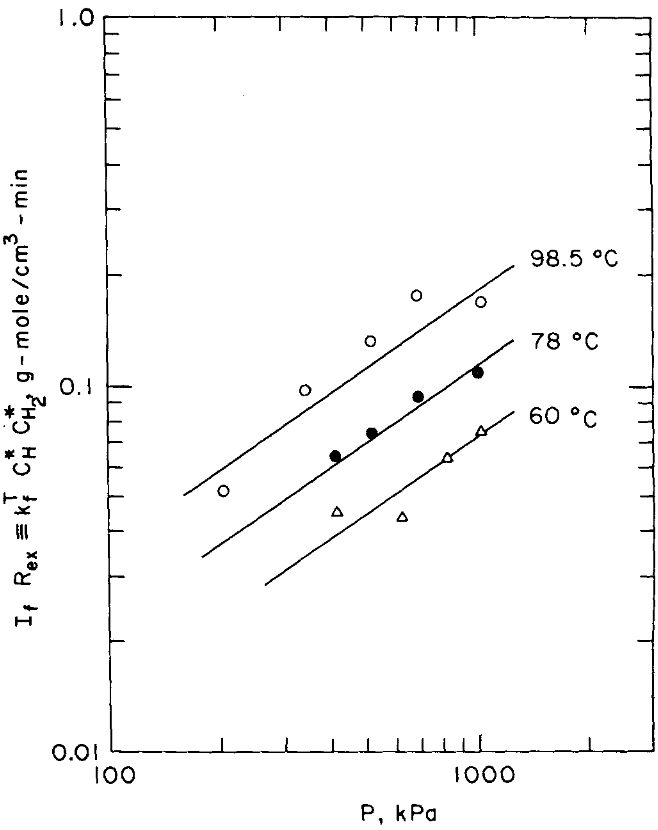

Fig. 6. Temperature and pressure dependence of $I_f R_{ex} \equiv k_f^T C^*_H C^*_{H_2}$

Table 1. Time Scales for External Mass Transfer, Solid Phase Diffusion and Surface Exchange Reaction

$r_p = 0.05$ cm

$D_s = 8 \times 10^{-5}$ cm²/s

T, °C	p, kPa (lb/in.²)	D_{HT-H_2}, cm²/s	$\theta_{ext} = \alpha/2\ K_{H_2} r_p^2/3D_{HT-H_2}$, s	$\theta_s = r_p^2/15D_s$, s	$\theta_r = \alpha/2\ K_{H_2}/k_fC^*_H$, s	$(\theta_{ext} + \theta_s)/\theta_r \times 100$, %
60	1 034 (150)	0.151	0.79	2.08	41.4	6.9
60	414 (60)	0.369	0.76	2.08	67.1	4.2
98.5	1 034 (150)	0.182	0.67	2.08	17.1	16.1
98.5	207 (30)	0.894	0.67	2.08	55.4	4.9

apparent later on, each value of $k_f{}^TC^*{}_H$ was then multiplied by $C^*{}_{H_2} = P/RT$, where the values of P and T were those corresponding to the experiments from which the value of $k^T{}_fC^*{}_H$ was derived. Values of $k_f{}^TC^*{}_HC^*{}_{H_2}$ so determined are shown in Figure 6. The temperature and pressure dependence of $k_f{}^TC^*{}_HC^*{}_{H_2}$ was found to be given by

$$k_f{}^TC^*{}_HC^*{}_{H_2} = 4.06\, P^{0.7} \exp\left(-\frac{24\,600}{RT}\right) \quad \text{g mole/cm}^3\text{-min} \qquad (21)$$

where P is in kilopascals and the activation energy is in joules per gram-mole.

It was surprising to find the surface exchange reaction controlling rather than solid phase diffusion. The latter process when present is usually limiting. Yet, by way of corroboration, Wiswall et al. (1977) made the observation following their stimulus-response experiments on the same system that, with step change stimuli, the total amount of hydrogen that emerged before breakthrough of the tritiated hydrogen front was about equal to the amount of hydrogen in the solid phase. They concluded from this finding that all of the hydrogen in the particles was chromatographically active and that solid state diffusion was not limiting.

The diffusion coefficient of hydrogen atoms in vanadium monohydride evidently has not been measured though the coefficient for diffusion in vanadium metal has and has been reported to be 8×10^{-5} cm² s⁻¹ (Schaumann, Völkl, and Alefeld, 1970). This value is used in calculations reported below on time scales of mass transfer and reaction.

A number of calculations were made to examine the reasonableness of the finding that the exchange reaction was controlling. For this purpose, estimates were made of D_{HT-H_2} using the Chapman-Enskog formula (Hirschfelder, Curtiss, and Bird, 1954). These estimates were used along with appropriate values of α, K_{H_2}, and r_p to evaluate $\theta_{ext} = \alpha/2\ K_{H_2}r_p{}^2/3D_{HT-H_2}$, the characteristic time for external mass transfer appearing in Equation (17). Estimates of $\theta_s = r_p{}^2/15\ D_s$, the time for solid phase diffusion, were calculated using the value indicated above for D_s. The exchange reaction time scale $\theta_r = \alpha/2\ K_{H_2}/k_f{}^TC^*{}_H$ was estimated using Equations (19) and (21) and values of α and K_{H_2}. The results calculated for the extremes of temperature and pressure used experimentally are shown in Table 1. The largest particle radius employed experimentally, $r_p = 0.05$ cm, was used in order to make conservative comparisons. It is seen in Table 1 that the time for external mass transfer was, at most, a few percent of the exchange reaction time. Evidently the diffusion coefficient of hydrogen atoms in vanadium monohydride is of the order of 8×10^{-5} cm²/s or larger, for even with the stated value the maximum solid phase diffusion time is of the order of 16% of the exchange reaction time.

For the purpose of examining the significance of the temperature and pressure dependence of the exchange reaction rate, it is convenient to proceed as follows. The rate of disappearance of HT is given by $k_f{}^TC^*{}_HC^*{}_{HT}$. This rate may be expressed in terms of the rate of the hydrogen exchange reaction

$$H_2(g) + H(s) \underset{k_r{}^H}{\overset{k_f{}^H}{\rightleftarrows}} H_2(g) + H(s) \qquad (22)$$

as follows:

$$k_f{}^TC^*{}_HC^*{}_{HT} \equiv \frac{k_f{}^T}{k_f{}^H} k_f{}^HC^*{}_HC^*{}_{H_2} \frac{C^*{}_{HT}}{C^*{}_{H_2}} = I_fR_{ex} \frac{C^*{}_{HT}}{C^*{}_{H_2}} \qquad (23)$$

As one can see, the product of the hydrogen exchange rate R_{ex} and the forward isotope effect I_f is identically the left-hand side of Equation (21). The forward isotope effect is independent of pressure and is a slowly varying function of temperature (Melander, 1960). Hence, all of the pressure dependence and substantially all of the temperature dependence of Equation (21) may be ascribed to the hydrogen exchange rate R_{ex}. The pressure dependence of the hydrogen exchange reaction rate may range from P^0 to P^1 according to the detailed nature of the mechanism of chemisorption and reaction of hydrogen. Three such mechanisms together with their pressure dependencies are those of Bonhoeffer and Farkas (P^0), Rideal-Eley, two site ($P^{0.5}$), and Riedal-Eley single site (P^1). A pressure dependence given by $P^{0.7}$ can be ascribed to a mixture of contributions from all three mechanisms. Alternately, the explanation of Scholten and Konvalinka (1966) may be valid. They found a pressure dependence of $P^{0.64}$ for the rate of hydrogen exchange on β palladium hydride. This pressure dependence closely approximated the variation with $P^{2/3}$ found for a mechanism based on a surface composition of Pd_3H_2 (approximately the composition of $PdH_{0.68}$ used experimentally) and the assumption that the rate of reaction was proportional to the number of hydrogen collisions with the surface and the chance of encounter with a free palladium atom. The same argument would apply to the β vanadium hydride system with its approximate composition V_3H_2.

The temperature dependence of the hydrogen exchange rate is in the range expected for activated chemisorption (Flanagan, 1977).

As can be seen from Equation (16), the slopes of second moment plots in the form shown in Figure 5 are related to the axial dispersion coefficient E_z. Values of E_z were calculated from the slopes of all such plots in combination with values of ϵ, α, K_{H_2}, and L. With values of E_z so derived and values of the molecular diffusion coefficients D_{HT-H_2} estimated as indicated previously, tortuosity factors q_{ext} were calculated from

$$E_z = \frac{\epsilon D_{HT-H_2}}{q_{ext}} \tag{24}$$

The average value of the tortuosity factors with 2σ limits was 1.12 ± 0.16, which is smaller than would be expected for purely laminar flow. (The Reynolds numbers based on the particle diameter varied from 0.2 to 2.2.) The presence of some mechanism of axial mixing in addition to molecular diffusion may account for the low values. A similar finding was reported by Padberg and Smith (1968).

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NOTATION

C^0_{HT} = concentration of HT in injected pulse
C_i = concentration of species i
$C^*_{HT}, C^*_{H_2}$ = gas phase interface concentrations of HT and H_2, respectively
C^*_T, C^*_H = solid phase interface concentrations of T and H, respectively
$\overline{C_i}$ = average concentration of species i in particle
D_s = diffusion coefficient of tritium atoms in solid particle
D_{HT-H_2} = diffusion coefficient of HT in H_2
D_p = particle diameter
E_z = axial dispersion coefficient
I_f = k_f^T/k_f^H, forward kinetic isotope effect
I_2 = intercept defined in Equation (17)
k_f^T, k_r^T = forward and reverse reaction rate constants for Equation (1) when occurring at gas-solid interface
k_f^H, k_r^H = forward and reverse reaction rate constants for Equation (22).
k_g = gas phase mass transfer coefficient
K_{H_2} = hydrogen distribution coefficient
L = column length
p_{mm} = hydrogen pressure, mm Hg
P = hydrogen pressure
q_{ext} = tortuosity factor
r = radial position
r_p = average particle radius
R = gas constant, 8.31 J/g-mole-°K
R_{ex} = hydrogen exchange rate, g mole/cm^3-min
S_1, S_2 = slopes defined by Equations (15) and (16)
t = time
t_0 = time of pulse injection
T = temperature, °K
u = superficial gas velocity
z = axial position

Greek Letters

α = HT-H_2 separation factor defined by Equation (13)
$\bullet$ = bed void fraction
θ = L/u, gas residence time
θ_{ext} = time scale for external mass transfer
θ_r = time scale for exchange reaction
θ_s = time scale for solid phase diffusion
μ_1' = first absolute moment
μ_2 = second central moment
ρ = hydrogen to vanadium atom ratio

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