TABLE V

KINETIC PARAMETERS FOR THE EXCHANGE OF ACETONITRILE ON DIVALENT METAL IONS

M^{n+}	$k_1(25°)$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Mn^{2+} [a]	$(1.2 \pm 0.3) \times 10^7$	7.25 ± 0.25	-1.8 ± 0.8 [c]
Fe^{2+} [a]	$(5.5 \pm 0.8) \times 10^5$	9.7 ± 0.7	0.3 ± 2.2 [d]
Co^{2+} [a]	$(3.2 \pm 0.3) \times 10^5$	11.4 ± 0.5	5.0 ± 2.0 [g]
Co^{2+} [b]	$(3.5 \pm 0.5) \times 10^5$	11.4 ± 0.5	5.2 ± 2.2 [g]
Co^{2+}, [b]	1.4×10^5	8.1 ± 0.5	-7.5 ± 2 [e]
Ni^{2+} [a]	$(2.1 \pm 0.3) \times 10^3$	16.4 ± 0.5	12.0 ± 2.0 [d]
Ni^{2+} [b]	$(2.8 \pm 0.5) \times 10^3$	11.7 ± 0.1	-3.6 ± 1.0 [f]

[a] Nitrogen-14 data. [b] Hydrogen-1 data. [c] W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, **9,** 1724 (1970). [d] R. J. West and S. F. Lincoln, *Aust. J. Chem.*, **24,** 1169 (1971). [e] Reference 2. [f] D. K. Ravage, T. R. Stengle, and C. H. Langford, *Inorg. Chem.*, **6,** 1252 (1967). [g] This work.

temperature range. The contributions of the dipolar terms T_{2M} and T_{2O} to the ^1H T_{2p} data are significant, and consequently the ^{14}N data provide a cross-check on the validity of the ^1H T_{2p} data treatment. The kinetic parameters derived from the ^{14}N and ^1H T_{2p} data sets are compatible within the limitations of the data treatment, as is the case for ^1H and ^{14}N studies of ammonia exchange[11–13] on $Ni(NH_3)_6{}^{2+}$.

The ^1H line-broadening study reported by Matwiyoff and Hooker[2] covered a narrower temperature range than that investigated in this work, and consequently the T_{2M} and T_{2O} contributions to T_{2p} were not observed in the earlier study. As a result the $\Delta H^{\ddagger}$ value derived by Matwiyoff and Hooker is too small, and k_1 and $\Delta S^{\ddagger}$ are proportionately at variance with the kinetic parameters derived from ^1H and ^{14}N data reported in this study (see Table V).

The *positive* ^{14}N A/h value is consistent with paramagnetic spin delocalization onto nitrogen by a σ-bonding interaction between cobalt(II) e_g orbitals and the orbital containing the nitrogen lone pair.[2] The *negative* ^1H A/h values observed over the experimental temperature range suggest a negative spin density at the hydrogen atoms, but the non-Curie temperature dependence of the ^1H shift data indicates that both Fermi contact and pseudocontact interactions may contribute to the ^1H shift. Kurland and McGarvey[14] have shown that for complexes with T_1 ground states a Zeeman mixing of excited states into the ground state may lead to a non-Curie temperature dependence. There appears to be no deviation from Curie behavior in the ^{14}N shift data, although it should be noted that the limiting shift region conforming to eq 7 is only just entered. This is consistent with the Fermi contact contribution associated with the coordinating ligand atom being significantly larger than the pseudocontact shift contribution to the observed shift.[14]

The kinetic parameters for the exchange of acetonitrile on divalent metal ions (Table V) exhibit a trend in which $k_1(25°)$ decreases from Mn^{2+} to Ni^{2+}, and the reverse trend for $\Delta H^{\ddagger}$. These trends are also observed for solvent exchange on these metal ions in ammonia, methanol, and water, which suggests a similarity in mechanism in these four solvents.[3] Recent crystal field calculations,[15] based on a square-pyramidal transition state for water exchange, which is consistent with the dissociative ligand substitution mechanism proposed[16,17] for these metal ions, predict the above trend in $\Delta H^{\ddagger}$.

Acknowledgments.—It is a pleasure to acknowledge the assistance of Helen Robjohns in obtaining A-60 pmr spectra at The Flinders University of South Australia. We thank the Australian Research Grants Committee for supporting the project of which this work is part.

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Inverse Hydrogen Isotope Effects in Some Metal Hydride Systems

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Several instances were found of metal hydrides in which replacement of hydrogen by deuterium or tritium resulted in a more stable compound. The experimental evidence consists in measurements of the dissociation pressures of pure isotopic species, and of the equilibrium distribution of hydrogen isotopes between gas and solid phases in systems of mixed isotopic content. Examples are VH_2, NbH_2, $(V,Nb)H_2$, and $LaNi_5H_6$. On the other hand, ternary hydrides formed by the intermetallics Mg_2Ni and TiFe exhibit an isotope effect which is in the opposite, and more usual, direction.

Introduction

An investigation of the reversible absorption of hydrogen by metals, mostly alloys, has been conducted at this laboratory over the past several years. It has resulted in the discovery, or improved characterization in terms of pressure–composition–temperature (P–C–T) relationships, of a number of new hydride phases.[1] Some attention has been given to properties other than P–C–T, as for instance magnetic properties;[2] and recently the effect of replacing normal hydrogen by deuterium was examined in vanadium di-

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[1] (a) J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.*, **6,** 2220 (1967); (b) *ibid.*, **7,** 2254 (1968); (c) *ibid.*, **9,** 1678 (1970).

[2] S. Aronson, J. J. Reilly, and R. H. Wiswall, Jr., *J. Less-Common Metals*, **21,** 439 (1970).

hydride (VH_2). It was immediately apparent that vanadium dideuteride (VD_2) was appreciably more stable than the corresponding dihydride. This was quite unexpected as, with few exceptions, it has been found that metal deuterides are less stable than the corresponding metal hydrides. Further, the exceptions were in cases where the stability differences were very small. The following list gives the references known to us on the effect of isotopic substitution on the stability of the metal hydride *vs.* deuteride as measured by their relative dissociation pressures. It also includes those which treat isotope-separation experiments involving hydrides. It does not include isotope effects on heat capacity, membrane diffusion rates, crystal parameters, nmr spectra, neutron scattering, magnetism, etc. To date there are published data on Ce,[3] Cs,[4] Dy,[5] Er,[5-7] Hf,[8] Ho,[5] K,[4,9] La,[3] Li,[10-12] Lu,[5] Mg,[13] Na,[4,14] Nb,[15] Pd[16-25] (partial list), Pd-Ag,[20] Pd-Pb,[20] Pd-Pt,[26,27] Pd-Rh,[20] Pr,[5] Pu,[28] Rb,[4] Ta,[29] Tb,[5] Ti,[29-38] Tm,[5] U[7,30-36] (partial list), Y,[5] and Zr.[37-40]

With three exceptions, these papers are unanimous in ascribing lower stability to metal deuterides as compared to the corresponding metal hydride. Two of these exceptions involve lithium[12] and uranium.[33] For both these elements, however, there have been published numerous and more detailed articles which support the opposite conclusion, *i.e.*, that for LiH and UH_3 the isotope effect is in line with all the other systems. The third exception concerns titanium, for which one research team found a zero isotope effect.[29] There is, however, an unresolved disagreement about the correct deuteride isotherms in this system. A convenient measure of the isotope effect is the ratio of the dissociation pressure of the deuteride to that of the protide and the literature cited gives values for this quantity which vary (if we discard the exceptions just mentioned) from 1.1 to 4.8. A typical value would be around 2. At room temperature, a value of 2 corresponds to a free energy difference, between protide and deuteride, of 410 cal/mol of hydrogen.

Our work thus far has been focused on the isotope effect in the vanadium dihydride–hydrogen system, since it is this system which departs from the usual more than any other. However, we are also including results on hydrogen isotope distribution in other metal hydride systems which, while not so detailed, we believe will prove of interest.

All the data presented herein were derived from pressure–composition isotherms of metal hydrides and deuterides, and from a number of hydrogen isotope exchange reactions involving a solid metal hydride in contact with a gas phase of known isotopic composition. A description of the experimental procedure follows.

Experimental Section

The hydrides studied were made from the following metals and alloys: V, Nb, VNb, TiFe, Mg_2Ni, and $LaNi_5$. In addition, an alloy of "Misch metal" and nickel in the proportion $MmNi_5$ was also used in several experiments (the atomic weight of Mm was taken as 140). In the case of V and Nb, both commercial grade and zone-refined materials were used for comparison purposes, since it has been found that the presence of impurities in V has a profound effect on the dissociation pressure of its hydride. Sources and specifications have been described in an earlier paper,[1c] as have those of the Mg and Ni.[1b] The Ti and Fe were zone-refined materials obtained from Materials Research Corp. of Orangeburg, N. Y. Lanthanum was supplied by Gallard Schlesinger Corp. of Carle Place, N. Y., and was of 99.5% purity. Misch metal was also obtained from the Gallard Schlesinger Corp. and had a nominal composition (in wt %) of 50 Ce, 27 La, 16 Nd, 5 Pr, and 2 other rare earths.

The Mg_2Ni alloy was prepared in an induction furnace using a graphite crucible; the TiFe, VNb, and $LaNi_5$ were prepared by arc melting. The VNb alloy was made from commercial grade ingredients. The source of normal hydrogen was Matheson's highest purity tank gas, with a stated purity of 99.999%. Deuterium of 99.5% isotopic purity was also obtained from Matheson, and from Air Products Corp. Tritium–hydrogen mixtures were made by treating tritiated water with hot zinc in a closed system.[41] The resulting gas was diluted with normal hydrogen until it had an activity of about 2×10^6 disintegrations $min^{-1}\,ml^{-1}$ (NTP).

The metals were hydrided, either with normal hydrogen or deuterium, by our usual technique.[1] Briefly this involved activation of the metal by repeated hydriding and dehydriding cycles,

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after which the sample was finally brought to the highest hydrogen-to-metal ratio that could be obtained at room temperature by exposure to gas at about 950 psia in the case of normal hydrogen and 500–600 psia for deuterium. The only exception to this was in the preparation of Mg_2NiH_4, which was hydrided at ~300° and 350 psia.

Data on equilibrium dissociation pressures were generally taken from decomposition isotherms which were determined at a number of temperatures. Details of the procedure used to gather such data have been published.[1] As in the past, we have chosen to standardize on desorption rather than absorption isotherms. Constant pressure is more quickly attained on desorption, and plateaus have longer horizontal portions. We believe, like Wicke and Nernst,[18] that these plateaus are more likely to correspond to true equilibrium.

Occasionally, experimental isochores were obtained directly on samples with compositions in the two-phase region. In this procedure, an almost completely hydrided sample was brought slowly to a series of successively higher temperatures and the pressure was measured at each temperature. Although the free volume was small, part of the solid necessarily dissociated at each step and thus the solid composition was not quite constant. However, provided the initial solid composition is in the plateau or two-phase region no significant error is incurred in this procedure, although care must be taken not to over-ride the temperature because of hysteresis effects. The two methods were compared in the case of VD_2 made from zone-refined vanadium and were found to give concordant results; that is, the rising-temperature isochore gave the same pressures, in the two-phase region, as were given by the decomposition isotherms.

Isotope exchange equilibria were determined by exposing hydrides made from metal and normal hydrogen to mixtures of a known amount of hydrogen–deuterium or hydrogen–tritium. The gas phase was sampled from time to time to permit isotope-ratio determinations, until the ratio became constant. At this point the solid phase was isolated and subsequently decomposed by heating. The amount of evolved gas was measured and analyzed for the appropriate hydrogen isotope. The separation factor α was then calculated from the equation $\alpha = [D\ (\text{or}\ T)/H_{\text{solid}}]/[D\ (\text{or}\ T)/H_{\text{gas}}]$. A material balance was also calculated from these data. In these experiments any net transfer of mass between solid and gas phase was minimized by careful control of gas pressure. When, as was usually the case, the solid was the highest hydride attainable, the pressure was maintained higher by a factor of >2 than the decomposition pressure in the plateau region of the pressure–composition isotherm. Beyond the plateau region, the typical isotherm is nearly parallel to the pressure axis, so that excess pressure will not result in an appreciable change of composition of the solid.

One exchange experiment was done with the lower hydride of vanadium, with composition about $VH_{0.9}$. Here too the isotherm has a steep slope over a large pressure range, and little or no mass transfer takes place within this range.

The first exchange experiments were done under static conditions. However, equilibrium was approached rather slowly and the rate-limiting step was evidently diffusion in the gas phase. An improved apparatus was built which consisted of a forced circulation loop in which gas was passed through a column of powdered hydride, supported by a porous frit. The column was ~2 in. in length and had a $^3/_8$-in. internal diameter. The powdered hydride was mixed with a small amount of Chromosorb A which served as an inert and porous diluent, thereby preventing the formation of a high pressure drop through the column. Circulation was provided by a novel type of pump in which the motive power was supplied by alternately decomposing and regenerating a hydride, using water as a heating and cooling medium; a description of this pump is given elsewhere.[42]

Hydrogen–deuterium analyses were done on a mass spectrometer. Tritium activity was determined in a proportional counter, after diluting each sample by a factor of 15 with "P-10" counting gas.

Results and Discussion

Equilibrium Pressure Measurements.—At room temperature, the vanadium metal phase (α) dissolves hydrogen until a composition of $VH_{0.05}$ is reached. At this point the monohydride (β) phase appears and coexists with the α phase until the composition reaches $VH_{0.45}$. From $VH_{0.45}$ to $VH_{0.95}$ only the pure β phase exists.[43] The region between $VH_{0.95}$ and $VH_{2.0}$ consists of a mixture of the monohydride (β) and dihydride (γ) phases.[10] It is possible to attain compositions as high as $VH_{2.08}$ by dissolving hydrogen in the γ phase. The phase relationships of the niobium–hydrogen system are similar.

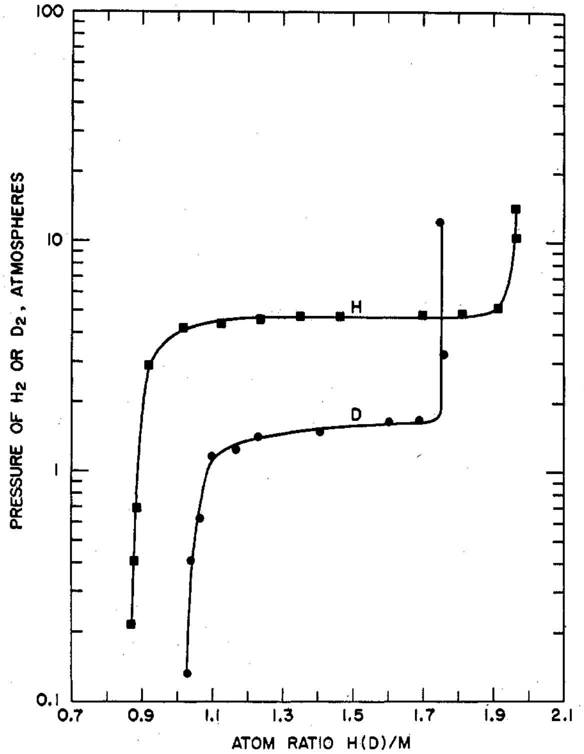

Figure 1.—Uptake of hydrogen and deuterium by zone-refined vanadium at 40°.

In Figure 1 are shown two pressure–composition isotherms, one for the VH–VH_2–H_2 system and the other for the VD–VD_2–D_2 system. The equilibrium dissociation pressure of the hydride is higher than the deuteride by a factor of ~3. In the deuterium isotherm it is interesting to note the γ dideuteride phase does not appear until the solid composition is $VD_{\sim 1.1}$. The fact that this isotherm does not extend over to the region of $VD_{\sim 2}$ is not significant as we believe that the sample was not completely deuterided; the reaction rate of V and D_2 is much slower than the corresponding hydrogen reaction. It may be noted that using commercial grade V, where the impurities catalyze the reaction, compositions as high as $VD_{1.92}$ have been obtained. In this regard we have found it necessary to specify the purity of the starting vanadium, as the impurities in commercial grade vanadium not only have a catalytic effect but also increase the dissociation pressure of the dihydride by a factor of over 2.[10] A number of pressure–composition isotherms for the vanadium system were constructed using both zone-refined and commercial grade metal. These data are summarized in Figure 2, which is a semilog plot of the equilibrium dissociation pressure (plateau region) *vs.* reciprocal temperature. From the plateau pressures

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(42) J. J. Reilly, A. Holtz, and R. H. Wiswall, Jr., *Rev. Sci. Instrum.*, **42**, 1485 (1971).

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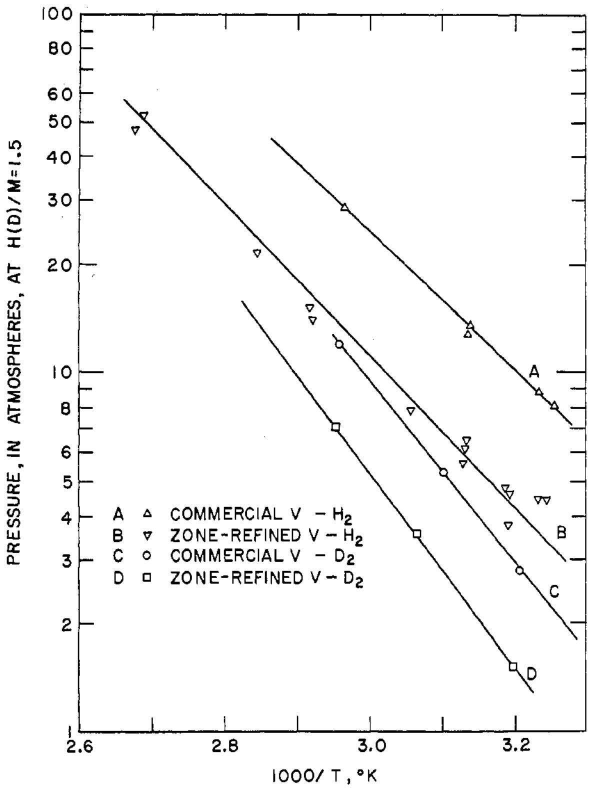

Figure 2.—Dissociation pressures of vanadium dihydride and dideuteride: temperature dependence.

and their temperature dependence one may derive the relative partial molar free energy, enthalpy, and entropy of hydrogen or deuterium in the solid phase; these are listed in Table I.

Table I

Hydrogen in Hydrides. Relative Partial Molar Quantities, per Gram-Atom of H or D, at 25°

Metal	H(D)/M	$\Delta\bar{G}$, cal	$\Delta\bar{H}$, cal	$\Delta\bar{S}$, cal/deg
V	H, 1.5	195	−4800	−16.8
V	D, 1.5	−160	−6000	−19.6
V (coml)[a]	H, 1.5	485	−4400	−16.4
V (coml)[a]	D, 1.5	38	−6000	−20.3
Nb	H, 1.5	−105	−4800	−15.7
Nb	D, 1.5	−195	−4900	−15.8
$V_{0.8}Nb_{0.2}$	H, 1.5	260 (at 45.5°)	...	...
$V_{0.8}Nb_{0.2}$	D, 1.5	30 (at 45.5°)	...	...

[a] coml = commercial grade.

In the case of Nb, the dihydride is only slightly less stable than the dideuteride, the pressure ratio being 1.3–1.4. The isotherms have the same shape and the appearance of the γ phase was at about the same composition for both systems. With niobium there was no essential difference between zone-refined and commercial grade metal. Figure 3 gives a pressure–composition isotherm for $Nb-D_2$, together with a previously published curve for $Nb-H_2$ for comparision. Other isotherms were obtained at 42.2 and 82.2°. From the plateau pressures (H/M = 1.5) the parameters A and B of the equation $\log P_{mm} = (A/T) + B$ were determined to be 2140 and 9.79, respectively. For $Nb-H_2$, they are 2090 and 9.75. The pressures calculated from these equations have a probable error of 4% in the $Nb-D_2$ system and 3% in the $Nb-H_2$.

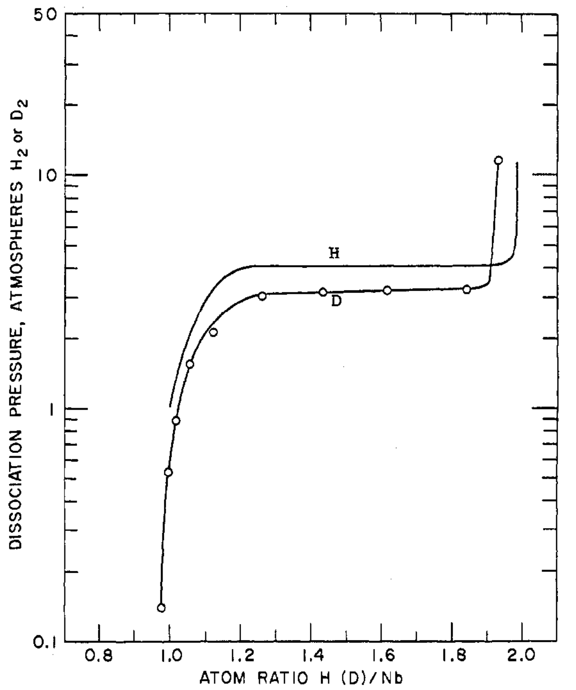

Figure 3.—Uptake of hydrogen and deuterium (lower curve) by niobium at 60.6°.

The thermodynamic quantities derived from the isochore are listed in Table I.

A few experiments were carried out with two alloys, $V_{0.8}Nb_{0.2}$ and TiFe. In the latter case consistent data were difficult to obtain as the dependence of the dissociation pressure on composition was very sensitive to sample history. In one pair of runs, however, we succeeded in getting well-defined plateaus with both deuterium and hydrogen in the H(D)/M range of 0.25–0.40. The respective plateau pressures were 5.8 and 4.8 atm at 30°, the deuteride being less stable than the hydride. On the other hand, as shown in Figure 4, the hydride of the V–Nb alloy is much less stable than the corresponding deuteride. While the alloy hydride structure has not been characterized, the isotherms are similar to those obtained using the elemental metals; our purpose here is merely to compare the hydride and deuteride stability.

Of the results presented, those pertaining to TiFe occasion no great surprise, but those for both forms (zone-refined and commercial) of vanadium, for Nb, and for VNb are significant. The ratios of dihydride to dideuteride dissociation pressure are, at 30°, 2.8 for zone-refined vanadium and 3.5 for the commercial grade. This inverse relationship is not, however, as novel as it first appears. The ratio of the dissociation pressures of hydride and deuteride is determined by the algebraic sum of a number of thermodynamic quantities, involving enthalpy and entropy differences between hydride and deuteride and between hydrogen and deuterium. The signs of some of the terms differ from one hydride to another. Thus, cases have been published in which the deuteride's enthalpy of formation was more negative than that of the corresponding hydride,[40,44] and other cases are known in which the

(44) W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, "Metal Hydrides," Academic Press, New York, N. Y., 1968, pp 512–513.

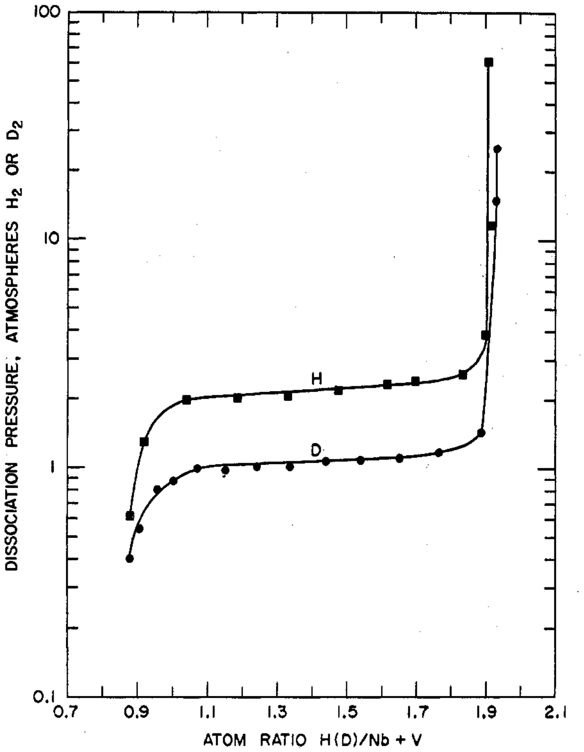

Figure 4.—Uptake of hydrogen and deuterium by alloy $Nb_{0.2}V_{0.8}$ at 45.5°.

reverse is true.[5,18] On the other hand, the entropy of formation, ΔS_f, is usually more negative for the deuteride because of the higher absolute entropy of deuterium gas (S_{298} = 34.62 eu) *vs.* that of hydrogen gas (S_{298} = 31.13 eu), although there are exceptions to this rule with rare earth hydrides.[5] In the present circumstances, the most conspicuous inversion of the pressure ratio is that found with VH_2–VD_2. This is evidently due to a combination of circumstances. The deuteride's heat of formation is more negative than that of the protide by an amount which is rather larger than usual, although not entirely without precedent, and the measurements were made at low enough temperature that the effect of the entropy difference, which operates in the opposite direction, is minimized. As the temperature is raised, the deuteride–protide stability difference diminishes, and eventually its sign changes. With commercial vanadium, for example. the crossover point can be calculated to be about 137°. With the exception of Pd, all of the previous work cited on the relative stability of metal hydrides and deuterides dealt with systems at relatively high temperatures. In such cases, even a slight negative entropy difference between the hydride and deuteride (the deuteride being more negative) would outweigh a favorable enthalpy difference.

Table II

Tritium–Hydrogen Separation Experiments

Hydride	T, °C	Presure range, psi	Separation factor	Tritium material balance, %
$VH_{0.65}$	210	188–162	1.10	
$VH_{0.85}$	30.6	98	1.40	102
VH_2	0	260–235	1.91	100.2
VH_2	0	271–263	1.79	98.1
VH_2	0	243–217	1.96	100.5
VH_2	28.0	137–124	1.72	102.1
VH_2	28.2	150–120	1.70	98.3
VH_2	28.2	279–263	1.77	101.6
VH_2	28.2	220–206	1.77	99.0
VH_2	45.2	315–298	1.61	100.4
VH_2[a]	27.6	283–240	1.79	98.1
Mg_2NiH_4[b]	325	244–180	0.46	96.3
Mg_2NiH_4[b]	251	212–137	0.48	104.0
$LaNi_5H_{6.6}$	0	234–220	1.25	102.3
$LaNi_5H_{6.6}$	29–30	253–240	1.23	
$LaNi_5H_{6.6}$	27.7	242–224	1.12	93.8
$LaNi_5H_{6.6}$	47.0	228–220	1.09	94.3
$MmNi_5H_{5-6}$[c]	0	230–226	1.29	95.7
$MmNi_5H_{5-6}$	0	228–227	1.29	94.9
$V_{0.9}Cr_{0.1}H_2$	28.4	219–207	1.66	104.5
$ZrNiH_3$	27.6	208–188	1.05	99.3

[a] Made from V of commercial purity; others were zone-refined. [b] Convective circulation only. [c] Mm is Misch metal: Ce, 50%; La, 27%; Nd, 16%; Pr, 5%; other rare earths, 2%.

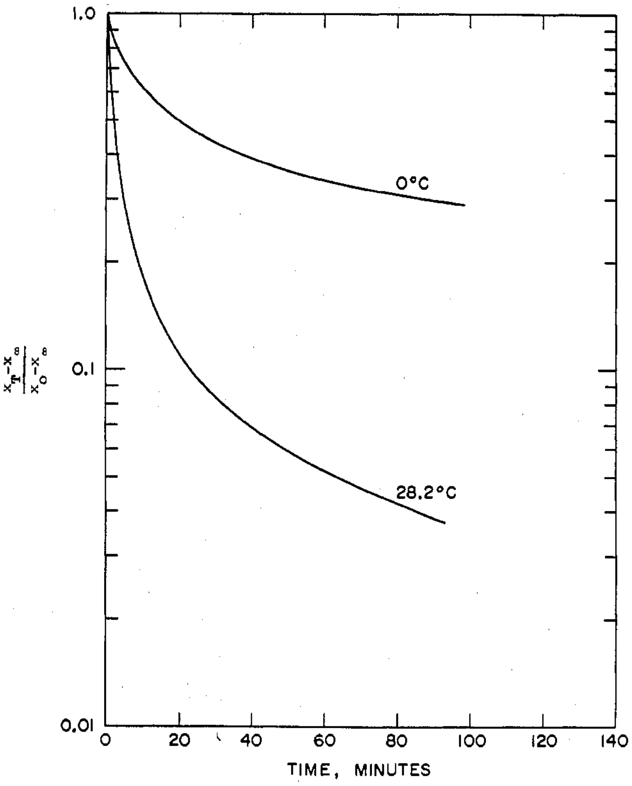

Figure 5.—Rate of tritium exchange with VH_2.

Exchange Experiments.—Our first isotope exchange experiments involved VH_2, made from commercial grade vanadium, and hydrogen–deuterium mixtures and were done under static conditions. In a typical experiment, VH_2 at 28° was exposed to a hydrogen–deuterium mixture containing 25–50% deuterium. The isotope ratio in the gas phase was followed for 120 hr. This and a few similar experiments were of a preliminary nature. The results were imprecise, largely because of the inadequacy of the only mass spectrometer available. Material balances were often too large or too small by 10–15%. Nevertheless, the results made it fairly certain that the separation factor was of the order of 1.7 ± 0.3 and are in agreement with the value which the dissociation pressure ratio of the pure isotopic species would lead one to predict. The required relationship can be derived by a method similar to that used by Bigeleisen and Kant[34] to relate separation factors in the system U–H–D and the relevant dissociation pressures. The present system presents an added complication in the fact that VH_2 decomposes in two stages instead of one, like UH_3. One needs to know the relative isotopic stabilities at each stage. We have no data on VH *vs.* VD, but an exchange experiment which was run with VH gave about the same separation factor as those run with VH_2. The isotopic pressure ratios were therefore taken as the same for the lower and higher hydride. Additional assumptions are that the isotope effect is independent of the $(H + D)/M$ ratio and of the (H/D) ratio in the solid.

A more extensive and much more reliable series of exchange measurements was made with tritium. In all the runs except those with Mg_2NiH_4 the gas was pumped continuously through the solid hydride, which greatly reduced the time necessary to attain equilibrium. Table II summarizes the results. The relation between T–H and D–H separation factors in the vanadium system is consistent with Bigeleisen's formula, $\ln \alpha_{T-H} = 1.4 \ln \alpha_{D-H}$.[45] Applying this to the 28° α_{T-H} value, 1.74, one predicts 1.48 for α_{D-H}, which agrees within its experimental error with the value found. For the rare earth alloys, whose hydriding properties were recently discovered by van Vucht, *et al.*,[46] the effect is in the same direction but smaller; a vanadium–chromium alloy resembles vanadium; zirconium–nickel hydride shows a very small effect in the same direction; while with Mg_2NiH_4, which is a relatively stable hydride, the heavy isotope becomes concentrated in the gas phase. There is no evidence for a dependence of separation factor on pressure. The temperature dependence is marked, however. Taking averages for all runs on VH_2 of similar origin at the same temperatures, one gets the following separation factors: 0°, 1.89; 28°, 1.74; and 45° (one run), 1.61.

Table III

Deuterium–Tritium Separation Factors in the Vanadium Dihydride–Hydrogen System

	0°	28.2°	28.6°	42.8°
$\alpha \equiv (T/D)_{solid}/(T/D)_{gas}$	1.078	1.044	1.036	1.009
Tritium material balance	96.8	101.3	101.9	100.7

Tritium–deuterium exchange was the subject of four runs. In these, the dideuteride, VD_2, of zone-refined vanadium was equilibrated in the forced-circulation loop with deuterium gas to which tritium tracer had been added. Table III gives the results. As before, a marked temperature dependence was found. However, the 28° value of the separation factor, 1.04, falls considerably short of the 1.17 figure which would be predicted from α_{T-H}.

The kinetics of the isotope exchange reactions do not appear to follow any simple rate law, although the exchange is rapid as shown in Figure 5. These curves have a shape very like that found by Bigeleisen and Kant[34] in a similar exchange experiment involving U as the metal substrate. Their conclusion that diffusion within the solid was rate determining very probably applies here.

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Preparation and Properties of Perfluoroammonium Tetrafluoroborate, $NF_4^+BF_4^-$, and Possible Synthesis of Nitrogen Pentafluoride[1]

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A new crystalline compound, $NF_4^-BF_4^-$, has been prepared by exposing the heterogeneous ternary system NF_3–BF_3–F_2 to 3-MeV bremsstrahlung at 77°K. The *G* value for the reaction (molecules isolated per 100 eV absorbed) is about unity. The compound is stable at room temperature in dry air; it decomposes above 250° to the reactants. It reacts rapidly with moisture and with organic substances. The indicated ionic structure is confirmed by infrared and Raman spectroscopy. The X-ray powder pattern can be indexed on the basis of a tetragonal unit cell with $a = 7.01$ and $c = 5.22$ Å. Irradiation of mixtures of nitrogen trifluoride and excess fluorine at 77°K has led to isolation in low yields of a white solid. It decomposes below 143°K to liberate nitrogen trifluoride and reacts with boron trifluoride at low temperature to form NF_4BF_4. Its most likely identity is perfluoroammonium fluoride.

Introduction

Synthesis of two salts of the previously unknown tetrafluoronitrogen(V) cation, NF_4^+ (perfluoroammonium), was recently reported by two groups of investigators.[2,3] Tolberg[2] and his colleagues prepared $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^-$ by a thermal reaction of NF_3 and F_2 with AsF_5 or SbF_5 at high pressures and moderately elevated temperatures. The perfluoroarsenate salt was also obtained by Christe, Guertin, and Pav-

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