SEPARATION AND ANALYSIS OF VARIOUS FORMS OF HYDROGEN BY ADSORPTION AND GAS CHROMATOGRAPHY

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CONTENTS

I. INTRODUCTION

The problem of the separation of the isotopes of hydrogen, their spin isomers, and their interisotopic molecular forms offers a uniquely fascinating challenge in analytical chemistry. The growth of knowledge about differential adsorption of gases on solids and the advent of the related science of gas–solid chromatography has offered a possibility of obtaining complete separation and analysis of a sample of hydrogen into all its identifiable components, and within the past few years a sizable literature has appeared on the subject. It is the purpose of this review to survey the progress that has been made on the experimental side, and the implications of the data so obtained relative to the adsorption of hydrogen on the solids employed as adsorbents in these experiments.

II. THE FORMS OF HYDROGEN

A. ISOTOPES—PROTIUM, DEUTERIUM, AND TRITIUM

There are three known isotopes of hydrogen: protium (H), deuterium (D), and tritium (T) of masses 1, 2, and 3, respectively, of which the last named is β-radioactive with a half-life of 12.4 years. The constant loss of tritium by radioactive decay is replenished from the following sources: (1) tritium produced in rocks by the action of neutrons on Li^6; (2) tritium produced by the action of high energy cosmic ray protons on atmospheric N_2 and O_2; (3) tritium injected into the earth's atmosphere from extraterrestrial sources, most likely, solar flares; and (4) tritium from the radioactive fallout following a thermonuclear explosion.

Of these, the first named source has been shown (64) to be of least significance, whereas the last named one (by its very nature an irregular source) has, at peak times, contributed more tritium than that from all other sources put together (6). Considerable literature has appeared on the subject of tritium equilibrium in nature, and the interested reader is referred to the recent publication of von Buttlar (13) from which earlier references may be procured.

The relative abundance of the isotopes of hydrogen in natural waters is a subject of great geophysical interest (53, 56), and a systematic study of the variations in the relative abundance has opened up the way to important conclusions in meteorology, oceanography, and hydrology. As an example, an examination of the tritium content of samples of water drawn off vertical profiles from the Mediterranean seems to indicate that the surface water does not usually penetrate below a depth of 150 m. Similar studies indicate areas of ocean up-welling in the Pacific off the coast of California. In order, therefore, to harmonize reports from various laboratories, the following conventional standards for reporting concentrations of deuterium and tritium in natural waters have been adopted: $D/H = 1:6328 = 1\ D/H\ (SMOW)$, where the letters SMOW stand for Standard Mean Ocean Water (20); $T/H = 1:10^{18} = 1\ T.U.$, which letters stand for Tritium Unit.

The concentrations of deuterium and tritium usually encountered in natural waters from various sources fluctuate within a few per cent around 1 D/H (SMOW) and 0.1–10 T.U., respectively.

Besides the importance in geophysical studies, both deuterium and tritium are extensively employed as tracers in all branches of physical and biological sciences, the use of tritium being far more common since it can be followed with less difficulty by virtue of its radioactivity. Applications of tracer methods are by no means restricted to laboratory experiments only; Kaufman and Todd (49) used tritium as tracers in field studies of canal seepage measurements. In practice, the concentrations of the isotopes, especially of tritium, in most tracer studies have to be kept low, the usual concentration of tritium employed in most tracer studies being of the order of 10^{-4} mole fraction.

Since the concentrations of the isotopes involved both in geophysical and in tracer studies are small and, further, since the conclusions in most instances have to be drawn from the differences in these small concentrations of the isotopes, analytical methods of a high degree of sensitivity and accuracy only can be usefully employed for the detection and estimation of the isotopes. The difficulties of the problem are further accentuated by the following complexities. (i) By a property of the nuclear spin, the diatomic homonuclear molecules of these isotopes are each capable of existence in two forms, ortho and para. (ii) Interisotopic molecules, HD, HT, and DT, may be formed by the combination of the isotopes

$$H_2 + D_2 \rightleftharpoons 2HD$$

$$H_2 + T_2 \rightleftharpoons 2HT$$

$$D_2 + T_2 \rightleftharpoons 2DT$$
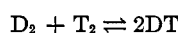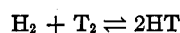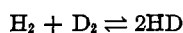
Apart from the interest in the separation of these molecular species per se, their existence often complicates the procedures for the detection and quantitative estimation of the isotopes in a mixture (see section III). It is appropriate, therefore, to take note of some relevant thermodynamic and kinetic considerations.

There seems to be some confusion regarding the nomenclature of the various forms of hydrogen, especially in respect to the interisotopic molecular species HD, HT, and DT. Hereafter, the term hydrogen will be used to denote the composite gas containing the various isotopes in natural proportions. As will be seen from the text of the review, the properties of protium have invariably been investigated with hydrogen, without purification from the heavier isotopes inherently present in the gas in trace quantities. However, the conclusions are unmistakably meant for the protium isotope only. HD will be referred to as protium deuteride, HT as protium tritide, and DT as deuterium tritide.
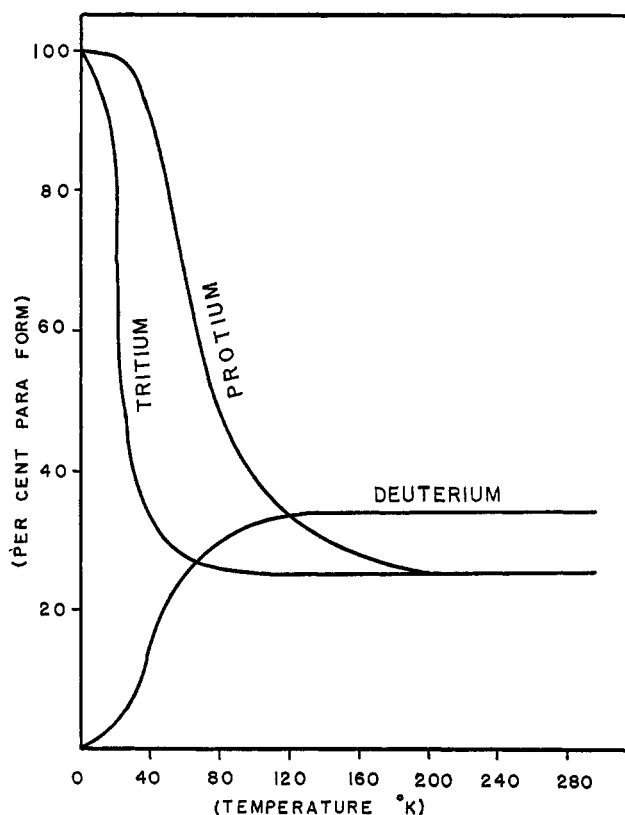

Fig. 1.—Equilibrium distribution of protium, deuterium, and tritium molecules in ortho and para states as a function of temperature.

B. SPIN ISOMERS—ORTHO AND PARA FORMS

The equilibrium proportions of the ortho and para forms of the three isotopes of hydrogen are functions of temperature. At low temperatures, para is the favored form for protium and tritium, but in the case of deuterium the equilibrium shifts in favor of the ortho form at these temperatures. At absolute zero, equilibrated protium and tritium consist of 100% para form each, whereas deuterium consists of 100% ortho form. As the temperature is raised, a limiting equilibrium proportion of 25% para and 75% ortho is reached in protium and tritium, the corresponding limiting proportion of the isomers in deuterium at infinite temperatures being 66.6% ortho and 33.3% para. It may be noted from Fig. 1 that although the limiting equilibrium proportions of ortho and para forms in protium and tritium are the same, the limit is approached at a far lower temperature in the case of tritium than in the case of protium (36, 45, 46).

Thus, it would appear that essentially pure paraprotium, orthodeuterium, and paratritium may be obtained by equilibrating the respective isotopes at near absolute zero temperatures. However, these interisomeric conversions are activated processes and, except in the case of tritium, the rates of spontaneous interconversions are extremely slow. No noticeable change,

for example, was observed in the composition of a sample of orthodeuterium even after 2–3 months when stored in clean vessels at room temperature (31). At higher temperatures, 600–750°, the interconversions proceed at measurable rates in protium and deuterium (28, 31), the order of the reaction being $^3/_2$. At the other end of the temperature scale, Cremer and Polanyi (21) studied the ortho–para transformation in protium in the condensed states. The ortho–para change in liquid protium has a conversion rate of 1% per hour at 100% orthoprotium (2), and this rate is nearly independent of temperature in the range 14–20 °K. The reaction is second order. The rate is somewhat greater in the solid state, and here again, it is independent of temperature in the range 4–12 °K. Even so, after a storage time of 145 hr., samples of solid protium were found to consist of only 75% para form against the equilibrium requirement of over 99%. The corresponding experimental studies on the spontaneous homogeneous para–ortho conversion of deuterium in liquid and solid phases do not appear to have been reported, but the theoretical studies of Motizuki (65) indicate an extremely small rate, 0.01% per hour, for para–orthodeuterium conversion in the solid state. The spontaneous ortho–para conversion of tritium in the solid phase has recently been investigated by Albers, Harteck, and Reeves (1) who report an unexpectedly fast rate (half-lifetime, 17 min.) for the conversion. Further, a measurable rate of homogeneous gas phase ortho–paratritium conversion, apparently not catalyzed by the walls of the reaction cell or by any paramagnetic impurity (e.g., O_2), was observed at 27 °K.

The processes of isomeric interconversions to equilibrium proportions may be expedited by paramagnetic substances, e.g., O_2, NO in homogeneous gaseous phase, Mn^{+2}, Fe^{+2} in solution, and charcoal or oxides of iron or chromium in the adsorbed phase. The mechanism (99) of these catalyzed interconversions is, of course, entirely different from that for the spontaneous homogeneous interconversions in gas phase discussed below. As for the slow apparently noncatalyzed conversion of ortho- to paraprotium in the condensed states, it has been suggested that it may be caused by the small magnetic moment of the ortho molecules (59).

C. THE INTERISOTOPIC MOLECULES

Table I contains the calculated values of equilibrium constants for the interisotopic exchange reactions of
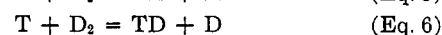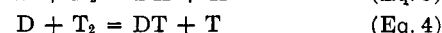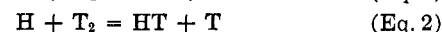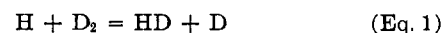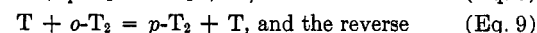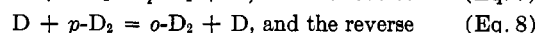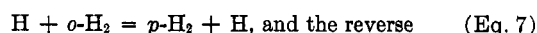
protium, deuterium, and tritium (93). The experimental values, where determined, agree reasonably well with these values (31, 58).

The formation of HD, HT, and DT from the parent molecules is, like the isomeric interconversions, each an activated process and proceeds at measurable rates only at higher temperatures. It has been suggested (26) that the formation of HD, HT, and DT and the isomeric interconversions proceed by similar mechanisms which may be represented by the following scheme: first there is dissociation of H_2, D_2, and T_2 into atoms followed either (a) by the formation of HD, HT, and DT according to the reactions

$$H + D_2 = HD + D \qquad \text{(Eq. 1)}$$
$$H + T_2 = HT + T \qquad \text{(Eq. 2)}$$
$$D + H_2 = DH + H \qquad \text{(Eq. 3)}$$
$$D + T_2 = DT + T \qquad \text{(Eq. 4)}$$
$$T + H_2 = TH + H \qquad \text{(Eq. 5)}$$
$$T + D_2 = TD + D \qquad \text{(Eq. 6)}$$

or (b) by isomeric interconversions according to the reactions.

$$H + o\text{-}H_2 = p\text{-}H_2 + H, \text{ and the reverse} \qquad \text{(Eq. 7)}$$
$$D + p\text{-}D_2 = o\text{-}D_2 + D, \text{ and the reverse} \qquad \text{(Eq. 8)}$$
$$T + o\text{-}T_2 = p\text{-}T_2 + T, \text{ and the reverse} \qquad \text{(Eq. 9)}$$

In a detailed formulation of the theory, reactions of the type

$$H + HD = H_2 + D \qquad \text{(Eq. 10)}$$
$$H + DH = HD + H \qquad \text{(Eq. 11)}$$
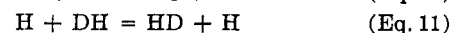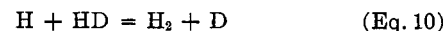
have also been taken into account. The calculated activation energies of the reactions 1 to 9 and of the reactions of type 10 and 11 are about 6–8 kcal. each. This agrees well with the experimental values where they have been determined (28, 31). It may be pointed out, inter alia, that the apparent activation energies for the interisomeric conversions and for the formation of HD, HT, and DT from the parent molecules, as calculated from the observed reaction rates at different temperatures, will also include half the heats of dissociation of H_2, D_2, and T_2 (about 51 kcal.), production of atoms being the first step in the total reaction.

In their very recent publication, Albers, Harteck, and Reeves (1) have shown that their observations on the ortho–paratritium conversion in the homogeneous gas phase at 27 °K. cannot be explained by this mechanism for reasons of energy considerations. The authors invoke the following ion chain mechanism to interpret their results.

$$T_2 \rightarrow T_2^+ + \bar{e} \qquad \text{(Eq. 12)}$$
$$T_2^+ + T_2 \rightarrow T_3^+ + T \qquad \text{(Eq. 13)}$$
$$T_3^+ + T_2 \text{ (ortho)} \rightarrow T_2 \text{ (para)} + T_3^+ \qquad \text{(Eq. 14)}$$
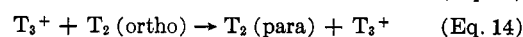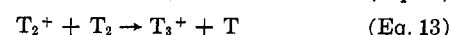
T_3^+ thus acts as the chain carrier. The T_2^+ ions are of course formed by the ionizing radiations from tritium,

TABLE I
INTERISOTOPIC EQUILIBRIA FOR HYDROGEN

Expression	K values[a]					
	0°	273.1°	298.1°	400°	500°	600°
$[HD]^2/[H_2][D_2]$	0	3.18	3.25	3.48	3.62	3.72
$[HT]^2/[H_2][T_2]$	0	2.42	2.56	2.97	3.24	3.44
$[DT]^2/[D_2][T_2]$	0	3.79	3.82	3.88	3.92	3.94

[a] Temperature in °K.

but reactions 13 and 14 must be postulated to proceed with zero heat of activation.

The interisotopic exchange reactions leading to the formation of HD, HT, and DT from their parent molecules are catalyzed, in general, by the metals effective in hydrogenation catalysis. The exchange reactions involving tritium are also catalyzed by the β-radiations from that isotope. The interaction $H_2 + D_2 \rightleftharpoons 2HD$ may be initiated, correspondingly, by an external flux of ionizing radiations (91).

An ordinary sample of hydrogen may, thus, be considered as a mixture of the following components: o-H_2, p-H_2, o-D_2, p-D_2, o-T_2, p-T_2, HD, HT, and DT. The slow rates of spontaneous ortho–para conversions and of the interisotopic combination is fortuitous, for, in view of this circumstance, the mixture may in the course of an analytical process be subjected to required variations of temperature without significantly affecting the original proportions of the various components *provided all contact with materials that catalyze any of the equilibrium processes is scrupulously avoided.*

III. METHODS OF DETECTION

A. THERMAL CONDUCTIVITY

A brief appraisal of only such methods for detecting and estimating the isotopes of hydrogen and their spin isomers will be given here as are principally employed in desorptive separation and chromatographic experiments with these gases. By far the most versatile method for the detection and estimation of the various forms of hydrogen is the one based on the differences in the heat conductivities of gases. If a piece of platinum wire, sealed inside a closed vessel, be supplied with a constant current and the vessel filled with different gases under standardized experimental conditions, the equilibrium temperature of the wire will be determined by the nature of the gas in the vessel. The temperature of the wire may be followed easily by measuring its resistance and, thus, if the vessel is filled successively with mixtures of different compositions of a two-component gaseous system, it should be possible to draw a calibration curve between the composition of the binary mixture and the resistance of the wire. The exact composition of an unknown gas mixture of the same components may then be determined empirically. Known as the thermoconductivity method, the classical technique developed by Bonhoeffer and Harteck (8) and improved to work with very small quantities of gas mixtures by Farkas (29) still remains the universally used method for the estimation of the composition of a mixture of ortho- and parahydrogen. Samples of hydrogen equilibrated at different temperatures and therefore of known ortho–para composition are used to obtain points for the calibration curve. Since the maximum concentration of orthohydrogen usually attain-

able is 75%, direct calibration of the cell above this value of orthohydrogen is not feasible. However, the error involved in extrapolation of the calibration curve, which is a straight line between 0 and 75% orthohydrogen, is believed to be less than 1% (23). Farkas (30) extended the method to estimate deuterium in gaseous admixture with protium. Inasmuch as mixtures of deuterium and protium will consist of o-D_2, p-D_2, o-H_2, p-H_2, and, possibly, HD, the experimental conditions have to be so arranged that (a) the ratios of o-D_2 to p-D_2 and of o-H_2 to p-H_2 in all the protium–deuterium mixtures used to obtain the calibration curve and in the unknown protium-deuterium mixture are the same; (b) HD is either absent altogether from all the mixtures or, if present, it is always in thermodynamic equilibrium with H_2 and D_2. In the former case, the calibration curve is a straight line and in the latter, concave towards the axis representing the composition of the gas mixtures.

For a review of the earlier work on thermoconductivity cells, the reader is referred to Farkas' monograph (32). A notable recent development in the design of thermoconductivity cells is the use of thermistors instead of wires of platinum or tungsten as the sensing device. Thermistors have a far larger temperature coefficient of resistance (albeit, with a negative sign) than wires of platinum or tungsten and, therefore, cells mounted with thermistors are far more sensitive to small changes in the composition of the gas mixtures as compared to the cells fitted with platinum or tungsten wires. Besides, the use of thermistors eliminates the chances of changes in the composition of the gas mixture due to exchange reactions of the type $H_2 + D_2 \rightleftharpoons 2HD$ during the process of measurement, since these reactions are catalyzed by heated wires of platinum or tungsten but not by thermistors.

Bucur, Mercea, and Mercea (11) have reported a modified experimental procedure for the use of thermoconductivity cells in isotope analysis in order to secure greater sensitivity of detection. By their method, as little as 10^{-9} part of deuterium in protium–deuterium mixtures are claimed to have been detected.

As used in the flow system employed for gas chromatography, the thermal conductivity detector is a double cell device known as a katharometer. One cell is connected to the exit end of the chromatographic column (sample cell) and the other cell to a regulated stream of pure carrier gas (reference cell). The two cells are placed in two arms of a Wheatstone bridge which is then zeroed to the flow of pure carrier gas through both the cells. The subsequent arrival of an eluted component in the sample cell causes an unbalance of the bridge, the magnitude of which is traced on a moving chart in terms of millivolts against time through a standard automatic recorder. The chromatogram so obtained consists of a series of peaks, one for each

eluted component, on one side of a steady base line which represents the flow of pure carrier gas in between the elution of the components. Under consistent experimental conditions, the time after sample introduction required for the emergence of a component through the chromatographic column, called the retention time, is a characteristic constant for the component and may be determined independently by introducing a dose of the pure component separately. The identity of the substance represented by each of the peaks in a chromatogram may thus be found out. The chromatogram may also be used for quantitative estimation of the components since the area of each peak is proportional to the amount of the component it represents.[1] The use of thermistors as the sensing elements in katharometers has been investigated by several workers (19, 66, 90, 95) and, indeed, thermistor katharometers are now available commercially. The conditions of maximum sensitivity for a katharometer must be determined empirically for each different carrier gas (19). The problem of noise in thermal conductivity detectors has been examined by Kieselbach (51) and measures to improve signal to noise ratio investigated.

In elution chromatography of the isotopes and isomers of hydrogen, the gas stream from the column is led into the katharometer either directly or through a heated (450–750°) copper oxide furnace (62). In the latter procedure, the eluted components are oxidized before entering the katharometer which is maintained at a temperature of 100° or higher to prevent condensation of the moisture. The detector is more sensitive to the oxides of protium and deuterium than to the isotopes themselves. Chromatograms obtained by this method have been used satisfactorily by several workers (34, 43, 94) for quantitative estimation of H_2, HD, and D_2.

B. MASS SPECTROSCOPY

An accurate method for the estimation of H_2, HD, and D_2 in a mixture is that of mass spectroscopy. First used in the analysis of protium–deuterium mixtures by Bleakney (7), it has often been employed (39, 43) to check the results derived from thermal conductivity measurements. The details of this technique may be found in standard text books on experimental physics.

(1) There is a reservation to this statement. It has been shown (57) that the thermal conductivity of mixtures of protium and helium is anomalous at certain gas concentrations. Consequently, if helium is being used as the carrier gas, the response of a katharometer to the elution of protium can be interpreted quantitatively only if the quantity of protium is within certain limits which will depend upon the rate of flow of the carrier gas, volume of the katharometer cell, column temperature, adsorbent, and column length. Measurements in this laboratory (85) indicate, for example, that the response of a thermistor katharometer (cell volume, ca. 2 ml.) was linear towards protium between 0–2.5 ml. (NTP) when the rate of flow of helium was 130–140 ml. per min.; column length, 8 ft.; adsorbent, Fe_2O_3–Al_2O_3; and column temperature, 77°K. The theory and significance of elution peaks obtained with gas chromatographic apparatus employing thermal conductivity detectors have been studied by Barsky (3).

C. RADIOACTIVITY

Although katharometers have been used for the detection of tritium (52, 75) in elution chromatography, this isotope of hydrogen is usually detected and estimated by methods based on its radioactivity. These methods permit a far lower concentration of tritium to be detected than is possible by thermal conductivity gages. Extremely sensitive static methods capable of detecting as little as a few parts of tritium in gaseous admixture with 10^{16} parts of hydrogen have been reported by Ostlund (71) and by von Buttlar and Stahl (12). These workers employed large size Geiger counters filled internally with the gas mixture to be assayed for tritium. Since the electrons emitted by tritium in radioactive decay have very low energy [$E_{max} = 18$ kev.] (40) and cannot pass through the walls of a counter, the isotope has to be present in the counting gas itself. Alternatively, the sample of hydrogen containing tritium may be converted into some suitable liquid, e.g., benzene, by a series of chemical reactions, and the tritium content of the liquid may then be estimated by a scintillation counter (87). However, not all these methods, howsoever admirably suited for static measurement of tritium in a sample of hydrogen, can be adopted for flow systems. The following devices have been used for detecting and estimating tritium in gas streams from chromatographic columns in the analysis of the isotopes of hydrogen: (1) ionization chambers, (2) proportional or Geiger counters.

Wilzbach, Van Dyken, and Kaplan (100) investigated the use of ionization chambers with a vibrating reed electrometer for the static determination of tritium. The technique was later adopted for the detection of tritium in the chromatographic analysis of tritium–protium mixtures by Gant and Yang (35) and by Carter and Smith (82). The ionization chamber is provided with entrance and exit holes for the gas stream and a high resistance ($\sim 10^{10}$ ohms) leak is installed between the input terminal and the feed-back line of the electrometer so that when the carrier gas has freed the chamber of the radioactive material, the charge on the probe bleeds through the leak and the system returns to the fixed background ionization current.

When tritium is estimated by proportional or Geiger counters, the gas stream is made to flow internally through the counter rather than around it. This imposes a limitation on the choice of the carrier gas in that it should also be a good counter gas. Fortunately, helium, the gas most extensively used for eluting isotopic mixtures of hydrogen through chromatographic columns, is a good counter gas if mixed with some suitable quencher, e.g., ethanol vapor or methane. The quencher is incorporated into the gas stream immediately before it enters the counter. It has been found (84) that hydrogen also behaves as a satisfactory counter

gas if bubbled through a mixture of benzene, ethanol, and toluene (equal volumes) prior to entry of the gas into the chamber. The counter is used in conjunction with a scaler, a pulse integrator, and an electronic recorder so that the elution of tritium is ultimately traced on a chromatogram in terms of millivolts against time (14). The technique was first developed by Wolfgang and Rowland (101) to detect and estimate tritium-labeled compounds in effluent gas streams from chromatographic columns.

The minimum level of tritium concentration detectable either by ionization chambers or by proportional or Geiger counters is, of course, not as small for flow systems as for corresponding static measurements. The parameter of importance in this connection is the total time of residence of the radioactive material in the active volume of the detector and this, in turn, will be determined by the volume of the detector and the rate of flow of the carrier gas. Since the detector is fed by the gas stream from a chromatographic column, neither the size of the detector nor the rate of flow of the carrier gas can be decided upon to the exclusive advantage of the detection system; too large a detector or too small a rate of flow of the carrier gas will prevent the resolution of the nearby peaks on the chromatogram.

IV. SEPARATION AND ANALYSIS OF SPIN ISOMERS

A. ORTHO–PARAPROTIUM

The separation of orthoprotium from paraprotium is of peculiar interest in that although pure paraprotium may be obtained readily simply by cooling normal protium (25% para, 75% ortho) to an appropriately low temperature on a suitable contact catalyst, it is not possible to obtain pure orthoprotium by simple equilibration; as has already been noted, the maximum equilibrium proportion of orthoprotium attainable is 75%. Pure orthoprotium can therefore only be obtained by separation from paraprotium.

1. Adsorption Experiments

From their studies on parahydrogen and mixtures of ortho- and parahydrogen (the heavier isotopes of hydrogen had not yet been discovered), Bonhoeffer and Harteck (8) showed that parahydrogen has a higher vapor pressure than orthohydrogen. This led Ubbelohde (92) to suggest that the average deformability of orthohydrogen along the different axes should be greater than that of parahydrogen, so that an adsorbent like charcoal should show greater adsorption for orthohydrogen than for parahydrogen. Furthermore, if the polarizability of the molecule is different along different axes, the more firmly bound molecules may no longer possess enough rotational energy to be able to complete a rotation and that this, in turn, may be expected to give rise to differences in the properties of the two spin iso-

mers in the adsorbed state. Ubbelohde tested the conclusions experimentally with the hydrogen–charcoal system at 90°K. It was observed that freshly evaporated gas from charcoal contains more orthohydrogen than the equilibrium mixture, indicating that orthohydrogen is adsorbed more than parahydrogen. Cremer (22) obtained evidence for similar preferential adsorption of orthohydrogen on silica at 20°K; after the adsorption equilibrium was established, the main fraction of the adsorbed gas was pumped out, after which the last fraction showed an enrichment of orthohydrogen. Later Sandler (77) confirmed the observation with titanium dioxide and charcoal adsorbents at 90 and 77°K., respectively.

A significant advance was made by Cunningham, Chapin, and Johnston (23) in 1958 when they not only proved a similar preferential adsorption of orthoprotium on γ-alumina at 20°K, but successfully separated practically pure o-H$_2$ from normal hydrogen by fractional desorption. Despite the subsequent development of the elegant chromatographic technique, Johnston's method still remains about the best practical way for obtaining pure o-H$_2$ in relatively large quantities. The apparatus consisted essentially of two concentric cylindrical copper containers of which the inner one, charged with γ-alumina, was wound on the outside with an electrical heating element. The apparatus was immersed in liquid hydrogen and normal hydrogen was allowed to flow through the adsorbent at a pressure of 50 mm. until the composition of the exit gas (in respect of ortho–para concentration) was constant. The flow of the gas was then stopped and the system evacuated for half a minute (to remove the gas contained in the dead space) following which the alumina was heated rapidly and fractions of the desorbed gas were collected in separate vessels at 1-min. intervals. An analysis of the fractions so collected showed that orthoprotium of over 90% purity could be obtained by collecting the gas desorbed between appropriate intervals of time. By using a three-stage apparatus wherein the desorbed gas from the first chamber was led through the second and the third chambers successively before fractions were finally collected, the authors obtained orthoprotium of over 99% purity.

The use of alumina had a definite advantage over the adsorbents used by earlier workers in that alumina is not a good catalyst for ortho–parahydrogen conversion. Such a high degree of separation cannot, evidently, be expected if the adsorbent has a significant catalytic activity in ortho–para interconversion. It is important that too high a pressure of hydrogen should not be used to saturate the adsorbent in these experiments, for the separation factor[2] for ortho- and parahydrogen on γ-alumina at 20°K. is dependent on surface cover-

(2) Defined as the ratio of the relative concentrations of ortho- and parahydrogen in the adsorbed and the bulk phases.

age (98) which in turn is determined by the equilibrium pressure of hydrogen. It is believed that the separation is greatest in the first molecular layer of the adsorbed gas; hence the use of 50 mm. pressure by Cunningham, Chapin, and Johnston in their experiments, at which pressure their adsorption measurements indicated the formation of the first adsorbed molecular layer.

2. Gas Chromatography

Concurrently with the work of Johnston and his co-workers, Moore and Ward (62) developed a method of elution chromatography for the separation of ortho-protium from paraprotium, using appropriately activated alumina columns at 77°K. with helium as the carrier gas. The homogeneity of the separated components was demonstrated by rechromatographing them individually when only one peak was obtained from each and, under standardized conditions, the individual retention times were reproduced. From observations with samples of protium of known ortho-para composition, obtained by equilibration at different temperatures, the authors further proved that no irreversible adsorption is involved during the passage of hydrogen through the column at 77°K. and that the method can be employed for quantitative estimation of the ortho and para components in a sample of hydrogen. Linde Molecular Sieve 13X has been shown to be an equally effective column material (2, 9) under the experimental conditions employed with alumina. It has further been noted that the total time of analysis with this material is appreciably reduced if the molecular sieve column is heated in a stream of CO_2 before the usual activation in a current of helium (2).

It is of paramount importance that the column materials used in chromatographic separation of ortho- from paraprotium be absolutely free from any paramagnetic impurity capable of rapidly catalyzing equilibration of the spin isomers, for otherwise no separation of the components will be achieved. It is known (2) that even trace contamination of molecular sieves with iron kills the efficacy of the column prepared with this material. Similarly, alumina contaminated with oxides of iron are known to be ineffective in separating ortho- from paraprotium.

In order to obtain pure ortho- or paraprotium free from the carrier gas (helium), Bachman, Bechtold, and Cremer (2) collected the appropriate fraction from the elution stream on a separate column, also packed with Molecular Sieve 13X and maintained at 77°K. The column was subsequently pumped out for 1 min. at the end of which time 60% of the original content of hydrogen was found still left on the adsorbent, but no trace of helium was detectable in the desorbed gas.

B. ORTHO–PARADEUTERIUM

Efforts to resolve the parallel problem of separating pure paradeuterium from normal deuterium by meth-ods analogous to those employed successfully in separating the protium counterparts met with less conspicuous success. Working with their two-stage apparatus, Cunningham, Chapin, and Johnston (23) obtained a maximum concentration of 76.7% paradeuterium. The magnitude of ortho–para separation factor over γ-alumina at 20°K. is far smaller for deuterium than for protium (98), and in order to obtain 100% para-deuterium by this method an apparatus with an appropriately larger number of stages will have to be employed.

Moore and Ward (62) tried to separate paradeuterium from orthodeuterium by elution chromatography under the conditions employed in successful resolution of orthoprotium from paraprotium, described earlier. Only partial resolution was obtained. In a later publication (63), the authors have stated, parenthetically, that virtually complete resolution of orthodeuterium from paradeuterium was accomplished at 65°K. (on an alumina column). The best published chromatogram showing completely resolved peaks for the spin isomers of deuterium is that of Mohnke and Saffert (61) obtained with a capillary column coated internally with a thin layer of silica. A more detailed consideration of the technique developed by these workers appears in a later section. With their 80-m. long column, Mohnke and Saffert were able to obtain the resolution at 77°K. Contrary to the order of elution with protium, orthodeuterium is eluted before paradeuterium indicating that, as in the case of protium, the molecules in the rotational state $J = 1$ are more strongly adsorbed.

The resolution of the spin isomers of tritium by fractional desorption or by chromatography does not appear to have been reported.

A proposed theory of ortho–para separation by adsorption at low temperatures has been formulated by White and Lassettre (97) and in the earlier publication of Sandler (77).

V. SEPARATION AND ANALYSIS OF ISOTOPES

The various solids that have been employed to obtain separation of the isotopes of hydrogen may be grouped as follows: (a) charcoal, silica gel, alumina, molecular sieves; (b) metallic palladium.

The classification is fundamental in that the principles involved in separation with palladium are different from those involved in separation with the solids of group a. In palladium, hydrogen dissolves, atomically, and separation of the isotopes is caused by differences in their solubilities; a chromatographic column packed with metallic palladium acts as a partition column (89). On the other hand, separation on a powder of group a at low temperatures is effected by differences in the adsorbabilities of the isotopes. From the point of view of analytical refinement, greater strides have been made with the use of the materials of
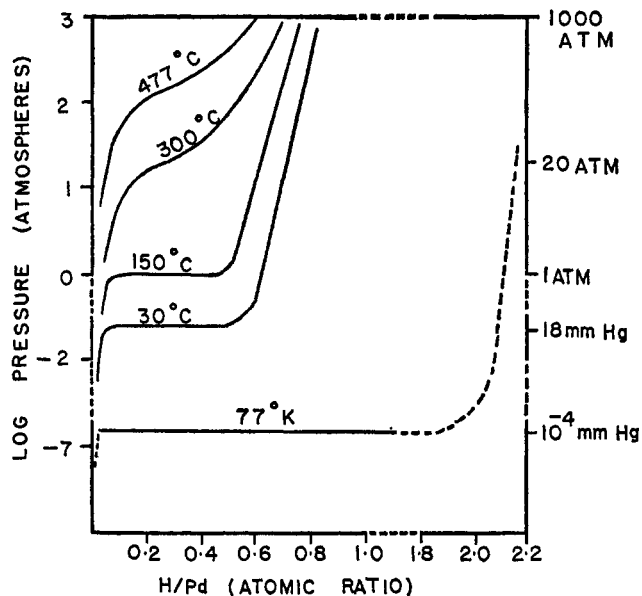
Fig. 2.—Distribution isotherms for the protium–palladium system.

type a, and the more recent developments relate almost exclusively to the use of alumina and molecular sieves. However, for large-scale separations the methods based on the use of palladium appear to be advantageous in as much as far larger quantities of gases can be handled with relatively small palladium-packed columns. Furthermore, since palladium catalyzes the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$ and $H_2 + T_2 \rightleftharpoons 2HT$, a three-component system as of H_2, HD, and D_2 is resolved by palladium into pure H_2 and D_2. The full potential of palladium still remains to be thoroughly investigated, to date work with this material being confined to the separation of H–D and H–T mixtures containing the heavier isotopes in appreciable proportions. The investigations involving palladium will be considered first so that a continuity of discussion may later be maintained with respect to the resolution of D–T and H–D–T mixtures in addition to H–D and H–T mixtures on alumina and molecular sieves.

A. PALLADIUM ABSORBENTS

Pressure–concentration–temperature relationships of Pd–H_2 and Pd–D_2 systems have recently been reinvestigated by several workers (54, 67, 72, 86). The results confirm the isotherms obtained earlier by Bruning and Sieverts (10) and by Gillespie and Downs (37) and extend the range of observation on the higher and lower sides of temperature and pressure scales. The available data are summarized in Fig. 2 and 3. Under comparable conditions of temperature and pressure, the absorption of deuterium is always less than that of protium. The absorption of protium and deuterium by palladium involves exothermic processes, the heat of absorption measured at 30° being about 1 kcal./mole
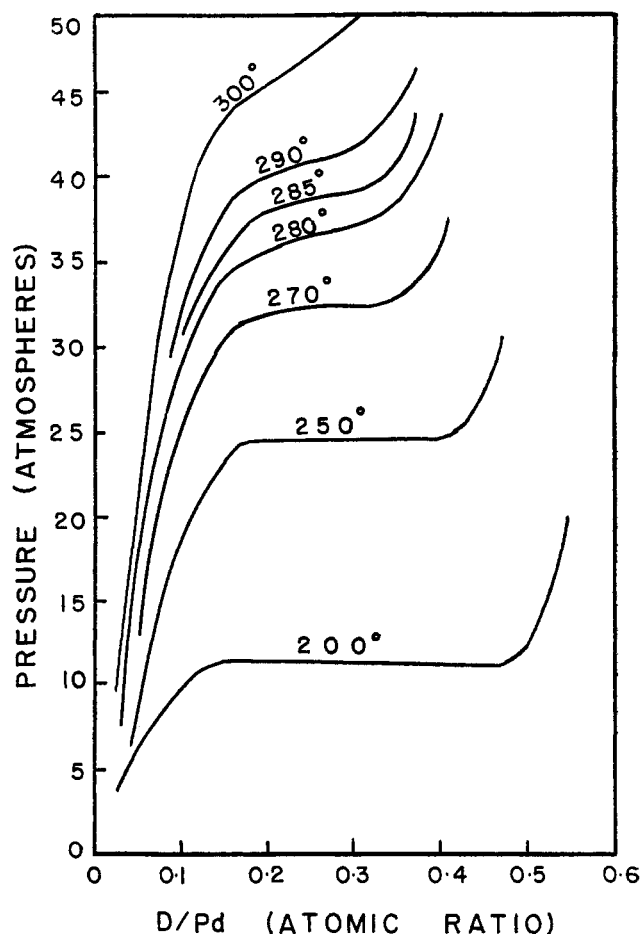

Fig. 3.—Distribution isotherms for the deuterium–palladium system.

higher for protium (9.5 kcal./mole vs. 8.5 kcal./mole). The difference in the absorption of protium and deuterium by palladium is more clearly brought out by a consideration of the absorption isobars (Fig. 4). The ratios H:Pd and D:Pd, each under a pressure of 1 atm., may be read directly from the figure for any temperature within the scale (55).

The physical constant of prime interest in connection with the separation of H–D mixtures by palladium is the separation factor which must be different from unity for successful resolution of the isotopes. The magnitude of separation factor at different temperatures has been determined by several different techniques and the results are summarized in Fig. 5 (89). It will be seen that both the equilibrium separation factor and the nonequilibrium separation factor as determined by break-through technique and elution experiments are different from unity. The separation factor is larger at lower temperatures and at 25° was found to be independent of the composition of the gas mixture in the range of deuterium concentration from 0.01 to 0.99 mole fraction (39). Since the process of gas chromatography with palladium as the fixed phase consists essentially of a series of absorption–desorption steps, it is
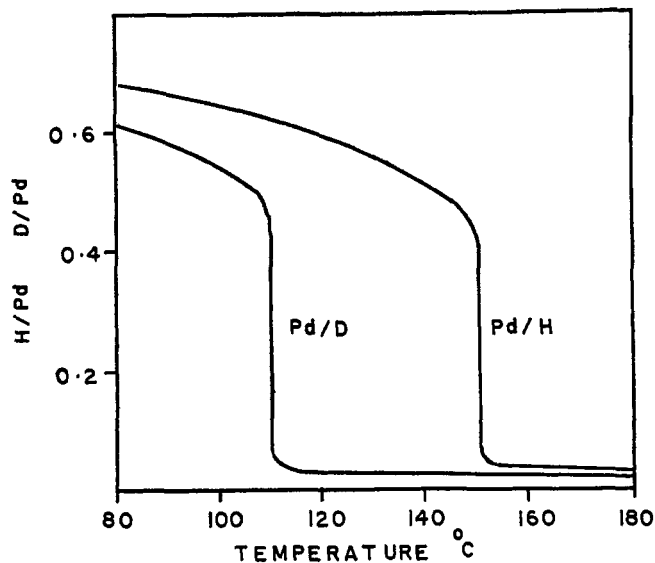
Fig. 4.—Comparison of absorption by palladium of protium and deuterium under a pressure of 1 atm. as a function of temperature.

Fig. 5.—Temperature dependence of deuterium–protium separation factor in a chromatographic column with palladium as the fixed phase.

relevant to note that a comparison of the absorption and desorption isotherms of hydrogen on palladium, obtained under conditions of equilibrium, indicates the existence of hysteresis loops (78, 80).

Protium–deuterium mixtures have been successfully separated on palladium columns (38, 39, 89) by the following techniques: (i) breakthrough chromatography, (ii) displacement chromatography (by adding pure H_2 to the column), (iii) self-displacement chromatography (by heating the column), (iv) elution chromatography (using argon as carrier gas).

In the break-through technique only one of the components, deuterium, is obtained in the pure state and only a portion of the total mixture is separated. These disadvantages disappear if the technique of displacement by hydrogen is employed. However, a small amount of deuterium is retained by the palladium column even after the displacement of the isotope apparently seems to be complete. The extent of this irreversible absorption was estimated (39) to be 1–2% when mixtures containing 40 volume % of deuterium were separated by displacement chromatography, presumably around room temperature. It should be possible to reduce the magnitude of this irreversible absorption by raising the temperature of the chromatographic column, but this will cause a decrease in the value of the separation factor and the efficiency of resolution will thus suffer. When the displacement chromatography was performed (89) at 80–85°, the intermediate mixed band of D_2 + HD + H_2 was correspondingly larger.

For the separation of large quantities, 16 l., of protium–deuterium mixtures, Glueckauf and Kitt (39) employed the technique of self-displacement where the palladium column, after it was charged with the mix-
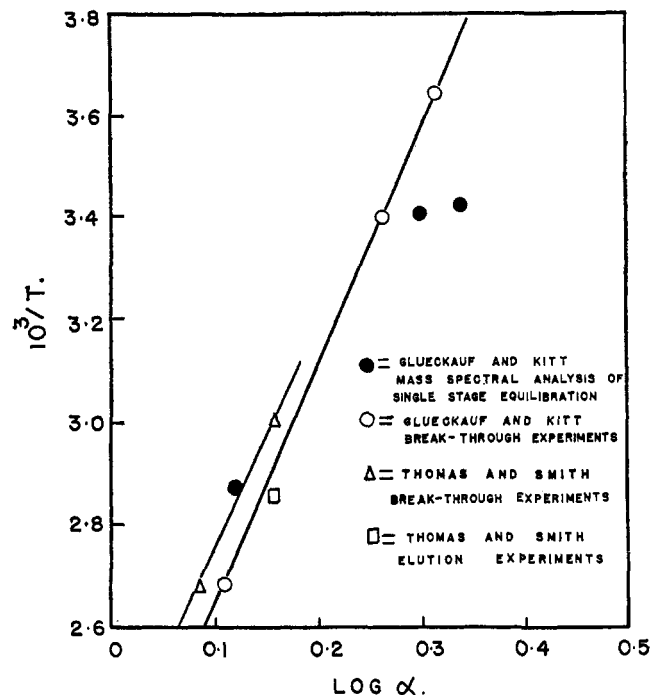
ture, was heated progressively from the entrance end to the exit end, thus forcing fractions of pure D_2 and pure H_2 out of the column.

Thomas and Smith (89) obtained partial resolution of protium–deuterium mixtures on a palladium column, 43 ft. long, by the technique of elution chromatography. Argon was used as the carrier gas and the column was maintained at a temperature of 175–180°. The technique is essentially of interest as an analytical method since only small doses of about 4 ml. of mixture can be chromatographed at a time.

Most of these experiments were done with protium–deuterium mixtures containing 40–50% by volume of the heavier isotope. Glueckauf and Kitt (39) reported resolution of a mixture containing a small proportion, 1.85 volume %, of deuterium by displacement chromatography. Despite the technological interest of the proposition, separation of protium–deuterium mixtures containing trace quantities of deuterium does not appear to have been attempted on palladium columns. Nor are experimental data for the values of separation factors at these concentrations of deuterium available.

The highest purity of deuterium obtained by the use of a palladium column is reported to be 99.5% (39). Since the separation factor is known to suffer a steep decline in the region of deuterium concentration of >99%, it may not prove possible to obtain 100% pure deuterium by these methods.

Although precise measurements of absorption isotherms for tritium–palladium system are not avail-

able, it is possible to state qualitatively that palladium absorbs protium more avidly than tritium. This knowledge was put to practical use by Salmon (76) to enrich the tritium content of protium–tritium mixtures by absorption–desorption cycles over a bed of finely divided palladium. The metal charged with a gas mixture containing a small proportion (presumably about 2%) of tritium was gradually heated, and the desorbed gas was collected in two fractions of approximately equal volumes. An analysis of the two fractions showed an enrichment of tritium in the earlier fraction (4.01% T) as compared to the later one (1.49% T).

Chadwick (18) separated mixtures of protium–tritium on a palladium column by displacement chromatography at room temperature. Hydrogen was used as the displacing gas. The palladium column, after thorough evacuation, was charged with 2 l. of the gas mixture and a slow stream of pure hydrogen, 3 l./hr., was then made to flow through the column. T_2 was eluted first, followed by a mixed band of T_2 + HT + H_2 and, finally, pure H_2. Up to 99% pure T_2 was obtained by the method in one operation from a mixture containing 16% of tritium.

Smith and Carter (82) attempted separation of protium–tritium mixtures by elution chromatography on the 43-ft. long Pd–quartz column which had been used earlier, with partial success, to separate protium–deuterium mixtures. Argon was used as the carrier gas and the column was maintained at a temperature of 150–175°. The protium–tritium mixtures used had tritium concentration at tracer level (10^{-4} mole fraction). No tritium activity was detected in the gas stream from the column even after prolonged passage of the carrier gas. When the temperature of the column was raised to 300°, a small amount of activity was detected in the exit gas, but there was no resolution of the components. A similar effort (84) to resolve protium–tritium mixtures on a column of $Pt–Al_2O_3$ by elution chromatography, using helium carrier, was also unsuccessful.

B. NONMETALLIC ADSORBENTS

In this section will be discussed the separation of the isotopes of hydrogen with charcoal, silica gel, alumina, and molecular sieves, the materials of group a in the classification outlined previously. The separation of the isotopes with these powders has been studied by the techniques both of desorptive enrichment and gas chromatography. The published data on the protium–deuterium system is far more extensive than on the systems involving tritium.

It may be stated most generally that on all of these powders deuterium is adsorbed preferentially to protium and, wherever evidence exists, tritium is adsorbed preferentially to both deuterium and protium. The contrast in this respect between the relative behavior of the isotopes in the process of adsorption on these powders on one hand and absorption in metallic palladium on the other may be noted. As was pointed out earlier, the lighter isotope is absorbed preferentially by palladium.

1. Protium–Deuterium System

Adsorption equilibria for pure protium, pure deuterium, and protium–deuterium mixtures on charcoal, silica gel, and Molecular Sieves 4A, 5A, and 13X at low temperatures (75–90°K.) have been investigated recently by Basmadjian (4). Together with the earlier data of Van Dingenen and Van Itterbeek (24) and of Melkonian and Reps (60) at lower temperatures and pressures, the results indicate that (1) the preferential adsorption of deuterium is observed on these powders at all temperatures between 20–90°K. and at all pressures in the range 10^{-5}–750 mm.; (2) the lower the temperature and pressure, the more marked the preferential adsorption of deuterium and, consequently, the larger the value of the separation factor; (3) under conditions of equilibrium, the magnitude of the separation factor is independent of the relative concentrations of the isotopes in the mixtures (4) (see below for observations under conditions of nonequilibrium).

Even before these adsorption equilibria had been studied experimentally, Eyring (27) had pointed out from a consideration of the differences in the zero-point energies of these isotopes that an enrichment of the heavier isotope by fractional desorption may be a practical possibility. Taylor, Gould, and Bleakney (88) tested the prediction by attempting enrichment of deuterium in ordinary hydrogen by desorption from charcoal. A sample of activated charcoal was charged with hydrogen, containing HD and D_2 in concentrations of the order of 10^{-4} mole fraction, to an equilibrium pressure of about 55 mm. at liquid air temperature. The charcoal was then pumped out for several hours during which fractions of the displaced gases were collected over appropriate intervals of time. Finally, the residual gas was desorbed rapidly by raising the temperature of the charcoal to obtain the end fraction. An analysis of the various fractions for HD and D_2 showed that there had been selective desorption of H_2 during the pumping operation, leading to an enrichment of the heavier molecules in the residual gas; the enrichment of the two molecular species HD and D_2 in the end fraction was found to be 2.2-fold and 4.3-fold, respectively. Peters and Lohmar (73) repeated the experiment with a starting mixture containing 18% HD and 1% D_2. Their final fraction consisted of 93.5% HD and 6.5% D_2 and was, thus, free from detectable protium. It will be noted that in these experiments desorption proceeds under conditions of nonequilibrium and of progressively diminishing coverage of the adsorbent surface as the pumping advances. Under

such circumstances, the value of the separation factor may be changing continuously, which fact will not be apparent from a consideration of only the initial and final data on the distribution of the isotopes. Edse and Harteck (25) made a detailed study of the changes in the value of the separation factor during the course of desorption of protium–deuterium mixtures from charcoal at 65°K. and from silica gel at 49, 52, 53, and 55°K. Since part of their objective was to determine the conditions under which maximum values for the separation factor may be obtained, these researches were conducted at very low coverages of the adsorbent surfaces (pressures of the order of 10^{-3} mm.). The isotopic mixture employed in the work contained, originally, around 50% deuterium. The separation factor on charcoal at 65°K. decreased from 5 to 2 as the desorption progressed. Studies with silica gel at the four different temperatures and with different charges of the gas mixture indicated that the separation factor is extremely sensitive to coverage, as will be seen from Table II which has been compiled from the published

TABLE II

SEPARATION FACTORS ACCOMPANYING DESORPTION OF PROTIUM–DEUTERIUM MIXTURES

Temp., °K.	Gas charge, cc./g. of silica gel	Range of value of separation factor	
		Initial	Final
49	1	40	10
52	2	30	8.5
53	4.5	6	4
55	2	20	7.5

curves of Edse and Harteck. Here, too, monotonous decrease in the value of the separation factor was consistently noted as the desorption progressed, despite the consequent decreasing coverage. These measurements under conditions of nonequilibrium are in contradistinction to observations under equilibrium conditions where the values of separation factor are always larger for lower coverages. Later when Harteck and Melkonian (41) studied the values of the separation factor on silica gel at 20°K. at similarly low coverages (10^{-4}–10^{-5} mm.), values of separation factor up to 140 were obtained. An important significance of these observations seems to be that a precise statement of the experimental conditions is called for in reporting values of separation factors. For obvious reasons, these high values of the separation factor cannot be put to any practical use for the separation of deuterium from natural hydrogen.

Fractional desorption by pumping with the adsorbent at liquid air temperature is an exceedingly time-consuming process, the total time of desorption reported by Taylor, Gould, and Bleakney (88), for example, being 50 hr. An alternative method for fractional desorption will be to raise the temperature of the adsorbent and to collect the evolved gases over suitably selected intervals of time. This will cut down appre-

ciably the total time required for an experiment. Keier and Roginskii (50) obtained practically pure fractions of deuterium by desorption from charcoal by the latter method, the isotopic mixture having been adsorbed on charcoal at liquid air temperature. Similarly, White and Haubach (96) fractionated deuterium from protium by desorption from γ-alumina, employing the apparatus and the technique developed earlier by Cunningham, Chapin, and Johnston to separate ortho- from parahydrogen (see section IVA1). A mixture of H_2 and D_2 was passed through the adsorbent, maintained at 20°K., to an equilibrium pressure of 50 mm., and, after a brief evacuation of the system, the alumina was heated rapidly and fractions of the desorbed gases were collected at 1-min. intervals. Fractionation was continued for 10 min. and a maximum concentration of 97% deuterium was noted in the final collection when the original feed gas contained 62% of the isotope. The efficiency of enrichment can obviously be improved by employing a multistage adsorption–desorption set-up. The procedure for enrichment of deuterium by low temperature gas adsorption reported by Ohkoshi, Tenma, Fujita, and Kwan (70) and the method of self-displacement chromatography of the isotopes of hydrogen described by Phillips, Owens, and Hamlin (74) are, in effect, applications of the multistage adsorption–desorption principle. Mixtures of protium and deuterium were introduced into columns packed with Molecular Sieve 5A and maintained at $-196°$. The gases were then made to travel through the column either by maintaining the exit end at a reduced pressure (70) or by heating the column progressively from the entrance end to the outlet by gradually lowering the liquid nitrogen container surrounding the column (74). An analysis of the outflowing gases showed that, as in the single stage enrichment by desorption, the first gas to arrive at the exit was a band of pure protium, followed by a protium-deuterium mixture in which the concentration of deuterium kept increasing progressively until, finally, a band of pure deuterium was evolved.

It will be noted that enrichment by desorption involves inescapably an intermediate band of mixed isotopes and, therefore, a quantitative separation of the components cannot be accomplished by this technique. The accumulated knowledge in respect to the differences in the adsorbabilities of the isotopes indicated, however, that one or more of the adsorbents discussed above might produce absolute separation of the isotopes by elution chromatography. The period from 1957 onwards has been one of simultaneous activity in this connection in many laboratories all over the world and, at times, success came independently in different places. Since this relates to a development of the relatively recent past, an effort has been made in the following discussion to take note of the priority of

publication and, where the published date of receipt of a paper so indicates, of independent success in research.

The first reported success in resolving a mixture of protium, protium deuteride, and deuterium came to Ohkoshi, Fujita, and Kwan (68) in 1958. The resolution was obtained on a column of Molecular Sieve 5A, 80 × 0.3 cm., at −196°. Cylinder hydrogen was employed as the carrier gas and, therefore, no peak for protium appeared on the chromatogram. The feasibility of alumina in separating (62) the spin isomers of protium by elution chromatography with helium carrier had already been demonstrated at the time and the possibility of separating the isotopes of hydrogen by elution chromatography on alumina was, as may be judged from the publications appearing in the following months, being investigated simultaneously in at least four laboratories, namely, University of Tokyo, Japan (Kwan), Johns Hopkins, U. S. A. (Emmett), Massachusetts Institute of Technology, U. S. A. (Moore and Ward), and the University of Tennessee, U. S. A. (Smith). If the isotopes could be resolved with alumina under the impressed flow of helium, or some other inert gas, separate peaks for H_2, HD, and D_2 in the chromatogram would provide estimates for each of the three molecular species. The chief difficulty lay, however, in the fact that alumina columns, under the usual low temperature experimental conditions, also resolved para- from orthoprotium, and since the separation factor of the latter isomer from HD is close to unity, the peaks for orthoprotium and HD overlapped. This could be prevented if the resolution of the spin isomers of protium could be suppressed without affecting the resolution of the isotopes. Smith and Hunt (81) did this by coating alumina with chromia, a paramagnetic substance which prevented resolution of the para- from orthoprotium by rapid equilibration of the isomers, and thus realized the first complete analysis of H_2, HD, and D_2 in clearly resolved peaks for each of the three. The separation was obtained on a 21-ft. long column of the chromia-coated alumina at 77°K. with neon carrier, and analyses of known mixtures showed that each component could be determined within 0.5–1.0% accuracy. Subsequently, Moore and Ward (63) accomplished the same objective by coating alumina with ferric oxide. On a 365 × 0.5 cm. column of the material at 77°K., resolution of H_2, HD, and D_2 was obtained with helium carrier. It was also observed that columns of strongly heated alumina (480°, 8 hr.), apparently iron free, lead to ortho–para equilibration, and satisfactory resolution of H_2, HD, and D_2 may be realized on such columns. In the meantime, Van Hook and Emmett (43) published a graphical method of calculating quantitative estimates of H_2, HD, and D_2 from the chromatogram obtained with alumina columns, with the usual overlapping of the

peaks for orthoprotium and protium deuteride. The combined peak for $o\text{-}H_2$ and HD was resolved empirically for the two components, and the results were found to be in agreement with those obtained by mass spectroscopic analysis of the gas samples, provided the proportion of HD in the mixtures was not below about 40%. Finally, Furuyama and Kwan (34) reported a method for obtaining separate peaks corresponding to $p\text{-}H_2$, $o\text{-}H_2$, HD, and D_2 on one chromatogram. Two columns were employed in series, the first one containing alumina and the second alumina coated with ferric oxide. Helium was used as the carrier gas. A mixture of H_2, HD, and D_2 was resolved by the first column into $p\text{-}H_2$, $o\text{-}H_2$ + HD, and D_2. The paraprotium separated by the first column underwent ortho–para equilibration during passage through the second column but emerged finally as one peak which represented the paraprotium content of the original mixture in the sample volume. Orthoprotium, likewise, underwent equilibration during passage through the second column and, concurrently with the process, the equilibrated protium was separated from HD. D_2 passed unaffected through the second column so that the four peaks ultimately traced on the chromatogram represented quantitatively the $p\text{-}H_2$, $o\text{-}H_2$, HD, and D_2 in the sample volume of the isotopic mixture analyzed.

Over a period of time, other column materials have been tested (9, 44), optimum conditions of activation and the influence of changes in other parameters (column length, rate of flow of the carrier gas) on the efficacy of resolution investigated (9, 79), and the reproducibility and quantitative accuracy of the analytical technique checked (33, 69, 94). The main features of these researches are summarized in Table III which also includes a summary of the corresponding data on the analysis of protium–tritium and protium–deuterium–tritium systems by elution gas chromatography. The interested reader is referred, in this connection, especially to the intensive investigations of Botter, de la Perriere, and Tistchenko (9) with several different adsorbents. These workers also made a comparative study of the values of separation factors for the various molecular species of hydrogen from each other as deduced from chromatograms on one hand and the values obtained by direct measurement with a static method on the other. Tables of values for separation factors derived from chromatograms have also been published by Carter and Smith (15) and by Mohnke and Saffert (61).

An interesting refinement of technique was reported by Mohnke and Saffert (61) who accomplished resolution of protium–deuterium mixtures with capillary columns. The method of column preparation was ingenious. A glass capillary was filled with a solution of aqueous ammonia, sealed at both ends and heated at 170° for 70 hr. The seals were then broken, and the

TABLE III

EFFICACY OF PACKING MATERIALS IN THE SEPARATION OF THE ISOTOPES OF HYDROGEN BY ELUTION GAS–SOLID CHROMATOGRAPHY[a]

Adsorbent	Carrier gas	Efficacy of isotope separation	Ref.	Remarks
Al_2O_3 (moderately activated)	H_2	Good: H, D	43	No peak for H_2
	He	Partial: H, D	9, 43	Empirical method for resolving the combined peak for (o-H_2 + HD) proposed
	Ne, He	Good: H, D	17	Capillary column used
		Good: H, D, T	75	
Al_2O_3 (strongly activated)	H_2	Good: H, D, T	15	No peak for H_2
	He	Good: H, D	63, 94	
		Good: H, T	14, 82	
		Good: H, D, T	15	
Cr_2O_3–Al_2O_3	He, Ne	Good: H, D	44	
		Good: H, T	82	
Fe_2O_3–Al_2O_3	He	Good: H, D	34, 63, 79	
		Good: H, T	82	
		Good: H, D, T	15, 52	
Molecular Sieves 5A, 13X with and without Fe_2O_3 additive	H_2	Good: H, D	9, 68	No peak for H_2
	He, Ne	Good: H, D	9	
		Good: H, T	35	Resolution temp. $-160°$ (boiling methane)
Silica gel	H_2	Good: H, D	44	No peak for H_2
		Good: H, T	82	No peak for H_2
	He, Ne	Isotopes not eluted at 77°K.	44	Partial resolution of H, D at $-160°$
	Ne	Good: H, D	61	Capillary column Separate peaks for p-H_2, o-H_2, HD, o-D_2, and p-D_2
Charcoal	H_2	Isotopes eluted but no resolution	9, 44, 84	Only one peak obtained
	He	Isotopes not eluted at 77°K.	9, 84	(See the discussion in section VB2)
Zeolon-H (diam. ~4 Å.)	He	Isotopes not eluted at 77°K.	83	At higher temperatures isotopes eluted but no resolution

[a] The resolution temperature is 77°K. unless otherwise stated. The notation H, D means the three component mixture H_2–HD–D_2; *mutatis mutandis*, H, T and D, T. The notation H, D, T stands for the six-component mixture H_2–HD–HT–D_2–DT–T_2.

residual liquid was removed by blowing compressed air through the capillary while its temperature was slowly raised to 190°; a layer of SiO_2, estimated to be 20 μ thick, was thus deposited on the inner walls of the bore. An 80-m. long column of glass capillary so treated resolved protium–deuterium mixtures into five fully separate peaks for paraprotium, orthoprotium, protium deuteride, orthodeuterium, and paradeuterium—eluted in that order. The resolution temperature was 77°K. and the carrier gas was neon. Cercy, Tistchenko, and Botter (16, 17) investigated the separation of protium-deuterium mixtures on capillary columns packed with finely divided alumina; at 77°K., the mixture was resolved into three peaks corresponding to H_2, HD, and D_2 on a column of Pyrex capillary, 18 m. $\times$ 0.4 mm. packed with alumina of 100–120 μ particle size. How-

ever, the spin isomers of protium and deuterium were not resolved. Exceedingly small quantities, a few mm.[3] only, of gas mixtures are required in these capillary gas chromatography experiments. In the work with packed capillary columns, the higher head pressure required to maintain the flow of carrier gas necessitates the use of a metallic apparatus.

Study of the problems associated with the separation of protium–deuterium mixtures by differential adsorption *on a technical scale* appears to have received only modest attention. An experimental investigation of interest in this connection has recently been reported by Basmadjian (5) who examined the concentration profile of H_2–D_2 mixtures in a moving bed adsorber, the adsorbent being charcoal at the temperature of liquid air. The powder was made to travel down a vertical column maintained at 86°K. and the situation, as obtaining in the steady state, may be described as follows. On entering the adsorber column, the charcoal was first saturated with protium which was then displaced, increasingly, by deuterium as the powder moved downward. The concentration of the heavier isotope rose to a maximum of about 30% toward the lower end of the column, where the charcoal was met by a rising stream of nitrogen which stripped the powder of adsorbed protium and deuterium. The gases so displaced traveled upward while the adsorbent, now charged with nitrogen, moved out of the cold column to be stripped, in turn, of the adsorbed nitrogen by passage through a heated tube; the charcoal thereafter was ready for recirculation. Under the experimental conditions employed, the displacement of protium and deuterium by nitrogen was noted to be complete in the lower 2 in. of the cold column, and no contamination of nitrogen above that zone was detectable. A measured amount of deuterium had been introduced into the column initially and after the attainment of equilibrium, samples of gases from different heights of the adsorber column were withdrawn for analysis. The experiments were conducted at a pressure of 1 atm. and the diameter of the adsorber column was 1.5 in.; the concentration profiles obtained with the set-up are claimed to corroborate the design equations for the adsorber derived by the author on certain assumptions.

2. Protium–Tritium System

In 1959, Gant and Yang (35) reported the separation of protium–protium tritide–tritium mixtures on a 6.1-m. long column of molecular sieves by elution chromatography. The resolution temperature was $-160°$ and helium was used as the carrier gas. The total tritium content of the mixtures analyzed was about 1%.

A comprehensive report on the analysis of protium–protium tritide–tritium mixtures by elution chromatography was presented by Smith and Carter (82) at the International Symposium on the Detection and

Uses of Tritium held at Vienna in 1961. Under appropriate experimental conditions, complete analysis of H_2–HT–T_2 mixtures was obtained on silica gel, chromia–alumina, ferric oxide–alumina, and alumina columns with hydrogen, neon, and helium carriers (refer to Table III). The concentrations of tritium in the isotopic mixtures employed in these investigations was of the order of 10^{-4} mole fraction which represents the order of concentration at which tritium is usually employed in tracer studies. In a later publication (14), analysis of mixtures containing much smaller mole fractions of total tritium was reported. A column of ferric oxide–alumina was employed in this work with helium as the carrier gas. The detection system for tritium consisted of a G.M. flow counter in conjunction with a pulse integrator and an electronic recorder. No visible peaks for HT and T_2 are obtained if mixtures of tritium concentrations lower than 10^{-10} mole fraction are analyzed. The limitation is probably imposed by the sensitivity of the detection method, for there seems to be no apparent reason why the column should not continue to resolve mixtures with still lower concentrations of tritium. Since, for practical reasons, it is not possible either to take significantly larger doses of the mixture or to allow longer residence time to the eluents in the counter (see section IIIC), it was decided (84) to look for a substance which would hold HT and T_2 fractions from a large number of repeat chromatographic analyses of standard doses of H_2–HT–T_2 mixtures containing total tritium in concentrations lower than 10^{-10} mole fraction, so that the HT and T_2 so stored could then be rechromatographed to determine the concentration of tritium in the original mixture. In order to be useful, the substance should conform to the following criteria.

(1) Under appropriate conditions, the substance should retain HT and T_2 quantitatively from the stream of the carrier gas (helium).

(2) If some particular condition were changed, it should give up HT and T_2 rapidly and quantitatively, so that the gases may be led into a chromatographic column as a plug.

(3) The substance must not react with HT and T_2 or affect the composition of the gases in any way.

Palladium black is known to remove HT and T_2 from a stream of argon or helium, and the isotopes are held very tenaciously by the metal. However, it is not practicable to recover HT and T_2 rapidly and quantitatively from the metal. Preliminary experiments indicated that activated charcoal conforms to all of the three criteria:

(i) At 77°K., a column of charcoal, 2 in. long, removes HT and T_2 quantitatively from a stream of helium, and no displacement of the isotopes is detectable when the flow of the carrier gas is maintained over reasonably extended periods, e.g., 4 hr.

(ii) If the liquid nitrogen bath surrounding the charcoal column is removed, the isotopes are desorbed rapidly and quantitatively in a plug, as could be judged from the quality of the chromatograms obtained by rechromatographing the evolved gases.

(iii) The composition of the adsorbed gases is not affected during contact with the charcoal. The peaks for HT and T_2 obtained by rechromatographing the desorbed gases are comparable, each to each, with the peaks obtained by chromatographing an equal dose of the original mixture under identical experimental conditions.

The tests were performed first with mixtures containing 10^{-10} mole fraction of tritium and then with a mixture containing 10^{-11} mole fraction of the isotope. In the case of the latter mixture, HT and T_2 from ten repeat analyses of standard doses were collected on the charcoal by directing the gas stream from the chromatographic column through the charcoal column, at predetermined time, after the elution of hydrogen was complete. The chromatogram obtained from this collection was comparable to the chromatogram obtained from one standard dose of the mixture containing 10^{-10} mole fraction of tritium. An automated chromatographic apparatus was then set up, and HT and T_2 from 100 repeat analyses of standard doses of a mixture containing 10^{-12} mole fraction of tritium were collected on charcoal. However, no peak for HT or T_2 was obtained when the evolved gases were rechromatographed. The nonappearance of the peaks for HT and T_2 may be due to either or both of the following reasons: (a) at these extremely low partial pressures of HT and T_2, the charcoal is no longer able to trap the gases quantitatively at 77°K.; (b) under the prolonged impressed flow of helium, the charcoal is not able to retain the gases at the temperature. It may be noted that helium had flowed through the charcoal for a total of 50 hr. while the isotopes from 100 repeat analyses of the mixture were being collected.

In either event, a more efficient performance may be expected from the charcoal if it be maintained at a lower temperature: HT and T_2 will be trapped more efficiently and retained more tenaciously. The possibility has not yet been investigated experimentally.

3. Protium–Deuterium–Tritium System

Analyses of mixtures containing all the three isotopes of hydrogen and their interisotopic molecular species have been reported independently by King (52) and by Carter and Smith (15). The most efficient resolution is realized on columns of ferric oxide–alumina at 77°K. with helium carrier. The order of elution of the components is as follows: H_2, HD, HT, D_2, DT, and, finally, T_2.

A composite detection system, consisting of a katharometer in series with an ionization chamber, enables

simultaneous detection of the nonradioactive components and the radioactive components, respectively, if the latter are present in concentrations too low to be detected by the katharometer. If the recorders connected to the katharometer and the electrometer are synchronized, the separate traces obtained from the two recorders may be combined to obtain a single chromatogram showing the positions of all the peaks.

The French group of workers at the Centre for Nuclear Studies, Saclay, have succeeded in resolving the multicomponent isotopic mixture under consideration on capillary columns packed with alumina (75). A copy of their chromatogram (unpublished), seems to indicate satisfactory resolution of the various components by their technique. Inasmuch as only a single detector, a katharometer, was used, the sensitivity had to be stepped up at selected points of time during the progress of the analysis to detect satisfactorily the arrival of the components present in small proportions.

From the data summarized in Table III it is not possible to formulate a theory that may enable a priori judgment on the likely efficacy of a hitherto untested material in the separation of the isotopes by elution chromatography. The ability to resolve the isotopes is a highly specific property of the adsorbent; Botter, de la Perriere, and Tistchenko (9) observed that samples of alumina obtained from different sources showed widely different efficacy of resolution. The remarkable tenacity with which the isotopes of hydrogen are adsorbed by silica gel, charcoal, and Zeolon-H at $-196°$ is to be noted; the isotopes cannot be eluted from these adsorbents by helium. The strength of the adsorptive bond, however, does not appear to be necessarily relevant to the resolvability of the isotopes, for no resolution is observed when the mixture is eluted from charcoal with hydrogen carrier.

In a series of publications (42, 47, 48, 96–98), Haubach, White, Lassettre, and their co-workers have developed a theory of hindered rotator for diatomic molecules adsorbed on a homogeneous surface to account for the separation of the isotopes of hydrogen and their spin isomers by adsorption and gas chromatography at low temperatures. Several of the known experimental facts may be inferred satisfactorily from the theory, namely, the order of elution of the molecular species, difficult separation of o-H_2 from HD, and increase in the values of the separation factors at lower temperatures. Quantitatively, however, the agreement between the experimental and the calculated values of separation factors are relatively modest (42, 97). The theory predicts that the separation factors of the homonuclear isotopes should be markedly dependent on their ortho–para composition, a prediction which may be amenable to experimental verification but does not appear to have been unequivocally (96) tested as yet.

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