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KNOLLS ATOMIC POWER LABORATORY

SCHENECTADY, NEW YORK

DIFFUSION STUDIES
I. THE PERMEABILITY OF TYPE 347 STAINLESS STEEL
TO HYDROGEN AND TRITIUM

D. Randall and O. N. Salmon

March 17, 1953

OPERATED FOR THE
U.S. ATOMIC ENERGY COMMISSION
BY THE
GENERAL ELECTRIC COMPANY

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Chemistry

General Electric Company
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ABSTRACT

The permeability of Type 347 stainless steel to hydrogen and to tritium as a function of temperature and pressure has been measured. The rate of permeation R in cc(STP)/hr is described for negligible back pressure by the equation

$$R = \alpha \sqrt{P} \frac{A}{d} \left[\frac{\beta d \sqrt{P}}{1 + \beta d \sqrt{P}} \right] = \frac{\gamma A P}{1 + \beta d \sqrt{P}}$$

where $\gamma = \alpha\beta$, P is the pressure in cm of mercury, A is the diffuser area in cm^2 , and d is the diffuser thickness in mm. For large values of P this becomes

$$R = \alpha \frac{A}{d} \sqrt{P}$$

and for very small values of P it approaches the form

$$R = \gamma A P$$

The temperature dependence of the coefficients α and γ are given by

$$\alpha = \alpha^0 e^{-E/2R_0 T}$$

$$\gamma = \gamma^0 e^{-E'/R_0 T}$$

where E is the high-pressure activation energy in cal/mole and E' is the low-pressure activation energy in cal/mole. R_0 is the gas constant, 1.987 cal/mole deg, and T is the absolute temperature in $^\circ\text{K}$.

Within the range $0 \leq P \leq 34$ cm and $550^\circ\text{C} \leq T \leq 700^\circ\text{C}$, the experimental values are given as follows:

	E	E'	α^0	γ^0
Hydrogen	33.01×10^3	16.86×10^3	105.6	616.0
Tritium	31.81×10^3	19.50×10^3	48.03	1332
Average deviation	3%	9%	4%	12%

The high-pressure ratio of the permeation rate of hydrogen to that of tritium increases with increasing temperature

$$\frac{\alpha_{\text{H}_2}}{\alpha_{\text{T}_2}} = 2.199 e^{-302/T}$$

This is in contrast to the behavior of H_2 and T_2 with palladium, in which case the ratio decreases with increasing temperature. The significance of this and other results is discussed.

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DIFFUSION STUDIES
I. THE PERMEABILITY OF TYPE 347 STAINLESS STEEL
TO HYDROGEN AND TO TRITIUM

D. Rendall and O. N. Salmon

INTRODUCTION

The objective of the present work has been the determination of the permeability of Type 347 stainless steel to hydrogen and to tritium as a function of temperature and pressure. The significance of the permeability equation has been examined with special emphasis being placed upon the moderately high-pressure region and upon the limiting case of very low pressure. The nature of the rate-controlling processes has been elucidated through consideration of the various activation energies involved.

From the practical point of view, the data obtained permit the calculation of the permeability of Type 347 stainless steel to H_2 or T_2 over a pressure range of essentially zero up to about half an atmosphere and within a temperature interval of about 550° to $700^\circ C$. The results are in good agreement with somewhat similar data obtained by other authors.

Briefly, the permeation rates have been determined by measuring the rate of increase of gas pressure in a constant volume on the downstream side of a cylindrical stainless steel diffuser for various constant upstream pressures and for two different diffuser temperatures. Precision of the results has been estimated to be 4 to 12% for various conditions. The necessary computations and corrections have been described (auth)

EXPERIMENTAL TECHNIQUE

Apparatus

The details of the diffuser chamber are shown in Figure K-6A4922 and the relevant portion of the vacuum system is shown schematically in Figure K-6A4923.

The diffuser proper* consists of a 5-1/2-inch-long Type 347 stainless steel cylinder, of wall thickness 10 mils (0.254 mm) and outer diameter 1/4 inch, closed at one end by a heavy-walled stainless steel plug and welded at the other end to a Kovar tube, outer diameter 1/4 inch. The effective length of the diffuser is 5 7/16 inches. Chromel-Alumel thermocouples are spot welded at three points along the length of the diffuser, namely, at $\ell = 0$, $\ell = 1$, and $\ell = 3.5$, where ℓ denotes the distance in inches downward from the Kovar to stainless steel weld. The thermocouple leads are brought into the diffuser chamber through Kovar tubes which are then sealed with soft solder. The wiring arrangement as shown permits the

*Supplied by P. S. Flint.

measurement of the temperature at these three points using four wires; thus, the potential across 1 and 2 is a measure of the temperature at $\ell = 0$, across 2 and 3 the temperature at $\ell = 1$, and across 3 and 4 the temperature at $\ell = 3.5$. Thus, temperature as a function of diffuser length is known. The diffuser is enclosed in a quartz chamber connected to the upper Pyrex portion through a graded seal. The diffuser tube is itself connected to the Pyrex outlet (1/4-inch inner diameter) by means of the Kovar tube. The entire assembly is positioned within a small resistance furnace (Powerstat-controlled) such that the Kovar tube is not strongly heated and diffusion occurs essentially through the stainless steel only. The direction of gas flow is indicated by the arrows. The main volume of the diffuser chamber is connected upstream in order to minimize any possible blanketing effect of gaseous impurities which would not diffuse and which would become concentrated upstream in the immediate vicinity of the diffuser surface.

In Figure K-6A4923, the diffuser is located at D, the arrows again indicating the direction of gas flow through the barrier. A mercury manometer M, located upstream, is read by a permanently mounted cathetometer to the nearest 0.01 cm pressure. Measurement of upstream pressures of 1 cm or less was accomplished by means of a double McLeod gauge (DMc) which covers the pressure range 11,000 microns to zero and 2000 microns to zero, respectively. On both sides of the diffuser are located liquid nitrogen cold traps T, between the diffuser and the stopcocks. These two traps were kept filled at all times in order to avoid contamination of the diffuser surface not only by mercury vapor but also by any stopcock grease and other condensable vapors. Cold traps elsewhere in the system are similarly indicated by T. Located upstream is B8, a 15-gram powdered uranium bed for storage of the tritium-rich gas, while downstream is B3, a similar bed for storage of pure hydrogen. Downstream there is also an ionization chamber (IC) developed by H. C. Matraw and F. G. LaViolette, volume about 890 cc, wrapped in aluminum foil electrically connected to the shielding mesh of the cable leading to a Beckman micromicroammeter. This external shielding of the entire body of the ionization chamber reduced fluctuations of the input current to the Beckman to virtually zero. The Beckman itself was modified by replacing the input resistors 10^8 and 10^{11} ohms by 10^6 - and 10^8 -ohm resistors, respectively, in order that macro quantities of tritium could be measured. A Pirani gauge (P) is connected downstream through a cold trap; the sealed-off reference arm of the Pirani, highly pumped out and containing one gram of palladium black, is immersed in the same cold trap. With these precautions it was found that the calibrations of the Pirani remained constant throughout the entire course of the experimental work. A large McLeod gauge (Mc) was, however, the means of accurately measuring the small downstream gas pressure built up during a run; the Pirani gauge served merely as a convenient means of continuously following the pressure. A Kurth-Ruggles two-stage mercury vapor pump DP_1^2 feeding into an automatic Toepler pump ATP^3 removes the downstream gas either to a temporary storage volume (V) or back to the upstream portion of the system. Two sample bulbs (SB) of approximately 100-cc volume each are located downstream, which together with the small volume (SV) between two stopcocks in the diffuser by-pass line permit the sampling of original and of freshly diffused gas. The system as a whole may be evacuated by means of a one-stage mercury vapor pump DP_2 backed by a Duo-Seal two-stage vacuum pump (OP) which is trapped as shown. Other features of the system, not pertinent to this particular study, have been omitted.

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THE VACUUM SYSTEM
SCHEMATIC

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All stopcocks in the system are mercury-sealed, and those which at any time might be contacted with tritium are greased with Fluorothene G, a polymer of $CF_2 = CFCl$ furnished by the Oak Ridge National Laboratory, rather than by Apiezon N. The high viscosity of Fluorothene G grease usually necessitated the warming of the stopcock for one to two minutes with an infra-red lamp before it could safely be turned. These measures avoid (a) any leakage of air into the system or of gas from within the system to the atmosphere, and (b) degradation of the tritium content of the gas by exchange with hydrogen in stopcock grease.

Calibration of the various volumes of the system was accomplished using high-purity* helium and the simple $PV = \text{constant}$ relationship with, of course, all liquid nitrogen traps filled. The upstream double McLeod gauge was calibrated, by successive expansions of a known quantity of helium, against the mercury manometer and also against the large downstream McLeod. The closely agreeing corrections were averaged for actual use. Volume calibration of the diffuser was carried out not only at room temperature but also over the range of diffuser temperatures to be encountered. The Pirani gauge was calibrated with known pressures of H_2 and of mixtures of known tritium content, as was also the Beckman. A combination of the Beckman reading with the Pirani gauge reading and/or the McLeod gauge reading enabled us to estimate to within 0.5% tritium the isotopic composition of the tritium-rich gas at any time. The accurate analyses of small portions of gas collected in the sample bulbs were made by H. C. Matraw and C. F. Pachucki, using a General Electric mass spectrometer.

Materials

The stainless steel diffuser was analyzed (by J. Marley), yielding the following results:**

Mn	1.52 %
Ni	10.51
C	0.097
Cb	0.81
Cr	18.49

The tritium-rich gas was analyzed with the following results:

H	4.72 atom %	} isotopic analysis
T	95.2 atom %	

*Passed twice through activated charcoal at liquid nitrogen temperature - Air Reduction Co.

**The sample of Type 347 stainless steel used by Hawkins⁵ (vide infra p. 23, 25) to obtain solubility data was analyzed with the following results: Mn 1.39%, Ni 10.66%, C 0.075%, Cr 18.8%.

CO ₂	0.03 %	} impurity analysis
N ₂	0.04 %	
H ₂ O	low	
He ³ , He ⁴ , A, O ₂	0.00 %	

The hydrogen used was supplied by the Matheson Company.

The gases were stored in uranium beds at room temperature, the hydrogen (or tritium) being evolved, when required, by heating the desired bed to about 430°C. It is safe to assume that such nonisotopic impurities as CO₂, N₂, O₂, and H₂O are completely and permanently removed from the hydrogen isotopes by reaction with hot uranium (reducing the bed storage capacity for H₂ or T₂ only very slightly). Furthermore, inert gases such as A, He³, and He⁴ are largely removed by pumping out all residual gas after sorption of the hydrogen isotopes on the uranium beds. Thus the purity of H₂ and T₂ should improve with use. Of course, the hot stainless steel inevitably contributes some H₂O, CO, and perhaps CO₂ during the initial activation runs which are then either permanently taken up upon a uranium bed or else evacuated from the system. Furthermore, the decay of tritium itself continually furnishes a small but measurable amount of He³; the accumulated He³ is, however, pumped out before each run. By the same token, any other gaseous contaminants (e.g. from stopcock grease degassing) would be either permanently combined in a uranium bed or else pumped out of the system just before and just after a run. After a short period of use, the gases may therefore be regarded as being virtually 100% pure hydrogen isotopes.

No attempt was made to enrich the tritium-rich gas. The data were instead corrected to correspond to 100% T₂ by the methods outlined in Appendix A.

Method

The rate of permeation of gas through the stainless steel diffuser was determined by measuring the rate of downstream pressure increase under constant volume conditions.

The experiments covered a pressure range of about 34 cm of mercury down to about 500 microns at two temperature levels of average temperature 569°C and 698°C, respectively.

A run consisted of several observations of such downstream pressure rise rates, each observation corresponding to a particular upstream pressure. During any one observation, the downstream pressure would be allowed to rise to a maximum of about 200 microns, which in comparison with the usual upstream pressure of 5 to 30 cm or so is sufficiently small (0.1 to 1%) to safely allow neglect of back-pressure. This is not quite as good an approximation for the few observations made at very low upstream pressures where the corresponding downstream pressure might approach 5% of the upstream pressure.

Another consequence of the low rate of permeation was the fact that during any one observation the upstream pressure did not decrease by more than 1 to 2% in the high-pressure region and up to about 10% in the low-pressure region. The upstream pressure was measured at the beginning and end of each observation, and the mean value was taken as the upstream pressure corresponding to the observed rate of permeation.

A typical observation would be carried out in the following manner. The gas, H_2 or T_2 , is confined in the upstream volume (ca. 250 cc) consisting of the manometer, the upstream portion of the diffuser, and the connecting leads. The diffuser is at operating temperature and the gas is diffusing freely although slowly into the downstream side (ca. 2202 cc) of the system. There the gas is being transferred by the mercury diffusion pump and Toepler pump (connected in series) into the temporary storage volume. The ionization chamber, Pirani gauge, and large McLeod gauge are open to the system. When a steady state has been reached as evidenced by a low but constant reading on the Pirani gauge, the McLeod gauge is read.* The stopcock between the downstream manifold and the diffusion pump is then shut off and simultaneously a stopwatch is started. As rapidly as possible the upstream manometer is read and the three thermocouple readings are recorded. The Pirani gauge is now closely followed. When it indicates a pressure corresponding to say 200 microns on the McLeod, the upstream pressure and diffuser temperatures are noted, and then the downstream McLeod gauge is read, the stopwatch being stopped just as the mercury passes the cut-off in the McLeod gauge. This completes the observation. The accumulated gas downstream is now pumped into the storage volume; the by-pass around the diffuser is "cracked" momentarily to the downstream manifold to drop the upstream pressure to the next lower value at which it is desired to measure the rate of permeation. After the by-pass has been closed, the downstream pressure will fall off to a new, slightly lower constant level as the mercury pump - Toepler pump combination just balances the rate of permeation. The system is now in a steady-state condition, ready for the next observation.

After a run, the gas in the storage volume is resorbed upon the appropriate bed. Both sides of the diffuser chamber are pumped out while the diffuser is cooled to room temperature. After completion of pump-out, the diffuser is closed off from the system and allowed to stand at room temperature (with traps always filled with liquid nitrogen) until the next run.

*The McLeod is read before (rather than just at or immediately after) closing the stopcock to the downstream diffusion pump, since the volume of the McLeod gauge is large and the time required to run the mercury up and down is about three minutes. Were this technique not adopted the effective downstream volume during an observation would seriously be changed. In fact, in quite a few cases the McLeod operating time would exceed the total observation time itself.

Reproducible results are not obtained from the first few runs. That is, although the experimental points for any one run may lie on a smooth curve, coincidence among curves for the same temperature conditions is not observed until quite a few runs have been made. The time required for "activation" may be reduced by treatments of the diffuser barrier with H_2 or T_2 at pressures up to about 40 cm and temperatures of the order of $700^\circ C$ for periods of one to several days. Apparently this "activation" involves clean-up of the metal surface (e.g. removal of any oxide and carbon present) as described in the Discussion of Results, page 29. Only on the eighteenth and subsequent runs were the rate data sufficiently reproducible to be satisfactory, not just within any one run but from one run to another (despite intervening runs under different conditions).

Calculation of Results

The rate of permeation R in cc(STP)/hr is given by (for a particular temperature and against negligible downstream P_2)

$$R = \frac{A}{d} \sqrt{P_1} \left[\frac{\beta d \sqrt{P_1}}{1 + \beta d \sqrt{P_1}} \right] = \frac{\gamma A P_1}{1 + \frac{\gamma d \sqrt{P_1}}{\alpha}} \quad (1)$$

where α , β , and $\gamma \equiv \alpha\beta$ are permeability coefficients to be determined from the experimental data. A is the geometrical area* of the diffuser in cm^2 , d is the thickness† of the diffuser wall in mm, Δ and P_1 is the upstream gas pressure in cm of mercury. For our particular diffuser of area A_0 and thickness d_0 , the permeation rate in cc(STP)/hr/ cm^2 area/mm thickness is given by

$$\frac{R d_0}{A_0} = \alpha \sqrt{P_1} \left[\frac{\beta d_0 \sqrt{P_1}}{1 + \beta d_0 \sqrt{P_1}} \right] \quad (2)$$

Values of $R d_0 / A_0$ were calculated from

$$\frac{R d_0}{A_0} = Z V_2 \frac{d_0}{A_0} \left(\frac{dP_2}{dt} \right) \quad (3)$$

where $Z = 273.2/(76)(299.2) = 0.012014$, which for an average room temperature of $26^\circ C$ corrects to STP; $A_0 = 2\pi r_0 \ell = 2\pi(1/8 \text{ in.})(5 \frac{7}{16} \text{ in.})(2.540)^2 = 27.55 \text{ cm}^2$, so that $d_0/A_0 = 0.2540 \text{ mm}/27.55 \text{ cm}^2 = 0.009219$; V_2 = constant downstream volume (approx. 2202 cc) in which the downstream pressure rise rate (dP_2/dt) is observed; dP_2/dt is observed in microns/minute which must be multiplied by 60×10^{-4} to obtain the pressure rise rate in the desired units, cm/hour. Inserting these numerical values, Equation (3) becomes

$$\frac{R d_0}{A_0} = 6.645 \times 10^{-7} (V_2, \text{cc})(dP_2/dt, \text{microns/min}) \quad (4)$$

*i.e. as would be measured by a ruler.

† Not to be confused with the symbol for differentiation.

Δ These "hybrid" units are adopted to conform to the practice of P. S. Flint.⁴

Strictly speaking, dP_2/dt decreases slightly as the upstream pressure falls, however slowly. But we have seen that in consequence of the low rate of permeation, the upstream pressure is very nearly constant throughout the time required for the completion of any one observation; hence for purposes of calculation the differential coefficient has been replaced by the difference ratio, or

$$\frac{dP_2}{dt} \approx \frac{\Delta P_2}{\Delta t} = \frac{P_2(\text{final}) - P_2(\text{initial})}{\Delta t} \quad (5)$$

where $P_2(\text{initial})$ and $P_2(\text{final})$ are the downstream pressures (in microns) at the beginning (steady-state condition) and conclusion of any particular observation over an interval of Δt minutes.

The values of Rd_0/A_0 so calculated for each observation, at an average upstream pressure level of $(\text{initial } P_1 + \text{final } P_1)/2$ for each observation, were fitted by the method of averages to Equation (2), and the permeability coefficients α , β , and γ were thus numerically evaluated for each run. These are listed in Tables I and II (see Tabulated Data).

The temperatures T_1 , T_2 , and T_3 , measured by thermocouples at positions along the length ℓ of the axis of the diffuser given by $\ell = 0$, $\ell = 1$, and $\ell = 3.5$, were customarily taken twice during each observation. The average run consisted of from five to seven observations, so that for each run there were usually available some 10 to 14 values for each T_1 , T_2 , and T_3 . For each run, these were averaged and the over-all average diffuser temperature T_g was computed by means of Equation (121), Appendix B.

The average of the over-all average diffuser temperatures for the high-temperature H_2 runs (18ss, 21ss, 22ss, 28ss) was found to be $970.5^\circ K$; the corresponding average values of α and γ were 0.02597 and 0.1276, respectively. Similarly the average of the over-all average diffuser temperatures for the low-temperature H_2 runs (19ss, 26ss, 27ss) was $841.6^\circ K$, and the average values of α and γ were 0.007217 and 0.03452.

In like fashion it was found that for the high-temperature tritium runs (24ss, 25ss) the average T_g was $971.85^\circ K$ for which α and γ had average values of 0.01594 and 0.07684, and for the low-temperature tritium runs (20ss, 23ss, 29ss) the average T_g was $843.7^\circ K$ for which α and γ had average values of 0.004698 and 0.01723.

These values of α and γ require correction. First, α and γ at each temperature level calculated for the tritium-rich gas (atom fraction $\omega = 0.9$, referring to total tritium content) must be corrected to correspond to 100% T_2 ($\omega = 1.0$). This correction is accomplished for each run in the manner described in Appendix A, using Equations (76) and (90), respectively. Values of α and γ before and after this correction for the composition effect appear in Table II. No such correction is required for the H_2 data.

Second, α and γ at each temperature for both H_2 and T_2 (now corrected to $w = 1.0$) must be corrected for the temperature gradient existing along the length of the diffuser. Briefly, the method as described in Appendix B is as follows: a quantity B , defined as $B = E/2R_0$ where E is the over-all activation energy for the high-pressure process, is determined from Equation (113) using the ratio of high-temperature α to low-temperature α . Similarly a quantity B' , defined by the relation $B' = E'/R_0$ where E' is the over-all activation energy for the low-pressure limiting process, is determined from Equation (117) using the ratio of high-temperature γ to low-temperature γ . In this fashion, activation energies free of any error resulting from the temperature gradient are calculated for both H_2 and T_2 . This permits calculation of α and of γ by Equations (126) and (128) corresponding precisely to a definite temperature. These definite temperatures were chosen as the average values of T_g for all H_2 and T_2 runs combined, at the two temperature levels encountered in this work, i.e. $T_g = 970.9^\circ K$ for all high-temperature runs, and $T_g = 842.7^\circ K$ for all low-temperature runs.

These completely corrected values for E , E' , α and γ (as well as the corresponding β) for both H_2 and T_2 are listed in Table III.

Precision

The assumed constancy of upstream pressure and of downstream pressure rise rate to within say 1% has been discussed. The total downstream volume is known to within $\pm 0.3\%$ or better. The "room temperature" within the hood never varied more than $\pm 1^\circ C$ from one run to the next, which is equivalent to no more than $\pm 0.2\%$ in the STP correction factor Z . The assumed constancy of upstream gas composition throughout the course of any one run is good to $\pm 1\%$ or better, in view of the fact that no more than 1 to 5% of the total amount of gas ever actually passed through the diffuser. Error in timing probably never exceeded ± 1 second which for most observations amounts to less than $\pm 0.5\%$. Other instrumental errors such as the measuring of downstream pressure (± 1 micron in 200 microns) and upstream pressure (± 0.02 cm in 5 to 30 cm) would also be of the order of $\pm 1\%$ or less. The aggregate of all these above-mentioned errors would run to no more than $\pm 2\%$.

The reproducibility actually attained was generally less than this figure would indicate. In the following table are listed the mean values* of α and γ for H_2 and T_2 (corrected to 100% T_2) together with their observed average deviations in %:

Permeability constant	At 842°K		At 971°K	
	Mean value	Avg dev, %	Mean value	Avg dev, %
α_{H_2}	0.007217	± 2.9	0.02597	± 4.0
α_{T_2}	0.004698	± 5.5	0.01594	± 4.2
γ_{H_2}	0.03452	± 15	0.1269	± 8.6
γ_{T_2}	0.01723	± 11	0.07684	± 12

*These values are the ones obtained before correction for the temperature gradient. Since this correction is so laborious, it was not carried out for each run individually but rather for the appropriately averaged constants; thus we have no individual values of α and γ , so corrected, available for the estimation of the average deviation.

The high-pressure permeability constant α is actually good, over-all, to $\pm 4\%$, and the low-pressure permeability constant γ is good to $\pm 12\%$. This variation is probably the result of small changes primarily in the surface structure of the stainless steel from run to run despite all precautions. It is doubtful whether this degree of error could ever be greatly reduced. Furthermore, measurements in the region of a few hundred microns upstream pressure are considerably more difficult to make and less reliable than are measurements made at moderately high pressures.

The question of whether or not the single sample of Type 347 stainless steel which we have studied is a truly representative sample, e.g. from the point of view of surface roughness, possible lattice rifting, strain content and perhaps other factors, is one that cannot be definitely answered. Comparison of our results with what literature data are available indicates their essential correctness. The extent to which the sample is or is not truly representative would affect the absolute values of the various permeability constants but would not be expected to exercise any very great influence upon the relative permeation rates of H_2 and T_2 . By the same token, inaccuracies in the value of the area A_0 and the thickness d_0 of the experimental diffuser would shift the absolute values of α_{H_2} , α_{T_2} , γ_{H_2} , and γ_{T_2} but would be entirely without effect upon the ratios $\alpha_{H_2}/\alpha_{T_2}$ and $\gamma_{H_2}/\gamma_{T_2}$ and upon the individual activation energies.

The observed average deviations in α_{H_2} , α_{T_2} , γ_{H_2} , and γ_{T_2} would result in no more than the following uncertainties in the over-all activation energies:

	E, %	E', %
H_2	± 2.7	± 9.5
T_2	± 3.8	± 8.5

Thus high-pressure activation energies are probably correct to $\pm 3\%$ and low-pressure activation energies to $\pm 9\%$.

It is interesting to estimate the magnitude of the error which would have afflicted the results had the effect of the temperature gradient been ignored. From the table below it is seen that the average ratio of the observed rate to the rate corrected for temperature gradient is not unity, but rather $R(\text{obs})/R(\text{corr}) = 1.33$.

	Hydrogen		Tritium	
	$\frac{\alpha(\text{obs})}{\alpha(\text{corr})}$	$\frac{\gamma(\text{obs})}{\gamma(\text{corr})}$	$\frac{\alpha(\text{obs})}{\alpha(\text{corr})}$	$\frac{\gamma(\text{obs})}{\gamma(\text{corr})}$
971°K	1.286	1.300	1.257	1.403
842°K	1.326	1.342	1.295	1.458

The absolute values of the permeability constants would have been high by some 33% on the average had no correction for the temperature gradient been applied. Closer inspection of the data reveals that the effect of the temperature gradient is greater at lower temperatures, at lower pressures, and to some extent for T_2 as compared to H_2 , i.e. for conditions associated with lower permeation rates. The consequent error in the relative permeabilities would, however, have been considerably smaller.

	Corrected		Uncorrected	
	$\alpha_{H_2}/\alpha_{T_2}$	r_{H_2}/r_{T_2}	$\alpha_{H_2}/\alpha_{T_2}$	r_{H_2}/r_{T_2}
971°K	1.592	1.792	1.629	1.661
842°K	1.500	2.178	1.536	2.004

The high-pressure permeability constant ratio $\alpha_{H_2}/\alpha_{T_2}$ would have been in error by roughly 2.3%, and the low-pressure permeability constant ratio r_{H_2}/r_{T_2} by roughly 7.9% if the temperature gradient correction had not been made.

There is little reason to doubt that a very close approximation to a steady-state condition was actually reached just before beginning any particular observation. This is evidenced not only by the levelling off of the downstream pressure readings but also by the fact that good checks were obtained even though the length of time between the start of pump-down by the diffusion pump - Toepler pump combination and the start of an observation was widely varied. Thus a prolonged pumping (say 10 to 20 minutes) yielded, for the same temperature and upstream pressure conditions, the same results as a considerably shorter (say only 2 to 3 minutes) pumping time. In practice, then, a steady-state condition invariably obtained.

TABULATED DATA

Summarized Experimental Data

TABLE I

HYDROGEN

<u>Run</u>	<u>$10^3\alpha$</u>	<u>β</u>	<u>10^3r</u>	<u>T_1</u>	<u>T_2</u>	<u>T_3</u>	<u>T_a</u>
19ss	6.935	4.406	30.55	504.5	761.3	880.9	843.0
26ss	7.527	4.108	30.92	510.1	762.5	879.2	842.1
27ss	7.190	5.854	42.09	505.7	758.0	877.9	839.7
18ss	25.65	4.123	105.8	586.5	866.7	1021.3	972.3
21ss	26.14	4.853	126.8	593.1	868.6	1017.5	970.1
22ss	24.23	6.138	148.7	585.9	864.4	1015.2	967.4
28ss	27.86	4.636	126.3	589.7	868.6	1020.2	972.1

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TABLE II

TRITIUM

<u>Run</u>	<u>w_{orig}</u>	<u>w_{diff}</u>	<u>(10³α)</u>	<u>(β)</u>	<u>(10³γ)</u>	<u>10³α</u>	<u>β</u>	<u>10³γ</u>	<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T_a</u>	<u>K_e(orig)</u>	<u>K_e(diff)</u>	<u>ρ</u>
20ss	0.8986	0.8336	5.053	3.272	16.53	4.803	3.017	14.50	510.7	763.0	881.8	844.5	3.94	4.10	1.77
23ss	0.8976	0.8243	4.634	4.659	21.59	4.314	4.662	20.11	511.3	763.0	881.0	843.8	3.49	3.41	1.87
29ss	0.8843	0.8083	5.259	3.629	19.08	4.972	3.432	17.06	510.0	762.1	880.4	842.9	2.81	3.74	1.81
24ss	0.8887	0.8331	17.73	4.814	74.20	16.62	4.063	67.50	594.1	896.6	1019.9	972.1	3.54	3.97	1.71
25ss	0.8941	0.8306	16.47	5.498	90.57	15.26	5.647	86.18	592.4	868.3	1019.8	971.6	3.83	4.53	1.72

841
017

No attempt has been made to list the unprocessed pressure-time data for each run from which the various coefficients have been calculated.

The columns headed by the parenthetically enclosed coefficients represent the tritium data uncorrected to 100% tritium. The corrected values appear in the following columns. $K_e(\text{orig})$ and $K_e(\text{diff})$ refer to the gas phase equilibrium constants (Appendix A Equation (64)) of the original gas and of a sample of freshly diffused gas. Similarly w_{orig} and w_{diff} refer to the atomic fraction of tritium (Appendix A Equation (63)) present in the original and in the freshly diffused gas. K_e and w are based on mass spectrometer figures. By way of comparison, the theoretical values¹⁷ of K_e are 3.715 at 842.7°K and 3.798 at 970.9°K. The resultant experimental separation factors (Appendix C Equation (139)) are given in the last column.

SUMMARY OF CALCULATED RESULTS

TABLE III			
	Hydrogen	Tritium	Units
B	8310	8007	°K
B'	8486	9815	°K
$E = 2R_0B$	33.01×10^3	31.81×10^3	cal/mole
$E' = R_0B = E_1$	16.86×10^3	19.50×10^3	cal/mole
α (842.7°K)	0.005513	0.003588	$\text{cm}^{\frac{1}{2}} \text{mm hr}^{-1}$
β (842.7°K)	4.729	3.248	$\text{cm}^{-\frac{1}{2}} \text{mm}^{-1}$
γ (842.7°K)	0.02607	0.01165	hr^{-1}
α (970.9°K)	0.02027	0.01258	$\text{cm}^{-\frac{1}{2}} \text{mm hr}^{-1}$
β (970.9°K)	4.861	4.311	$\text{cm}^{-\frac{1}{2}} \text{mm}^{-1}$
γ (970.9°K)	0.09854	0.05424	hr^{-1}
α^0	105.6	48.03	$\text{cm}^{\frac{1}{2}} \text{mm hr}^{-1}$
γ^0	616.0	1332	hr^{-1}
ΔH_s	3356	3661	cal/mole
K^0	20.61	18.49	$\text{micromoles}/(100 \text{ g})(\text{mm}^{\frac{1}{2}})$
$v = \Delta H_s/2R_0$	844.8	921.5	°K
E_2	13.50×10^3	15.84×10^3	cal/mole
E_3	14.83×10^3	14.08×10^3	cal/g atom
$D^0 = \alpha^0/K^0$	5.127	2.597	$\text{cm}^{\frac{1}{2}} \text{mm}^{\frac{3}{2}} (100\text{g}) \text{hr}^{-1} \text{micromole}^{-1}$
$\sigma = E_3/R_0 = B - v$	7465	7086	°K

The computation of α , β , γ , B , B' , E , and E' was carried out as indicated previously. Values of ΔH_g , K^0 , and v were calculated from the data of N. J. Hawkins. The calculation and significance of α^0 , γ^0 , E_2 , E_3 , σ , and D^0 are described in the Discussion of Results.

In Figures MH-9A8189 and MH-9A8190 are plotted the permeation rates Rd_0/A_0 (in cc(STP)/hr/cm² area/mm thickness) for H₂ against the square roots of the upstream pressures (in cm mercury) for the high- and the low-temperature series of runs. The individual points are the experimentally observed rates at average diffuser temperatures of 970.5°K and 841.6°K, respectively. In both Figures MH-9A8189 and MH-9A8190 Curve I represents Equation (2) fitted directly to these observed points before correction for the temperature gradient. Curve II represents the permeation rates calculated from Equation (2) using values of α and γ corrected for the temperature gradient in the manner outlined under Calculation of Results; that is, Curve II shows the rates that would have been observed had the diffuser been uniformly at 970.9°K and 842.7°K in each case.

In Figures MH-9A8191 and MH-9A8192 are plotted Rd_0/A_0 for tritium against $\sqrt{P}$ for the high- and the low-temperature cases. The individual points are the observed permeation rates of tritium-rich gas at average diffuser temperatures of 971.8°K and 843.7°K. Curve I is Equation (2) fitted directly to these points before correction to 100% T₂ and before correction for the temperature gradient. Curve II shows the permeation rates calculated by Equation (2) using values of α and γ corrected to correspond to 100% T₂ but still uncorrected for the temperature gradient. Curve III shows the rates calculated using α and γ corrected to 100% T₂ and also corrected to correspond to uniform diffuser temperatures of 970.9°K and 842.7°K.

In all four figures, Curve I demonstrates the goodness of fit of Equation (2) to the experimental points. Curves II for H₂ and Curves III for T₂ represent the fully corrected permeation rate data at the two temperatures 970.9°K and 842.7°K. These curves are shown together in Figure KH-9A2717, permitting a direct graphical comparison of the behavior of H₂ and T₂. In effect, Figure KH-9A2717 is a summary of the entire body of permeation rate data gathered in the course of this study.

DISCUSSION OF RESULTS

The Permeability Equation

The Effect of Pressure

In what follows, it is assumed that the downstream pressure is negligibly small or zero.

It is known that at moderately high pressures the rate of permeation of a diatomic gas such as hydrogen through a metal barrier varies as the square root of the upstream pressure. At very low pressures the rate becomes proportional to the first power of the pressure. The situation for very

high pressure is not unambiguous; apparently saturation of the upstream metal surface with dissolved gas may be ultimately approached^{6,7} and the rate may become independent of pressure. Since the data at hand have been obtained for the low- and intermediate-pressure regions only, this last case will not be treated further.

The variation of permeability rate with pressure for a given temperature is expressed by Equation (1), which for large values of P approaches

$$R = \frac{A}{\alpha_d} \sqrt{P} - \frac{\alpha^2 A}{rd^2} \approx \frac{A}{\alpha_d} \sqrt{P} \quad (6)$$

and for very low pressures assumes the limiting form

$$R = ArP \quad (7)$$

In Equation (1) it is perhaps tempting to identify $[\beta d \sqrt{P} / (1 + \beta d \sqrt{P})]$ with the fraction of the metal surface covered by hydrogen atoms in the manner of a Langmuir adsorption isotherm. This interpretation encounters several difficulties,^{8,9} for example, the fact that it would predict that as $[\beta d \sqrt{P} / (1 + \beta d \sqrt{P})]$ approaches unity, the rate should become independent of pressure rather than proportional to $\sqrt{P}$ as is actually the case. Nonetheless, with or without theoretical significance, Equation (1) serves as a convenient means of accurately representing the rate-pressure data, and valid conclusions as to the activation energies may be drawn from its limiting forms. More complex relationships have been proposed,^{10,11,12,13} but their very complexity seriously detracts from their utility.

The geometry factors appearing in Equation (1) perhaps require clarification. The presence of A is obvious, since at all pressures the quantity of gas transported per unit time will vary directly with the area exposed to the gas. Further, at all pressures sufficiently high such that diffusion proper (i.e. migration of gas ions through the metal lattice) is rate-limiting, the rate will vary inversely with the thickness d . At very low pressures, however, the permeability becomes surface-process-limited (i.e. lattice migration is rapid compared to the surface process), and hence the permeation rate becomes independent of the thickness.¹⁴

Equations (6) and (7) may be compared with the permeation rate equations we have developed.¹⁴ Defining R_1 as the rate of penetration of the upstream surface layer by gas atoms, R_2 as the rate of diffusion of gas atoms through the body of the metal, and R_3 as the rate of removal of gas from the downstream surface, we may write

$$R_1 = R_1' - R_1'' = AaP_1(1 - C_1/C_s)^2 - AbC_1^2 \quad (8)$$

$$R_2 = \frac{AD}{d} (C_1 - C_2) \quad (9)$$

$$R_3 = R_3'' - R_3' = AbC_2^2 - AaP_2(1 - C_2/C_s)^2 \quad (10)$$

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where D is the lattice diffusion coefficient, a and b are surface constants related to the solubility constant K by

$$K = \sqrt{a/b} \quad (11)$$

and C_1 , C_2 , and C_s are the gas concentrations in the surface layers upstream and downstream and the saturation value, respectively. If $C_1 \ll C_s$, the limiting equations can be shown from Equations (8), (9), and (10) to be

$$R = \frac{ADK}{d} \sqrt{P_1} - J^* \approx \frac{ADK}{d} \sqrt{P_1} \quad (\text{where } C_1 \gg C_2) \quad (12)$$

at high pressures, and at very low pressures,

$$R = \frac{a}{2} AP_1 \quad (\text{where } C_1 \approx C_2) \quad (13)$$

Comparing Equations (12) and (13) with Equations (6) and (7),

$$\alpha = D\sqrt{a/b} = DK \quad (14)$$

$$\gamma = a/2 \quad (15)$$

It has been asserted earlier that "activation" of the stainless steel diffuser primarily involves clean-up of the metal surface rather than, say, rift-formation within the bulk of the metal. This is evidenced by the observation that α , which is a function of lattice diffusion proper, is not greatly increased by activation procedures, whereas γ , which is a function of surface sorption, is markedly increased. Thus in Figure MH-9A8188, as the number of runs increases, we find a small change in slope α (plotting rate vs $\sqrt{P}$) but a considerable shift of the straight line portion of the curve closer to the origin, straightening the "toe" of the curve (i.e., increased γ).

The Effect of Temperature

The increase of permeation rate at high pressures with increasing temperature is theoretically given¹⁵ by an equation of the form

$$R = Q \frac{A}{d} \sqrt{P} \sqrt{T} e^{-B/T} \quad (16)$$

(which neglects the small, essentially constant, term appearing in the limiting Equations (6) and (12), where Q and B are constants to be determined experimentally. Since the effect of T in the exponent is much greater than that of the $\sqrt{T}$ term, Equation (16) is generally written with little loss of accuracy as

$$R = \alpha \frac{A}{d} \sqrt{P} e^{-B/T} \quad (17)$$

* $J = \frac{A}{\sqrt{8}} \left(\frac{DK}{d} \right)^{3/2} (P_1)^{1/4}$ which behaves essentially as a constant over moderate pressure ranges for "active" metal diffusers and is treated as such in the study.¹⁴

Since Equation (1) holds only for one specific temperature, it is evident that both α and r must be functions of temperature. Comparison of Equations (6) and (17) leads to

$$\alpha = \alpha^0 e^{-B/T} \quad (18)$$

Similarly we may write

$$r = r^0 e^{-B'/T} \quad (19)$$

The Permeability Equation Coefficients

Experimentally we have found the following values for the various coefficients:

	α^0	r^0	B	B'	E	E'
H ₂	105.6	616.0	8309.6	8486.2	33,014	16,858
T ₂	48.03	1332	8007.3	9814.8	31,813	19,497

α^0 is in cm² mm hr⁻¹, r^0 is in hr⁻¹, B and B' are in degrees absolute, E, the over-all activation energy for the high-pressure rate in cal/mole, is given by

$$B = E/2R_0 \quad (20)$$

since in the $\sqrt{P}$ law region, the rate-limiting step is the diffusion of atoms. E', the over-all activation energy for the low-pressure rate in cal/mole, is given by

$$B' = E'/R_0 \quad (21)$$

since at very low pressure the rate-limiting step involves sorption of molecules.

The ratio of the high-pressure permeation rates of H₂ and T₂ increases with increasing temperature

$$\frac{\alpha_{H_2}}{\alpha_{T_2}} = \frac{\alpha^0_{H_2}}{\alpha^0_{T_2}} e^{\frac{B_{H_2} - B_{T_2}}{T}} = 2.199 e^{-302.3/T} \quad (22)$$

whereas the experimentally measured separation factor ρ for hydrogen and tritium, defined as

$$\rho = \frac{(1-w)/w}{(1-w_0)/w_0} \quad (23)$$

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where ω and ω_0 represent the atom per cent tritium in the diffused and original gas, respectively, decreases with increasing temperature. At first sight this would appear to conflict with the fact that the high-pressure separation factor (i.e. $\sqrt{P}$ law region for all constituents) varies directly with the ratio of the high-pressure coefficients $\alpha_{H_2}/\alpha_{T_2}$ as shown in Appendix C. Since, however, the measured separation factors were obtained at upstream pressures of about 11.5 cm, they are not directly comparable with the limiting high-pressure separation factors calculated (for an average composition of $\omega = 0.9$) from the ratio $\alpha_{H_2}/\alpha_{T_2}$.

Temperature, °K	Observed Separation Factors		High-pressure ρ (calc.)	$\frac{\alpha_{H_2}}{\alpha_{T_2}}$	$\frac{\gamma_{H_2}}{\gamma_{T_2}}$
	ρ (all runs)	ρ ("activated" runs)			
842.7	1.71 ± 0.13	1.82 ± 0.04	1.58	1.54	2.24
970.9	1.65 ± 0.06	1.715 ± 0.005	1.64	1.61	1.82

The separation factors were measured in a pressure region where the effect of the surface process is significant. Therefore they cannot be expected to parallel $\alpha_{H_2}/\alpha_{T_2}$ since (as is evident from the last column) the ratio $\gamma_{H_2}/\gamma_{T_2}$ decreases (whereas $\alpha_{H_2}/\alpha_{T_2}$ increases) with increasing temperature according to the relation

$$\frac{\gamma_{H_2}}{\gamma_{T_2}} = \frac{\gamma_{H_2}^0}{\gamma_{T_2}^0} e^{-\frac{B'_{H_2} - B'_{T_2}}{T}} = 0.4623 e^{+1329/T} \quad (24)$$

It is noteworthy that the observed separation factors correspond more closely to the ratios of the permeation rates at 11.5 cm pressure, 1.67 at 842.7°K, and 1.65 at 970.9°K.

As a consequence of the opposing trends of $\alpha_{H_2}/\alpha_{T_2}$ and $\gamma_{H_2}/\gamma_{T_2}$ with changing temperature, there must exist an intermediate pressure at which the separation factor will be constant, independent of temperature for a moderate range of temperature.

Activation Energies

An interpretation of the over-all activation energies mentioned in the preceding section is possible in the following manner.

In the high-pressure region the steady-state lattice diffusion rate R_2 is given by

$$R_2 = \frac{A}{d} DC_1 = \frac{A}{d} D_0 C_1 e^{-E_3/R_0 T} \quad (\text{assuming } C_1 \gg C_2) \quad (25)$$

where D is the diffusion constant proper, assumed independent of concentration but, of course, a function of temperature, thus

$$D = D^0 e^{-E_3/R_0 T} \quad (26)$$

E_3 is the activation energy in cal/gram atom for the migration of protons (or tritons) through the metal lattice. The rate of production of protons just inside the upstream surface by sorption of H_2 molecules from the gas phase is given by

$$R_1' = A s P_1 = A s_0 P_1 e^{-E_1/R_0 T} \quad (27)$$

where s (Equation (8)) is the sorption rate constant which varies with temperature according to the relation

$$s = s_0 e^{-E_1/R_0 T} \quad (28)$$

E_1 is the activation energy for sorption. Similarly, the rate of loss of protons from the plane just inside the upstream surface as a result of recombination followed by evaporation into the gas phase, can be written as

$$R_1'' = A b C_1^2 = A b_0 C_1^2 e^{-E_2/R_0 T} \quad (29)$$

where b (Equation (8)) is the desorption rate constant which varies with temperature. Thus

$$b = b_0 e^{-E_2/R_0 T} \quad (30)$$

E_2 is the desorption activation energy.

In the high-pressure region the rate of lattice diffusion is slow compared to the rates of sorption and desorption, i.e. $R_1, R_2 \gg R_3$. Since in the steady state $R_3 = R_1 - R_2$, this means that $R_1 \approx R_2$, or

$$s_0 P_1 e^{-E_1/R_0 T} = b_0 C_1^2 e^{-E_2/R_0 T} \quad (31)$$

This is another way of stating that a condition of quasi-thermodynamic equilibrium exists between the molecules in the gas phase and the protons just beneath the metal surface. This condition is the basis for the correction (in the high-pressure region) of the data for the tritium-rich gas mixture to 100% T_2 . Solving Equation (31) for C_1 we find

$$C_1 = \sqrt{\frac{s_0}{b_0}} \sqrt{P_1} e^{-(E_1 - E_2)/2R_0 T} \quad (32)$$

which upon substitution in Equation (25) yields

$$R = R_3 = \frac{A}{d} D^0 \sqrt{\frac{a_0}{b_0}} \sqrt{P_1} e^{-(E_1 - E_2 + 2E_3)/2R_0T} \quad (33)$$

or

$$R = \frac{AD^0}{d} \sqrt{\frac{a_0}{b_0}} \sqrt{P_1} e^{-(\Delta H_s + 2E_3)/2R_0T} \quad (34)$$

where the heat of solution of one mole of the gas in the metal, ΔH_s , is given by

$$\Delta H_s = E_1 - E_2 \quad (35)$$

Comparison with Equations (17) and (20) shows that $\Delta H_s + 2E_3 = E$, the observed over-all high-pressure activation energy, so that E_3 , the activation energy for diffusion proper, may be computed from

$$E_3 = \frac{1}{2} (E - \Delta H_s) \quad (36)$$

In the region of very low pressure, on the other hand, the migration of protons within the lattice becomes very rapid compared to recombination and evaporation from either the upstream or the downstream metal surface and is no longer rate-limiting. Indeed, in the limit of vanishingly small upstream pressure, migration of protons within the metal lattice merely serves to shuttle the protons to-and-fro between the two surfaces, such that the proton concentration gradient $(C_1 - C_2)/d$ across the metal approaches zero. That is, the proton concentration is very nearly the same everywhere within the metal. As before protons are supplied to the metal at a rate given by Equation (27), and protons are lost by desorption from the upstream surface at a rate given by Equation (29). But as a consequence of the essentially zero concentration gradient, the same rate of desorption will be experienced at both the upstream and the downstream surfaces (assuming identical surface properties upstream and downstream). Then the total loss rate from both surfaces will be just $R_1'' + R_3'' = 2R_1''$ which will balance the rate of sorption R_1' at the upstream surface. In the steady state

$$R_1' = 2R_1'' \quad (37)$$

so that the observed rate of permeation R is

$$R = \frac{R_1'}{2} = \frac{As_0P_1}{2} e^{-E_1/R_0T} \quad (38)$$

where E_1 may be identified with the over-all low-pressure activation energy, i.e.

$$E_1 = E' \quad (39)$$

Our conclusion that $R = R_1'/2$ is at variance with the reasoning of Melville and Rideal¹⁶ who consider that desorption from the upstream surface is negligible compared to the rate of lattice diffusion ($R_2 \gg R_1''$) and that consequently the observed permeation rate is equal to the rate of sorption ($R = R_1'$). This overlooks that fact that if the upstream and downstream surfaces have similar properties (as must be assumed in the absence of a statement to the contrary), desorption from one surface must be about the same as from the other in the absence of a large concentration gradient. Since the observed rate of permeation is obviously the downstream desorption rate which in turn is equal to the rate of lattice diffusion (net rate of transfer of protons through the bulk of the metal), the upstream desorption rate is not negligible compared to the lattice diffusion rate; on the contrary, it is always equal to or greater than the lattice diffusion rate ($R_1'' \gg R_2 = R_3''$), equality being approached in the limit of very low pressure where $C_1 = C_2$.

From the solubility data of N. J. Hawkins⁵ ΔH_s for hydrogen is 3356 cal/mole and for 96% tritium ΔH_s is 3661 cal/mole. Then by Equation (36), $2E_3 = 33,014 - 3356 = 29,658$ cal/mole for H_2 and $2E_3 = 31,813 - 3661 = 28,152$ cal/mole for T_2 .

By Equation (39), the activation energies for the solution process are $E_1 = 16,858$ cal/mole for H_2 and $19,497$ cal/mole for T_2 . The activation energies for the reverse process are, by Equation (35), $E_2 = 16,858 - 3356 = 13,502$ cal/mole for H_2 and $E_2 = 19,497 - 3661 = 15,836$ cal/mole for T_2 .

From the data on molecular frequencies collected by Urey¹⁷ one finds that for T_2 , $\omega = 2546.50$ cm^{-1} , $x\omega = 41.88$ cm^{-1} , and for H_2 , $\omega = 4405.3$ cm^{-1} , $x\omega = 125.32$ cm^{-1} for the ground states. The zero-point energies may then be calculated from the usual relation,¹⁸

$$E_0 = \frac{1}{2} h c \omega - \frac{1}{4} h c x \omega + \dots \quad (40)$$

with the result that $E_0(H_2) = 6204$ cal/mole, $E_0(T_2) = 3608$ cal/mole, or $E_0(H_2) - E_0(T_2) = 2596$ cal/mole. More recently Jones¹⁹ has calculated the zero-point energy of T_2 from the existent data for H_2 , by means of the theoretical isotope effect upon the spectrum of diatomic molecules.²⁰ He finds that $E_0(H_2) = 6193.8$ cal/mole, $E_0(T_2) = 3603.4$ cal/mole, or $E_0(H_2) - E_0(T_2) = 2590.4$ cal/mole. Now the observed difference in the low-pressure activation energies is $E'(H_2) - E'(T_2) = 16,858 - 19,497 = -2639$ cal/mole. The agreement between the difference in zero-point energies (2.59 kcal/mole) and the difference in low-pressure activation energies (-2.64 kcal/mole) lends added support to the concept that at very low pressures a surface process is rate-controlling, since it seems probable that for a surface process, the principal difference in behavior between the two isotopes (at the temperatures studied) should be that due to their difference in zero-point energy. Since it is reasonably well established

*Frequency is in wave numbers, not atom per cent tritium as elsewhere in this report.

that the potential energy curves of the isotopes are identical,²¹ it would be expected that there would be little if any difference in the force constants of the bonds, metal-proton and metal-triton; the greater zero-point energy of H_2 should then facilitate its dissociation at the metal surface relative to the dissociation of T_2 , with the result that the sorption of H_2 should require that less energy be supplied, as compared to that required by T_2 , in order to surmount the potential energy barrier associated with the rate-limiting process. On this basis it would be anticipated that the low-pressure activation energy for H_2 should be less than that for T_2 by very nearly the amount by which the zero-point energy of H_2 exceeds that of T_2 . Within experimental error, this is what has been found.

Solubility and Diffusion Constants

In view of Equations (14) and (22) the ratio of the high-pressure permeation rate of H_2 to that of T_2 may be written for the same temperature and pressure as

$$\frac{R_{H_2}}{R_{T_2}} = \frac{D_{H_2} K_{H_2}}{D_{T_2} K_{T_2}} = 2.199 e^{-302.3/T} \quad (41)$$

With increasing temperature this ratio increases in the case of stainless steel as above, but decreases in the case of palladium.²² At high pressures the isothermal permeation rate is given by the usual relationship

$$R = \frac{ADK}{d} \sqrt{P} \quad (42)$$

and the isobaric permeation rate is described by

$$R = k \frac{A}{d} e^{-B/T} \quad (\text{where } k = D^0 K^0 \sqrt{P} = DK \sqrt{P} e^{B/T} = \alpha^0 \sqrt{P}) \quad (43)$$

and the rate for temperature and pressure both variable is

$$R = \frac{D^0 K^0 A}{d} \sqrt{P} e^{-B/T} \quad (44)$$

where we have defined

$$DK = D^0 K^0 e^{-B/T} \quad (45)$$

We may separate the effects of lattice diffusion and solubility in the usual manner^{23,24,25} by writing Equation (45) as

$$D = D^0 e^{-\sigma/T} \quad (D \text{ always increases with increasing temperature}) \quad (46)$$

and

$$K = K^0 e^{-v/T} \quad (\text{for endothermic solution}) \quad (47)$$

where

$$B = \sigma + v = E/2R_0 \quad (48)$$

σ and v are positive quantities (in $^{\circ}\text{K}$) which are already known, viz.

$$v = H_s/2R_0 \quad (49)$$

$$\sigma = B - v = 2E_3/2R_0 \quad (50)$$

For palladium, on the other hand, Equation (47) involves a positive exponent,

$$K = K^0 e^{v/T} \quad (\text{for exothermic solution}) \quad (51)$$

and Equation (48) becomes

$$B = \sigma - v \quad (52)$$

In general the high-pressure rate ratio is

$$\frac{R_{H_2}}{R_{T_2}} = \frac{\alpha_{H_2}}{\alpha_{T_2}} = \frac{(DK)_{H_2}}{(DK)_{T_2}} = \frac{(D^0K^0)_{H_2}}{(D^0K^0)_{T_2}} e^{\frac{B_{H_2} - B_{T_2}}{T}} \quad (53)$$

For stainless steel it is

$$B_{H_2} - B_{T_2} = (\sigma_{H_2} + v_{H_2}) - (\sigma_{T_2} + v_{T_2}), \quad (54)$$

but for palladium

$$B_{H_2} - B_{T_2} = (\sigma_{H_2} - v_{H_2}) - (\sigma_{T_2} - v_{T_2}) \quad (55)$$

Thus, there is no basis for predicting a priori whether $\alpha_{H_2}/\alpha_{T_2}$ will increase or decrease with increasing temperature, for either stainless steel or palladium, since $B_{H_2} - B_{T_2}$ may be either positive or negative according to the magnitude of the various energies involved.

On the basis of simple kinetic theory one might expect the ratio of the lattice diffusion constants D_{H_2}/D_{T_2} to approach $\sqrt{m_T/m_H} = \sqrt{3}$ as the temperature increases. That is, as the temperature rises the effect of the difference in potential energy between hydrogen and tritium in the metal lattice becomes progressively less important than the effect of the difference in atomic masses m_H and m_T upon the respective diffusion constants. Since $\alpha = DK$, the limiting diffusion constant ratio is given by

$$\frac{D^0_{H_2}}{D^0_{T_2}} = \frac{\alpha^0_{H_2}}{\alpha^0_{T_2}} \cdot \frac{K^0_{T_2}}{K^0_{H_2}} \quad (56)$$

where $\alpha_{H_2}^0/\alpha_{T_2}^0 = 2.199$, and from the solubility data* $K_{H_2}^0/K_{T_2}^0 = 1.114$; hence, $D_{H_2}^0/D_{T_2}^0 = 1.974$, a value not too different from $\sqrt{3} = 1.732$. The 14% discrepancy is probably experimental error rather than the result of an unjustifiable extrapolation of Equation (53). Even though the physical system is drastically altered as the temperature increases without limit, still the interaction of whatever new environment is created should be very nearly identical with both protons and tritons, with only the mass effect remaining of importance. By Equation (46) we may write the diffusion constant ratio as

$$\frac{D_{H_2}}{D_{T_2}} = \frac{D_{H_2}^0}{D_{T_2}^0} e^{-\frac{\sigma_{H_2} - \sigma_{T_2}}{T}} \quad (57)$$

For a particular temperature range T' to T'' , $\sigma_{H_2} - \sigma_{T_2}$ will have a particular value; suppose that at T'' a phase change occurs, then in general $\sigma_{H_2} - \sigma_{T_2}$ will assume a different value over the succeeding temperature interval T'' to T''' . Although the shape of the exponential curve is altered by each phase change, the asymptote $D_{H_2}^0/D_{T_2}^0$ might be expected to be the same for all such curves. Thus D is given by absolute reaction rate theory²⁶ as

$$D = \frac{\lambda^2}{v_f^{1/3}} \left(\frac{kT}{2\pi m} \right)^{1/2} \left[e^{-\Delta E_{\text{vap}}/nR_0 T} \right] \quad (58)$$

where v_f is the "free volume" of the medium, λ is the distance between minima in the free-energy vs diffusion length curve, n is an empirical constant, and the other symbols have their usual meaning. Now it is reasonable that λ and v_f will be essentially identical at any given temperature for both protons and tritons, being properties of the metal lattice. Then considering the ratio of the diffusion constants,

$$\frac{D_{H_2}}{D_{T_2}} = \frac{\sqrt{\frac{m_T}{m_H}}}{\sqrt{\frac{m_T}{m_H}}} e^{-\frac{\sigma_{H_2} - \sigma_{T_2}}{T}} \quad (59)$$

where the potential energy terms have been identified with our σ 's. To the extent then that the above assumptions regarding λ and v_f are correct, we should expect $D_{H_2}^0/D_{T_2}^0 = \sqrt{3}$.

*For H_2 $\log K = 1.314 - 366.9/T$ and for 96% T_2 , $\log K = 1.267 - 400.2/T$, where $K = S/\sqrt{P}$, S in micromoles/100 gram steel, P in mm mercury.⁵ Consequently, for Equation (47), $K_{H_2}^0 = 20.61$, $K_{T_2}^0 = 18.49$, $v_{H_2} = 844.8$, $v_{T_2} = 921.5$, so that $\Delta H_s (H_2) = 3356$ cal/mole, $\Delta H_s (T_2) = 3661$ cal/mole.

The ratio of the solubility constants is given by

$$\frac{K_{H_2}}{K_{T_2}} = \frac{K_{H_2}^0}{K_{T_2}^0} e^{-\frac{v_{H_2} - v_{T_2}}{T}} = \frac{K_{H_2}^0}{K_{T_2}^0} e^{-\frac{\Delta H_s(H_2) - \Delta H_s(T_2)}{2R_0T}} = 1.114 e^{304.7/2R_0T} = 1.114 e^{76.7/T} \quad (60)$$

which allows Equation (57) to be evaluated as

$$\frac{D_{H_2}}{D_{T_2}} = \frac{D_{H_2}^0}{D_{T_2}^0} e^{-\frac{E_3(H_2) - E_3(T_2)}{R_0T}} = 1.974 e^{-752.9/R_0T} = 1.974 e^{-379.0/T} \quad (61)$$

Comparison with Existing Data

The results of Edwards²⁷ for the diffusion of H_2 through pure iron in the temperature range 10° to $100^\circ C$ may be expressed by $D = D^0 e^{-E/R_0T}$, where $D^0 = 1.65 \times 10^{-2} \text{ cm}^2/\text{sec}$ and $E = 9200 \text{ cal/gram atom}$. To permit comparison, our results must be converted to cgs units

$$\alpha \left(\frac{\text{cm}^3}{\text{hr}} \right) \times \text{mm} \times \frac{1}{\text{cm}^2} \times \frac{1}{\text{cm}^{1/2}} \times \left(\frac{0.1 \text{ cm}}{3600 \text{ sec}} = 2.7778 \times 10^{-5} \right) = \alpha \left(\frac{\text{cm}^{3/2}}{\text{sec}} \right)$$

$$K \left(\frac{\mu\text{-moles}}{100 \text{ g} \times \text{mm}^{1/2}} \right) \times \left(\frac{10^{-6} \times 22414 \text{ cm}^3}{\frac{100}{7.86} \text{ cm}^3 \times 0.3162 \text{ cm}^{1/2}} = 5.5810 \times 10^{-3} \right) = K (\text{cm}^{-1/2})$$

assuming the density of Type 347 stainless steel to be 7.86 gram/cc; then

$$D = \frac{\alpha \left(\frac{\text{cm}^3}{\text{hr}} \right) \times \text{mm} \times \frac{1}{\text{cm}^2} \times \frac{1}{\text{cm}^{1/2}}}{K \left(\frac{\mu\text{-moles}}{100 \text{ g} \times \text{mm}^{1/2}} \right)} \times \left(\frac{2.7778 \times 10^{-5}}{5.5810 \times 10^{-3}} = 4.9772 \times 10^{-3} \right) = D (\text{cm}^2/\text{sec})$$

By Equation (46) the diffusion coefficients for H_2 and T_2 are given by

$$D_{H_2} = 5.126 e^{-7460/T} \text{ in mixed units, } = 2.551 \times 10^{-2} e^{-7460/T} \text{ in cm}^2/\text{sec}$$

$$D_{T_2} = 2.598 e^{-7081/T} \text{ in mixed units, } = 1.293 \times 10^{-2} e^{-7081/T} \text{ in cm}^2/\text{sec}$$

We have then the following comparison for the diffusion of hydrogen:

Material	E_3 , kcal/g atom	D^0 , cm^2/sec	D at 842.7°K, cm^2/sec
Pure iron	9.2	0.0165	6.8×10^{-5}
Type 347 stainless steel	14.8	0.0255	3.6×10^{-6}

Flint⁴ found that the permeability of Type 347 stainless steel to hydrogen in the temperature range 200° to 600°C could be expressed by

$$\log R = 2.19 - 3.18 \times 10^3/T$$

where R = rate of permeation in $\text{cc(STP)}/\text{hr}/\text{cm}^2$ area/mm thickness at 760 mm H_2 pressure. The corresponding activation energy is $E = 2.303(2R_0)(3.18 \times 10^3) = 29.1$ kcal/mole. The comparison with our results for H_2 , extrapolated to one atmosphere pressure, follows below:

	Flint	Present Study
E (kcal/mole)	29.1	33.0
R (842.7°K) ($\text{cc, STP}/\text{hr}/\text{cm}^2/\text{mm}$)	0.026	0.044
R (970.9°K) ($\text{cc, STP}/\text{hr}/\text{cm}^2/\text{mm}$)	0.082	0.162

Flint observes that the rate of permeation above 600°C is greater than that predicted by his equation, so that E would be expected to be somewhat higher than 29.1 kcal/mole, in agreement with our findings. Moreover, the permeability at 970.9°K would then be expected to be greater than 0.082, i.e. toward closer agreement with our rate at the same temperature and pressure.

We did not observe the decrease of permeability with time ("aging" effect) mentioned by Flint and attributed by him to oxidation of the metal surface by traces of O_2 in his H_2 . This is doubtless the result of our hydrogen isotopes being essentially oxygen-free, having been multidiffused through palladium and stored in uranium beds. The only "aging" effect we observed was the previously discussed initial increase in permeability during the first seventeen runs. For example, before clean-up (run 2ss) a rate of approximately 0.032 cc, STP/hr/ cm^2/mm at 9 cm pressure and $T_g = 698^\circ\text{C}$ was observed (Flint's data would predict a rate of 0.025 under these conditions) which ultimately would reach 0.048 according to our later data.

The generally satisfactory agreement between the two sets of results, despite quite different experimental techniques, is indicative of the absence of gross error in each.

SUMMARY AND CONCLUSIONSNumerical Values

	H ₂	T ₂
High-pressure over-all activation energy E, cal/mole	33.01x10 ³	31.81x10 ³
Low-pressure over-all activation energy E' = E ₁ , sorption activation energy, cal/mole	16.86x10 ³	19.50x10 ³
Heat of solution ΔH _s , cal/mole ⁵	3356	3661
Lattice diffusion activation energy E ₃ , cal/g atom	14.83x10 ³	14.08x10 ³
Desorption activation energy E ₂ , cal/mole	13.50x10 ³	15.84x10 ³
α ^o , cm ^{1/2} mm hr ⁻¹	105.6	48.03
γ ^o , hr ⁻¹	616.0	1332
K ^o , micromoles (100 g) ⁻¹ mm ^{-1/2}	20.61	18.49
v = ΔH _s /2R _o , deg absolute	844.8	921.5
D ^o , cm ^{1/2} mm ^{3/2} (100 g) (micromoles) ⁻¹ hr ⁻¹	5.127	2.597
σ = E ₃ /R _o , deg absolute	7465	7086
Zero-point energy difference E _o (H ₂) - E _o (T ₂), kcal/mole ^{17,19}	2.59	
Low-pressure over-all activation energy difference E'(T ₂) - E'(H ₂), kcal/mole	2.64	
Limiting high-pressure permeability constant ratio α ^o _{H₂} /α ^o _{T₂}	2.199	
Limiting solubility constant ratio K ^o _{H₂} /K ^o _{T₂}	1.114	
Limiting diffusion constant ratio D ^o _{H₂} /D ^o _{T₂}	1.974	

Conclusions

The values of the various permeability coefficients and activation energies listed above permit the prediction of the rate of permeation of H₂ and T₂ through Type 347 stainless steel for pressures from zero up to about half an atmosphere within the temperature interval of approximately 550° to 700°C and by extrapolation for higher pressures and a wider temperature range.

The high-pressure activation energy for the entire permeation process for hydrogen exceeds that for tritium, whereas the over-all low-pressure activation energy for T_2 is greater than for H_2 .

The ratio of the high-pressure permeability constant of H_2 to that of T_2 increases with increasing temperature, in contrast to the case of permeation through palladium. The low-pressure permeability coefficient ratio decreases with increasing temperature.

The lattice diffusion activation energy of H_2 exceeds that for T_2 . Thus the ratio of the diffusion constant of H_2 to that of T_2 increases with increasing temperature, approaching the value 1.97 in the limit. That is, D_{H_2}/D_{T_2} is not greatly different from $\sqrt{3}$ at higher temperatures.

The difference in the low-pressure activation energies $E'(T_2) - E'(H_2)$ is very nearly equal to the difference in the zero-point energies $E_0(H_2) - E_0(T_2)$. This is in agreement with the hypothesis that at very low pressures the surface process is rate-controlling.

"Activation" of the diffuser involves primarily clean-up of the surface of the metal membrane (e.g. removal of surface carbon and oxide).

The diffusion coefficient at 570°C of H_2 in Type 347 stainless steel is about $1/20$ that of H_2 in pure iron. The activation energy for the case of stainless steel is higher than that for iron.

The permeability of Type 347 stainless steel to H_2 as measured here is somewhat greater and the activation energy a little higher than would be indicated by the data already available. The degree of agreement is, however, satisfactory.

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APPENDIX A

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APPENDIX A. COMPOSITION CORRECTION

We are assuming, as usual, negligible back pressure. Let us define the quantities ϕ , μ , and θ as follows:

$$P_{H_2} = \phi P, P_{HT} = \mu P, P_{T_2} = \theta P \quad (62)$$

where P is the total pressure in the gas phase, and P_{H_2} , P_{HT} , P_{T_2} are the equilibrium partial pressures of H_2 , HT , and T_2 , respectively. The atom fraction of tritium in the gas phase is then given by

$$\omega = \frac{P_{T_2} + \frac{1}{2} P_{HT}}{P} = \theta + \frac{1}{2} \mu \quad (63)$$

The gas phase equilibrium constant for the reaction $H_2 + T_2 \rightarrow 2HT$ is given by

$$K_e = P_{HT}^2 / P_{H_2} P_{T_2} = \mu^2 / \phi \theta \quad (64)$$

Of course,

$$P = P_{H_2} + P_{HT} + P_{T_2}, \text{ or } 1 = \phi + \mu + \theta \quad (65)$$

In the $\sqrt{P}$ law region, lattice diffusion is rate-limiting which means that the rate of sorption of gas molecules at the upstream surface and the rate of desorption of gas molecules from the upstream surface back into the gas phase are both much more rapid processes than migration through the bulk of the metal. Under these conditions thermodynamic equilibrium is closely approached between the partial pressures P_{H_2} , P_{HT} , and P_{T_2} in the gas phase and the respective numbers of atoms n_H and n_T present in the upstream surface layers of the metal. That is,

$$k_1 = n_H^2 / P_{H_2} \quad \text{or } n_H = \sqrt{k_1 P_{H_2}} \quad (66)$$

$$k_2 = n_T^2 / P_{T_2} \quad \text{or } n_T = \sqrt{k_2 P_{T_2}} \quad (67)$$

Note that the equally valid equation $k_3 = n_H n_T / P_{HT}$ adds nothing since it is a dependent relationship, derivable from Equations (64), (66), and (67). This is another way of saying that while the presence of HT is of course not without effect upon the rate of permeation, its influence is calculable in terms of P_{H_2} , P_{T_2} , and K_e ; P_{HT} itself does not appear. In this high-pressure region, permeation is diffusion-limited, and since diffusion occurs by virtue of a concentration gradient, it is apparent that the rates of permeation of H atoms and of T atoms will be proportional to the numbers of H and T atoms on the upstream surface.

$$R_H = k_1' n_H \quad (68)$$

$$R_T = k_2' n_T \quad (69)$$

and the total rate of transfer of H and T atoms across the barrier is

$$R = R_H + R_T \quad (70)$$

From Equations (66) and (68) we obtain

$$R_H = k_H \sqrt{P_{H_2}} = k_H \sqrt{\phi P} \quad (71)$$

and from Equations (67) and (69)

$$R_T = k_T \sqrt{P_{T_2}} = k_T \sqrt{\theta P} \quad (72)$$

where k is a combination of constants, viz. $k = k' \sqrt{k} = \alpha A/d$. Experimentally the tritium-rich gas mixture obeys the $\sqrt{P}$ law over the same general pressure range as does pure H_2 , so that

$$R = k_m \sqrt{P} \quad (73)$$

where k_m refers to the mixture. From Equations (70), (71), (72), and (73) we have

$$k_m \sqrt{P} = k_H \sqrt{\phi P} + k_T \sqrt{\theta P} \quad (74)$$

or

$$k_T = \frac{k_m - k_H \sqrt{\phi}}{\sqrt{\theta}} \quad (75)$$

Since A/d cancels out,

$$\alpha_{T_2} = \frac{\alpha_m - \alpha_{H_2} \sqrt{\phi}}{\sqrt{\theta}} \quad (76)$$

Equation (76) permits calculation of α_{T_2} , the coefficient α for pure T_2 , from a measurement of α_{H_2} , the coefficient α for pure H_2 , and a measurement of α_m , the coefficient α for the tritium-hydrogen mixture whose composition is given by ϕ , θ . The values of ϕ and θ depend in turn upon the atom fraction of tritium, ω , and upon the gas phase equilibrium constant, K_e , which is a function of temperature. The necessary equations are readily derived as follows: from Equation (64),

$$\mu = \sqrt{K_e \phi \theta} \quad (77)$$

Substitution of Equation (77) into Equations (63) and (65) yields

$$\omega = \theta + \frac{1}{2} \sqrt{K_e \phi \theta} \quad (78)$$

$$1 = \phi + \sqrt{K_e \phi \theta} + \theta \quad (79)$$

Solving Equation (78) for ϕ ,

$$\phi = \frac{4}{K_e \theta} (\omega^2 - 2\omega\theta + \theta^2) \quad (80)$$

which upon substitution in Equation (79) yields

$$\theta = \frac{[8\omega - K_e(2\omega - 1)] - \sqrt{[8\omega - K_e(2\omega - 1)]^2 - 16\omega^2(4 - K_e)}}{2(4 - K_e)} \quad (81)$$

The negative sign on the radical rather than the positive sign is selected in order that $P > P_{T_2}$, i.e. $1 > \theta$. Once a numerical value for θ has been obtained by substitution of the appropriate values of ω and K_e into Equation (81), a numerical value of ϕ is readily obtained, since by Equations (63) and (65),

$$\phi = 1 + \theta - 2\omega \quad (82)$$

Values of K_e were estimated from the data of Jones¹⁹ to be 3.798 at 970.9°K and 3.715 at 842.7°K. Thus for each gas mixture run the correction procedure was to calculate θ by Equation (81) using the appropriate value of K_e and the value of ω as determined by mass spectrometer analysis, then to calculate ϕ by Equation (82), and finally to calculate α_{T_2} from Equation (76) using the value of α_m found for that particular run together with the average value of α_{H_2} obtained from all runs with pure H_2 at that same temperature.

Mention should be made of two further points. First, we have considered that $\omega = \text{constant}$ throughout the duration of any given run; since but a very small portion of the upstream gas ever diffused through the barrier (as a consequence of the low rate of permeation), the isotopic fractionation would be negligible. Second, the average temperature of the metal surface was used to select K_e (despite the obvious fact that the average temperature of the gas phase as a whole would be somewhat lower) since it is the gas in the immediate vicinity of this surface that is in most intimate equilibrium with the gas atoms on the surface.

In the low-pressure limiting case the rate of permeation is not controlled by the rate of diffusion through the lattice but is rather controlled by some surface process involving sorption and dissociation. Although the rate of transport of H and T atoms through the metal lattice is still proportional to the number of H and T atoms in the surface layer, yet the diffusion process is rapid compared to whatever process supplies the H and T atoms to the surface of the metal from the gas phase and serves merely to "shuttle" the atoms to-and-fro within the bulk of the metal. The rate-controlling steps are those of evaporation from both the upstream and downstream surfaces. This situation is significantly different from the high-pressure case considered above, in that we no longer have a state of quasi-thermodynamic equilibrium prevailing between the gas phase and the atoms on the surface of the metal, and consequently we must consider directly the contribution

by HT to the rate of permeation. Now in the low-pressure region the rate-controlling surface process involves molecules colliding with the surface, and hence the over-all permeation process appears to be one involving molecules. Thus,

$$R_{H_2} = r_{H_2} P_{H_2} = r_{H_2} \phi P \quad (83)$$

$$R_{HT} = r_{HT} P_{HT} = r_{HT} \mu P \quad (84)$$

$$R_{T_2} = r_{T_2} P_{T_2} = r_{T_2} \theta P \quad (85)$$

$$R_m = r_m P = R_{H_2} + R_{HT} + R_{T_2} \quad (86)$$

so that

$$r_m = r_{H_2} \phi + r_{HT} \mu + r_{T_2} \theta \quad (87)$$

or

$$r_{T_2} = \frac{r_m - r_{H_2} \phi - r_{HT} \mu}{\theta} \quad (88)$$

where unfortunately r_{HT} is not known. If we assume that

$$r_{HT} = \frac{r_{H_2} + r_{T_2}}{2} \quad (89)$$

then

$$r_{T_2} = \frac{r_m - r_{H_2}(\phi + \frac{\mu}{2})}{\theta + \frac{\mu}{2}} \quad (90)$$

which is probably the best simple approach to the problem of correcting the low-pressure data to $\omega = 1$. Thus, having available values of ϕ and θ as well as μ by Equation (65) for each gas mixture run and knowing the average values of r_{H_2} obtained from all runs with pure H_2 at the same temperature, the corrected value of the low-pressure constant r_{T_2} is obtained at once, from Equation (90).

As a refinement we might write

$$r_{H_2} = r_{H_2}^0 e^{-\lambda_1/T} \quad (91)$$

$$r_{HT} = r_{HT}^0 e^{-\lambda_2/T} \quad (92)$$

$$r_{T_2} = r_{T_2}^0 e^{-\lambda_3/T} \quad (93)$$

$$r_m \approx r_m^0 e^{-\lambda_m/T} \quad (94)$$

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Now instead of the above assumption, Equation (89), we might assume that at very high temperatures the only factor involved is the square root of the molecular mass, i.e. $r_{H_2}^0 : r_{HT}^0 : r_{T_2}^0 = \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{6}}$, so that

$$r_{HT} = \frac{r_{H_2}^0}{\sqrt{2}} e^{-\lambda_2/T} \quad (95)$$

$$r_{T_2} = \frac{r_{H_2}^0}{\sqrt{3}} e^{-\lambda_3/T} \quad (96)$$

In view of Equation (87) we have, for a given temperature T,

$$\frac{r_m}{r_{H_2}^0} = \phi e^{-\lambda_1/T} + \frac{\mu}{\sqrt{2}} e^{-\lambda_2/T} + \frac{\theta}{\sqrt{3}} e^{-\lambda_3/T} = \frac{r_m^0}{r_{H_2}^0} e^{-\lambda_m/T} \quad (97)$$

and at a second temperature T',

$$\phi e^{-\lambda_1/T'} + \frac{\mu}{\sqrt{2}} e^{-\lambda_2/T'} + \frac{\theta}{\sqrt{3}} e^{-\lambda_3/T'} = \frac{r_m^0}{r_{H_2}^0} e^{-\lambda_m/T'} \quad (98)$$

where $\lambda_1 = 16,858/R_0 = 8486^\circ K$, $r_{H_2}^0 = 616.0$, and λ_2 and λ_3 are unknown. If a value of r_m^0 (or, equivalently, r_m at T and T') corrected for the temperature gradient were available, it would then be possible to solve (by successive approximation) Equations (97) and (98) simultaneously for λ_2 and λ_3 . Knowing λ_3 , r_{T_2} would then be available from Equation (96) directly, or, equivalently, from Equations (88) and (95).

Alternatively, λ_2 and λ_3 might be evaluated in the following fashion. For the reaction $H_2 + T_2 \rightarrow 2HT$, the heat of reaction ΔH is given by

$$\frac{d \ln K_e}{dT} = \frac{\Delta H}{R_0 T^2} \quad (99)$$

Integrating between the limits T and T', assuming ΔH to be constant within this temperature interval,

$$\Delta H = \frac{2.303 R_0 T T'}{T - T'} \log \frac{K_e}{K_e'} \quad (100)$$

and substituting $K_e = 3.798$ at $T = 970.9^\circ K$ and $K_e' = 3.715$ at $T' = 842.7^\circ K$, $\Delta H = 279.6 \text{ cal/2 moles}$. Since the heat content of two moles of HT exceeds that of one mole of H_2 plus one mole of T_2 by 280 cal, one would expect the activation energy for HT to be less by 140 cal/mole than the mean activation energy of H_2 and T_2 , i.e.

$$\lambda_2 = \frac{\lambda_1 + \lambda_3}{2} - \frac{\Delta H}{2R_0} \quad (101)$$

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Simultaneous solution of Equations (97) and (101) for λ_2 and λ_3 is possible. From Equation (101), $\lambda_3 = 2\lambda_2 - (\lambda_1 - \Delta H/R_0) = 2\lambda_2 - u$. Substituting this into Equation (97) yields

$$\frac{r_m}{r_{H_2}^0} = \phi e^{-\lambda_1/T} + \frac{\mu}{N^2} e^{-\lambda_2/T} + \frac{\theta}{N^3} e^{-\frac{2\lambda_2 - u}{T}} \quad (102)$$

which is of the form $z e^{-\lambda_2/T} + v e^{-2\lambda_2/T} = w$, where $z = \frac{\mu}{N^2}$, $v = \frac{\theta}{N^3} e^{u/T}$, and

$$w = \frac{r_m}{r_{H_2}^0} - \phi e^{-\lambda_1/T}$$

This quadratic in $e^{-\lambda_2/T}$ is readily solved with the result that

$$e^{-\lambda_2/T} = \frac{-z + \sqrt{z^2 + 4vw}}{2v} \quad (103)$$

or

$$\lambda_2 = -2.303 T \log \left[\frac{-z + \sqrt{z^2 + 4vw}}{2v} \right] \quad (104)$$

Knowing λ_2 , r_{HT} is available from Equation (95) and r_{T_2} follows from Equation (88). While this procedure is easier than the simultaneous approximate solution of Equations (97) and (98), it still requires a value of r_m corrected for the temperature gradient. Since it has been our practice to correct to $w = 1$ before correcting to constant temperature, r_m so corrected is not available except by laborious solution of Equation (117).

The method actually adopted in this work was, therefore, the assumption of Equation (89) and the resultant corrective relationship, Equation (90).

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APPENDIX B

APPENDIX B. TEMPERATURE GRADIENT CORRECTION

Calculation of Activation Energies

A sharp temperature gradient exists along the length of the cylindrical stainless steel diffuser as a result of the attempt to confine the diffusion of gas to the steel as completely as possible by maintaining the Kover portion at a substantially lower temperature than the steel diffuser proper. At a given pressure the rate of permeation is given by Equation (43). If we let r_o = radius of diffuser and ℓ = length of diffuser, then by Equation (43), the rate per unit length, r , may be written as

$$r = k \frac{2\pi r_o}{d} e^{-B/T} \quad (105)$$

For the case of a uniform temperature along the length of the diffuser, $dT/d\ell = 0$,

$$R = r\ell \quad (106)$$

but in the present instance the temperature varies along the length of the diffuser, i.e. $T = f(\ell)$, and Equation (104) becomes

$$R = \int_0^\ell r d\ell = \frac{2\pi r_o k}{d} \int_0^\ell e^{-B/f(\ell)} d\ell = k_o \int_0^\ell e^{-B/f(\ell)} d\ell \quad (107)$$

Now the observables are R and T (as a function of ℓ) so that if we have data at two different temperature levels, we can in principle calculate both k_o (a function of α , i.e. $k_o = \alpha^o \sqrt{P} (2\pi r_o/d)$ and B providing that we can find a function $T = f(\ell)$ which (a) allows integration of Equation (107) and (b) fits the observed temperature-length data sufficiently well. This is not a simple matter; quite a few functions were examined and it was found either not to represent the data satisfactorily or else not to permit integration in closed form in terms of elementary functions. The best such function tested was found to be

$$\ell = a + bx + cx^2 \quad (108)$$

where

$$x = 1/T \quad (109)$$

and

$$d\ell = (b + 2cx)dx \quad (110)$$

Substituting into Equation (107) one obtains

$$R = k_0 \int_{x_1}^{x_2} e^{-Bx} d\ell = k_0 \int_{x_1}^{x_2} e^{-Bx} (b + 2cx) dx \quad (111)$$

where $x_1 = 1/T_1$ at $\ell = 0$ and $x_2 = 1/T_2$ at $\ell = \ell$. Integrating,

$$R = k_0 b \int_{x_1}^{x_2} e^{-Bx} dx + 2k_0 c \int_{x_1}^{x_2} e^{-Bx} x dx = -\frac{k_0 b}{B} e^{-Bx} \Big|_{x_1}^{x_2} + \frac{2k_0 c}{B^2} e^{-Bx} (-Bx-1) \Big|_{x_1}^{x_2}$$

so that

$$R = \frac{k_0 b}{B} \left[e^{-Bx_1} - e^{-Bx_2} \right] + \frac{2k_0 c}{B^2} \left[e^{-Bx_1} (1 + Bx_1) - e^{-Bx_2} (1 + Bx_2) \right] \quad (112)$$

Equation (112) can be solved for B only by successive approximation and with considerable labor providing a value of k_0 is known. Since this is not the case, B was obtained by considering the ratio of permeation rates R/R' at two different temperature levels T (high-temperature run) and T' (low-temperature run) solving by successive approximation Equation (113).

$$\frac{R}{R'} = \frac{\alpha}{\alpha'} = \frac{b \left[\frac{e^{-Bx_1}}{e^{-Bx'_1}} - \frac{e^{-Bx_2}}{e^{-Bx'_2}} \right] + \frac{2c}{B} \left[(1 + Bx_1) e^{-Bx_1} - (1 + Bx_2) e^{-Bx_2} \right]}{b' \left[\frac{e^{-Bx'_1}}{e^{-Bx'_2}} - \frac{e^{-Bx'_1}}{e^{-Bx'_2}} \right] + \frac{2c'}{B} \left[(1 + Bx'_1) e^{-Bx'_1} - (1 + Bx'_2) e^{-Bx'_2} \right]} \quad (113)$$

where $\alpha > \alpha'$, both being α 's corrected to $\omega = 1$ for the case of the tritium-rich mixtures, and for the case of pure hydrogen, the α 's are the directly measured coefficients, no correction of course being necessary. In addition, for the high-temperature run at T, $x_1 = 1/T_1$ at $\ell = 0$, $x_2 = 1/T_2$ at $\ell = \ell$, and for the low-temperature runs at T', $x'_1 = 1/T'_1$ at $\ell = 0$ and $x'_2 = 1/T'_2$ at $\ell = \ell$. Also, $B = E/2R_0$ in degrees absolute, where E is the over-all high-pressure activation energy in cal/mole. The high-temperature run constants are a, b, c, and a', b', c' are the low-temperature run constants obtained by fitting the temperature-length data to Equation (108).

The correction procedure is then as follows: the ratio α/α' is known numerically, the temperature-length data is determined for both the high- and the low-temperature runs by means of the thermocouples spot-welded along the length of the diffuser at known intervals. Using these data, a, b, c, and a', b', c' are computed, x_1 and x'_1 are directly measured by the particular thermocouple positioned at $\ell = 0$; x_2 and x'_2 ($1/T$ and $1/T'$ at $\ell = 5.4375$ in.) are computed from Equation (108) using the values of a, b, c, and a', b', c' just calculated. The only remaining quantity in Equation (113), B, is then found by successive approximation. Knowing B, the activation energy E follows at once. This is carried out for hydrogen to obtain E_{H_2} ; then the entire procedure is repeated for tritium to obtain E_{T_2} (using of course α 's corrected to $\omega = 1$ as shown in Appendix A).

The correction for the low-pressure case is similarly obtained. From Equations (7) and (19)

$$R = k'Ae^{-B'/T} = 2\pi r_0 k'e^{-B'/T} \quad (k' = \gamma^0 P) \quad (114)$$

$$r = 2\pi r_0 k'e^{-B'/T} \quad (115)$$

$$R = \int_0^l r dl = 2\pi r_0 k' \int_0^l e^{-B'/T} dl = k'_0 \int_0^l e^{-B'/f(l)} dl = k'_0 \int_{x_1}^{x_2} e^{-B'x} (b+2cx) dx \quad (116)$$

so that

$$\frac{R}{R'} = \frac{\gamma}{\gamma'} = \frac{b \left[e^{-B'x_1} - e^{-B'x_2} \right] + \frac{2c}{B'} \left[(1+B'x_1) e^{-B'x_1} - (1+B'x_2) e^{-B'x_2} \right]}{b' \left[e^{-B'x'_1} - e^{-B'x'_2} \right] + \frac{2c'}{B'} \left[(1+B'x'_1) e^{-B'x'_1} - (1+B'x'_2) e^{-B'x'_2} \right]} \quad (117)$$

where a, b, c and a', b', c' have the same numerical values as above, as also do $x_1, x_1',$ and $x_2, x_2',$ but where now $B' = E'/R_0$ in degrees absolute, E' being the over-all low-pressure activation energy in cal/mole. The ratios γ/γ' are known for both hydrogen (no correction needed) and for tritium (corrected to $\omega = 1$), and k' and k'_0 are constants of proportionality for the low-pressure region analogous to k and k_0 for the high-pressure data. Calculation of B'_{H_2} and B'_{T_2} and hence E'_{H_2} and E'_{T_2} proceeds as before with equal labor.

In practice, $a, b, c,$ and a', b', c' for H_2 were determined from all of the readings (for all H_2 runs combined) of each thermocouple for the given temperature levels averaged together. A slightly different set of values for $a, b, c,$ and a', b', c' for tritium was similarly obtained. As a result, we had one set of x_1, x_1', x_2 and x_2' for hydrogen and another very slightly different set for the tritium-rich mixture. The rather good temperature constancy obtained at each thermocouple for a given gas and a given temperature level permitted this procedure. These values were used in both Equations (113) and (117) as indicated.

Calculation of the Average Temperature

Let us define the average temperature T_a as

$$T_a = \frac{\int_0^l T dl}{\int_0^l dl} = \frac{1}{l} \int_0^l T dl = \frac{1}{l} \int_0^l f(l) dl \quad (118)$$

where $f(\ell)$ is given by Equation (108). From Equation (108) we find

$$x = \frac{1}{T} = - \frac{b - \sqrt{b^2 - 4c(\ell - a)}}{2c} \quad (119)$$

which upon substitution into Equation (118) yields

$$T_a = \frac{1}{\ell} \int_0^\ell \frac{2cd\ell}{-b - \sqrt{b^2 - 4c(\ell - a)}} \quad (120)$$

Integration proceeds as follows: let $z = b^2 - 4ac$, $s = 4c$; then we have

$$T_a = - \frac{2c}{\ell} \int_0^\ell \frac{d\ell}{b + \sqrt{z + s\ell}}; \text{ now let } u = \sqrt{z + s\ell}, \text{ or } d\ell = \frac{2}{s} \sqrt{z + s\ell} du = \frac{2u}{s} du,$$

whence

$$T_a = - \frac{4c}{4\ell c} \int \frac{udu}{b+u} = - \frac{1}{\ell} \left[b+u - b \ln(b+u) \right] = - \frac{1}{\ell} \left[b + \sqrt{b^2 - 4ac + 4c\ell} - b \ln(b + \sqrt{b^2 - 4ac + 4c\ell}) \right]_0^\ell$$

or

$$T_a = - \frac{1}{\ell} \left[\sqrt{b^2 - 4ac + 4c\ell} - \sqrt{b^2 - 4ac} - b \ln \frac{b + \sqrt{b^2 - 4ac + 4c\ell}}{b + \sqrt{b^2 - 4ac}} \right] \quad (121)$$

T_a calculated from this equation compares closely with that obtained by graphical integration of Equation (118), not assuming any analytical form for $T = f(\ell)$ but merely drawing a smooth curve through the experimental points. The average temperature for a low temperature level run T_a' may be similarly calculated, using a' , b' , and c' .

Correction of α and γ to Constant Temperature

Up to this point the values of α and γ correspond to the observed rates of permeation of pure H_2 and pure T_2 when a temperature gradient exists along the length of the diffuser. Since α and γ , unlike E and E' , are both functions of temperature, it is necessary to calculate values of α and γ for both H_2 and T_2 , at each temperature level, which correspond to some definite temperature, say T_1 , which lies between the temperature extremes T_1 at $\ell = 0$ and T_2 at $\ell = \ell$. Thus by Equation (18) we have

$$\alpha_1 = \alpha^0 e^{-B/T_1} \quad (122)$$

For the case of variable temperature the observed α_v is related to the observed rate R by

$$R = \alpha_v \frac{A}{d} \sqrt{P} = \alpha_v \frac{2\pi r_0 \ell}{d} \sqrt{P} \quad (123)$$

Since the observed rate is also given by Equation (107) as

$$R = k_0 \int_0^{\ell} e^{-B/T} d\ell = \frac{2\pi r_0 \alpha^0 \sqrt{P}}{d} \int_0^{\ell} e^{-B/T} d\ell \quad (124)$$

it follows that

$$\alpha^0 = \alpha_v \frac{\ell}{\int_0^{\ell} e^{-B/T} d\ell} \quad (125)$$

which together with Equation (122) leads to

$$\alpha_1 = \alpha_v \frac{\ell e^{-B/T_1}}{\int_0^{\ell} e^{-B/T} d\ell} \quad (126)$$

which relates α_1 (corresponding to a definite temperature T_1 , where $T_1 \leq T_1 \leq T_2$) to α_v (the observed coefficient corresponding to a temperature gradient between the extremes of T_1 at $\ell = 0$ and T_2 at $\ell = \ell$). α_1 reduces to α_v as it should, for the special case of constant temperature. Of course, $\alpha_1 = f(T_1)$ and will vary according to the value of T_1 selected for use in the numerator. Since T_a obviously lies between T_1 and T_2 , it is convenient to assign $T_1 = T_a$, where T_a is already known from Equation (121). That is, α_1 will correspond to a very definite temperature T_a , the average temperature of the diffuser. This in no way implies that α_1 is an approximate or averaged value; it refers precisely to a temperature which we have arbitrarily but reasonably taken as equal to the average diffuser temperature. It could just as well have been calculated to correspond to any other specified temperature within the range T_1 to T_2 .

The procedure is then to calculate T_a by Equation (121) and to use this value in the numerator of Equation (126) together with the known numerical value of B (by Equation (113)). The integral is also known, within the range T_1 to T_2 :

$$\int_0^{\ell} e^{-B/T} d\ell = \frac{1}{B} \left[b \left\{ e^{-Bx_1} - e^{-Bx_2} \right\} + \frac{2c}{B} \left\{ (1+Bx_1)e^{-Bx_1} - (1+Bx_2)e^{-Bx_2} \right\} \right] \quad (127)$$

The fact that the integral is known only within this interval is the reason for restricting T_1 to the range T_1 to T_2 . α_v is known for both hydrogen and tritium (corrected to $w = 1$); in all cases, $\ell = 5.4375$ in. In Equation (127) x_1 and x_2 are used to compute the fully corrected $\alpha = \alpha_1 = \alpha_a$ at the higher temperature level, and x_1' and x_2' are used for the lower temperature level.

The values selected for T_a are $T = 970.9^\circ\text{K}$ and $T' = 842.7^\circ\text{K}$, which represent the mean of all average temperatures for both hydrogen and tritium calculated individually by Equation (121) for each run; i.e. 970.9°K is the average of all the average temperatures for the high-temperature runs and 842.7°K is the average of all the average temperatures for the low-temperature runs.

Similarly we can derive

$$r_i = r_v \frac{\int_0^l e^{-B'/T_1} dl}{\int_0^l e^{-B'/T} dl} \quad (128)$$

starting with

$$R = r_{iAP} = k_o' e^{-B'/T_1} = \text{rate for constant temperature } T_1 \quad (129)$$

and

$$R = r_{vAP} = k_o' \int_0^l e^{-B'/T} dl = \text{observed rate with temperature gradient.} \quad (130)$$

As above, we have assigned $T_1 = T_a$ where T_a assumes the values 970.9°K for the high-temperature runs and 842.7°K for the low-temperature runs. The corresponding values of the fully corrected $r = r_i = r_a$ for both hydrogen and tritium are obtained from Equation (128).

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APPENDIX C

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APPENDIX C. THE THEORETICAL ISOTOPE SEPARATION FACTOR

In a mixture of the simultaneously diffusing gases, the relative rate of permeation ψ by hydrogen as compared to tritium is

$$\psi = \frac{R_H}{R_T} \quad (131)$$

That is, ψ is the ratio of the rate at which H atoms are actually transported under the existing conditions of P_{H_2} , P_{HT} , P_{T_2} to the rate at which T atoms are transported. It is not equal to the high-pressure permeation rate ratio $R_{H_2}/R_{T_2} = \alpha_{H_2}/\alpha_{T_2}$ of the pure gases each diffusing at the same total pressure.

At pressures sufficiently high, where the $\sqrt{P}$ law holds, this becomes

$$\psi = \frac{\alpha_{H_2}}{\alpha_{T_2}} \sqrt{\frac{P_{H_2}}{P_{T_2}}} = \frac{\alpha_{H_2}}{\alpha_{T_2}} \sqrt{\frac{\phi}{\theta}} \quad (132)$$

which, since θ is given by Equation (81) and ϕ by Equation (82), may be written as

$$\psi = \frac{\alpha_{H_2}}{\alpha_{T_2}} \left[\frac{8(1-\omega) + K_e(2\omega-1) - \sqrt{[8\omega - K_e(2\omega-1)]^2 - 16\omega^2(4-K_e)}}{8\omega - K_e(2\omega-1) - \sqrt{[8\omega - K_e(2\omega-1)]^2 - 16\omega^2(4-K_e)}} \right]^{\frac{1}{2}} \quad (133)$$

The theoretical isotope separation factor ρ is given by

$$\rho = \frac{(1-\omega')/\omega'}{(1-\omega)/\omega} \quad (134)$$

where ω = atom fraction of tritium in the upstream gas and ω' = atom fraction of tritium in the diffused gas. Now

$$\omega' = \frac{n'_T}{n'_H + n'_T} \quad (135)$$

where n'_T is the number of T atoms present in the diffused gas as T_2 and HT , and n'_H is the number of H atoms present in the diffused gas as H_2 and HT . But in the diffused gas,

$$n'_H = \frac{R_H}{R_T} n'_T = \psi n'_T \quad (136)$$

whence

$$\omega' = \frac{n'_T}{\psi n'_T + n'_T} = \frac{1}{1 + \psi} \quad (137)$$

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Then by Equation (137), $1 - \omega' = \psi / (1 + \psi)$ so that Equation (133) yields

$$\rho = \frac{\omega}{1 - \omega} \psi \quad (138)$$

Equation (138) together with Equation (133) gives us the separation factor as a function of permeability constants and gas composition (temperature of course affects both α 's and K_e):

$$\rho = \frac{\alpha_{H_2}}{\alpha_{T_2}} \left(\frac{\omega}{1 - \omega} \right) \left[\frac{8(1-\omega) + K_e(2\omega-1) - \sqrt{[8\omega - K_e(2\omega-1)]^2 - 16\omega^2(4-K_e)}}{8\omega - K_e(2\omega-1) - \sqrt{[8\omega - K_e(2\omega-1)]^2 - 16\omega^2(4-K_e)}} \right]^{\frac{1}{2}} \quad (139)$$

Computation of ρ is probably slightly easier using the equivalent form

$$\rho = \frac{\alpha_{H_2}}{\alpha_{T_2}} \left(\frac{\omega}{1 - \omega} \right) \sqrt{\frac{1 + \theta - 2\omega}{\theta}} \quad (140)$$

where θ is obtained from Equation (81).

It is evident then that the separation factor is directly proportional to the ratio of the high-pressure permeability constants when the total pressure is such that the gas mixture obeys the ΔP law, the constant of proportionality being a function of gas composition.