the steps, 2-methyl-1-butynylmagnesium bromide, 2,5-dimethyl-3-hexyne-2-ol (86%) and 2-chloro-2,5-dimethyl-3-hexyne[19] (80%) to 2,2,5-trimethyl-3-hexyne (54%; overall, 20%).

2,2,5,5-Tetramethyl-3-hexyne.—This was prepared from pinacol through the steps, pinacolone,[31] 2,2-dichloro-3,3-dimethylbutane, 3,3-dimethyl-1-butyne[32,33] (from pinacol, 26%), 3,3-dimethyl-1-butynylmagnesium bromide, 2,5,5-trimethyl-3-hexyne-2-ol (83%), 2-chloro-2,5,5-trimethyl-3-hexyne[19] (89%), and 2,2,5,5-tetramethyl-3-hexyne (55%; from 3,3-dimethyl-1-butyne, 35%).

2-Heptyne.—This was prepared by methylation of 1-hexyne.[28,34]

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[31] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 462.

[32] P. Ivitzky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

[33] The subsequent steps are those of Hennion and Banigan.[29]

[34] (a) J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949); (b) G. F. Hennion and J. Pillar, *ibid.*, **72**, 5317 (1950).

PASADENA, CAL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

The Separation of Hydrogen and Deuterium by the Reaction of Iron with Steam

BY HILTON A. SMITH AND JOHN C. POSEY

RECEIVED SEPTEMBER 26, 1956

The separation of hydrogen and deuterium during the reaction of steam and iron was measured over the range of 118 to 340°. Separation factors from 1.4 to 3.2 were observed. The data were found to be correlated by the equation $\log \alpha = 273.1/T - 0.2039$ where α is the isotope separation factor and T is the absolute temperature. Isotope separation factors obtained with cadmium agreed within experimental error with those obtained with iron. The separation of hydrogen and deuterium occurring during the reduction of magnetic iron oxide was measured and found to approach the equilibrium value. This is believed to have been caused by isotope exchange catalyzed by the freshly reduced iron.

The separation of hydrogen isotopes as a result of the reaction of steam and metals has been observed by previous workers. Horiuti and Polanyi[1] observed that when iron reacted with an excess of steam at 500° the hydrogen which was produced contained a lower concentration of deuterium than the steam. A separation factor of 1.6 can be calculated from their data. Bleakney and Gould[2] investigated the same reaction at 510° and obtained data from which a separation factor of 1.3 can be calculated. Henderson[3] measured the separation factor for this reaction using freshly reduced iron over the range 200 to 400°. He obtained values from 1.60 to 1.42 which were in fair agreement with the values of the equilibrium separation factor and concluded that the separation was caused by isotope exchange between the steam and the hydrogen.

Horiuti and Szabo[4] measured the separation of these isotopes in the reaction of water vapor and sodium and found a separation factor of 2.2. Henderson and Bernstein[5] measured this separation in the reaction of steam and zinc over the range of 295 to 415°. The separation factor was found to be 1.6 at 400° and had a temperature gradient of −0.0011 per degree.

Eyring and Cagle[6] have calculated the separation of hydrogen and deuterium in the electrolytic process by means of the absolute rate theory assuming that the breaking of the hydrogen–deuterium bond is the rate-controlling step. They obtained the equation

$$\alpha = \frac{\sinh\,(h\nu_{\text{OH}}/2kT)}{\sinh\,(h\nu_{\text{OD}}/2kT)} \qquad (1)$$

For ordinary temperatures this may be simplified to

$$\alpha = e^{708/T} \qquad (2)$$

According to Fricke, Walter and Loher[7] steam reacts with iron to produce hydrogen and magnetic iron oxide, Fe_3O_4, at temperatures below 540–560°. At higher temperatures ferrous oxide is formed. All of the work reported in this paper fell in the lower temperature range.

Experimental

The steam-iron and steam-cadmium reactions were carried out in the apparatus shown in Fig. 1. The water flowed from the buret down into the reaction tube. It was volatilized in a heated trap at the top of the tube. From here it passed in the form of steam down through the heated bed of the powdered metal and down through a condenser and water collection flask. After this it passed through a glass wool packed cold trap which was immersed in a mixture of Dry Ice and acetone. This removed the last of the unreacted water from the hydrogen. The hydrogen then entered a tube containing copper oxide at a temperature in excess of 300° where it was oxidized quantitatively to water. This water was collected in a second cold trap.

The reaction tube was constructed of standard 3/4-inch copper tubing and standard brass flare fittings. All joints other than the flare joints were silver soldered. The condenser and the tube from the buret to the reaction tube were also made of copper. The rest of the system with the exception of the Bourdon gages was made of Pyrex glass. All glass parts were connected with ground glass joints lubricated with Apiezon M stopcock grease.

The reaction tube was heated in a furnace which consisted of a Pyrex tube wound with nichrome wire and insulated with glass wool held in place by asbestos tape. The temperature was controlled by means of a variable transformer. The temperature was measured by means of a potentiometer and a copper–constantan thermocouple located in a copper thermocouple well which projected up inside the reaction tube into the bed of powdered metal.

The iron powder was Merck Iron by Hydrogen. It had a surface area of 1.63 square meters per gram as determined by nitrogen adsorption using the B.E.T. method. The iron had 90.4% of the reducing capacity of pure iron as determined by the amount of hydrogen evolved in the reaction of a known weight of iron with hydrochloric acid.

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[1] J. Horiuti and M. Polanyi, *Nature*, **132**, 819 (1933).

[2] W. Bleakney and A. J. Gould, *Phys. Rev.*, **44**, 265 (1933).

[3] W. G. Henderson, Masters Thesis, Illinois Institue of Technology, Chicago, Illinois, 1954.

[4] J. Horiuti and A. L. Szabo, *Nature*, **133**, 327 (1934).

[5] W. G. Henderson and R. B. Bernstein, THIS JOURNAL, **76**, 5344 (1954).

[6] H. Eyring and F. W. Cagle, *J. Phys. Chem.*, **56**, 889 (1952).

[7] R. Fricke, K. Walter and W. Loher, *Z. Elektrochem.*, **47**, 487 (1941).

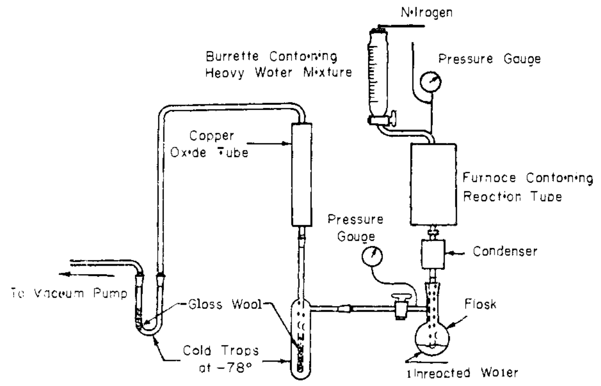

Fig. 1.—Apparatus for the reaction of steam and metals.

The cadmium was produced by the reaction of concentrated cadmium chloride solution with less than the stoichiometric equivalent of zinc dust. This reaction produced porous lumps of metal. After four hours reaction the metal was rinsed four times with distilled water and was stored under acetone. Before use this metal was reduced in place in the reaction tube by flowing hydrogen at 300°.

The reacting mixture of light and heavy water was produced by mixing 99.8% heavy water from the Stuart Oxygen Company with laboratory distilled water.

The following procedure was used in the reaction of steam and iron. The system was evacuated and filled with dry nitrogen while the metal sample was held at the reaction temperature. The cold traps were then immersed in the Dry Ice–acetone mixture. The isotopic water mixture was admitted by opening the stopcock on the buret. When the water hit the hot trap at the top of the reaction tube a sharp pressure increase occurred. When the pressure had fallen appreciably due to the passage of steam through the bed of powdered metal more water was admitted. At the end of the run the system was swept with dry nitrogen. This forced the last of the water through the reaction tube and carried the unreacted hydrogen into the copper oxide tube. The system was then evacuated to pull the last of the water into the second cold trap.

The average time of contact of the steam with the iron varied from 4.9 to 37 seconds. The shorter times occurred at the higher temperatures. The contact times of the steam with the cadmium were somewhat less due to the greater porosity of the beds of this material.

The iron used in all runs at temperatures above 134° was already partially oxidized by use in previous runs. This oxide film was desired to reduce the rate of reaction and to reduce the catalytic activity of the iron for the isotope exchange between the hydrogen gas and steam. It was not considered necessary to preoxidize the slower reacting cadmium.

The equipment used in the reduction of iron oxide by a hydrogen–deuterium mixture differed from that previously described in some respects. The buret was replaced by a gas cylinder with an ordinary diaphragm pressure regulator, a needle valve and an orifice flow meter for flow control and measurement. The second cold trap and the copper oxide tube were also greatly increased in size.

The mixture of hydrogen and deuterium gases was prepared by adding hydrogen to a cylinder containing 99.5% deuterium from the Stuart Oxygen Company. The deuterium content of the mixture was analytically determined to be 49.44%.

Iron oxide was prepared by treating the previously described iron powder with an excess of steam over a period of five hours while the temperature was increased slowly from 200 to 320°. It contained 13.4% magnetic iron oxide as calculated from the gain in weight. A single 59.6-g. sample of the material was used in all the reduction tests. It was not reoxidized between runs.

The falling drop method was used for the determination of the deuterium concentration. This method and the equipment have been described by Combs, Googin and Smith.[8] The maximum analytical error in this work is estimated to be 0.3 mole %. In most of the analyses the error was much less.

Results and Discussion

The separation factors for the reaction of steam and iron were calculated by means of eq. 3

$$\alpha \log\left(1 - \frac{MX}{M_0X_0}\right) = \log\left[1 - \frac{M(1 - X)}{M_0(1 - X_0)}\right] \quad (3)$$

where M_0 is the number of moles of water entering the reaction tube, M is the number of moles collected in the second cold trap, X_0 is the mole fraction of deuterium in the water before the reaction, and X is the mole fraction of deuterium in the water in the second cold trap. This equation assumes that the separation was due to different rates of production of hydrogen and deuterium.

The separation factors are presented in Fig. 2 as a function of the temperature. The data were correlated by eq. 4

$$\log \alpha = \frac{273.1}{T} - 0.2039 \quad (4)$$

or

$$\log \alpha = \frac{1250}{2.303RT} - 0.2039$$

where T is the temperature on the Kelvin scale. This equation was obtained by the application of the least mean squares method to the values of log α and $1/T$. All of the values obtained with iron at temperatures up to 281°, inclusive, and all of the values obtained with cadmium were used in this calculation.

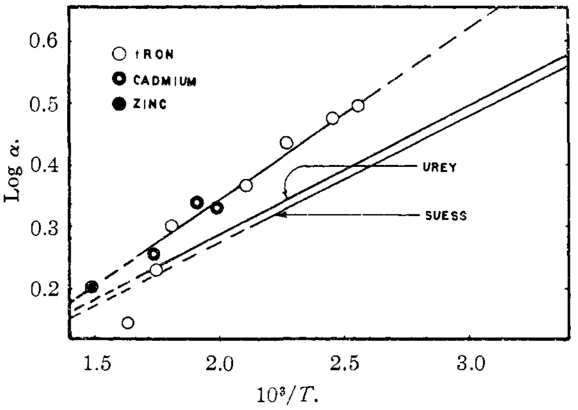

Fig. 2.—Separation factors as a function of temperature.

Similar plots of the equilibrium separation factor as calculated by Urey[9] and as measured by Suess[10] are shown on the figure. The calculated values are for low concentrations of deuterium. However, according to Suess the total variation of α with concentration does not exceed 3%. The values therefore should be comparable.

The separation factor obtained by Henderson and Bernstein[5] for the reaction of steam and zinc is also shown. They used deuterium concentrations of 0.864 and 1.049% as compared to the 50% deuterium concentration of the water used in this work. The excellent agreement of this value with the extrapolated data of this work and the agreement of the values obtained with cadmium with those obtained with iron suggest that the kinetic separation

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(8) R. L. Combs, J. M. Googin and H. A. Smith, *J. Phys. Chem.*, **58**, 1000 (1954).

(9) H. C. Urey, *J. Chem. Soc.*, 562 (1947).

(10) H. E. Suess, *Z. Naturforsch.*, **4A**, 328 (1949).

factor like the equilibrium separation factor is not greatly affected by the isotopic concentration and that the size of the separation factor may be the same for many different metals.

The separation factor of 2.2 obtained by Szabo and Horiuti[4] for the reaction of sodium and water vapor at 25° and the value of 5.2 obtained by extrapolation of the data of this work are not in agreement. The speed of the reaction involving sodium may have resulted in the selective removal of hydrogen from the water vapor at the metal surface at such a rate that the isotopic composition of this water differed appreciably from that of the bulk of the vapor. Local heating is also possible.

Except for the values obtained with iron at the two highest temperatures the effect of isotopic exchange is probably small. Hirota and Horiuchi[11] have shown that iron is a catalyst for the exchange of deuterium between hydrogen and water at temperatures as low as 100°. However the iron particles were covered with a layer of oxide in this work so that free metal was not exposed. The oxide is undoubtedly a less effective catalyst than pure iron. Evidence for this point will be presented under the reduction of iron oxide. This is also indicated by the work of Clark[12] who found that the activity of an iron oxide as a catalyst for the reaction

$$H_2 + D_2 \longrightarrow 2HD$$

was increased 64-fold by reduction of the iron oxide. The lack of appreciable exchange also is indicated by the agreement among the values obtained with zinc, cadmium and iron. As can be seen in Fig. 2 the values obtained with iron at 300 and 340° fall appreciably below the line of the rest of the data. This may be caused by isotope exchange. If the experimental separation factor at 340° is recalculated assuming that equilibrium existed, a value of 1.59 is obtained. This falls between the value of the equilibrium separation factor obtained by the extrapolation of the data of Suess[10] and the calculated value of Urey[9] at this temperature. Because of the probability of isotope exchange, agreement between the data obtained by other workers at higher temperatures and eq. 4 is not to be expected.

According to classical kinetic theory the value 1250 cal. in eq. 4 is the difference in the activation energies of the two isotopic species. This value is in fair agreement with similar values calculated from the data of other workers for the separation of hydrogen and deuterium in the electrolytic production of hydrogen from water. A value of 1210 cal. was calculated from the data which Walton and Wolfenden[13] obtained using a silver cathode over the range of 15 to 95°. The data obtained with a nickel cathode over the same temperature range by these workers gives a value of 974 cal. Okamoto[14] according to Rome and Hiskey[15] obtained a value of 1200 cal. with a nickel cathode. The equivalent value from the equation of Eyring and Cagle[6] is 1410 cal. All of the values were obtained with electrodes at which the reduction of hydrogen occurs by the mechanism called the "catalytic" mechanism by Horiuchi and Okamoto.[16] Rome and Hiskey[15] give a value of 140 cal. for "electrolytic" reduction mechanism at a mercury cathode.

Reduction of Iron Oxide.—The separation factors observed in the reduction of iron oxide by a mixture of hydrogen and deuterium are given in Table I. These values were calculated by eq. 6 which is based on the assumption that the separation was caused by the equilibrium distribution of deuterium between the two compounds.

$$\alpha = \frac{X/(1 - X) \quad \text{trap 1}}{X/(1 - X) \quad \text{trap 2}} \tag{6}$$

TABLE I

ISOTOPE SEPARATION OBSERVED IN THE REDUCTION OF MAGNETIC IRON OXIDE BY A MIXTURE OF HYDROGEN AND DEUTERIUM GASES

Temp., °C.	Contact time (sec.)	Separation factor	Temp., °C.	Contact time (sec.)	Separation factor
205	74	1.55	208	42	1.73
294	32	1.59	314	110	1.57
299	24	1.60	301	65	1.59
208	24	1.67	300	74	1.60
207[a]	20[a]	1.70[a]	296	10	1.59

[a] The gas was saturated with water vapor at room temperature before entering the reaction tube.

Here X is the mole fraction of deuterium in the sample. Values of α larger than unity mean that the deuterium tended to concentrate in the steam produced in the reaction. Also given are the contact times of the hydrogen–deuterium mixture with the contents of the reaction tube. At temperatures near 300° the separation factor remained nearly constant while at temperatures near 200° it increased from run to run. The factor causing this increase was important enough to outweigh a more than three-fold decrease in the contact time as can be seen by comparing the first run with the fourth, fifth and sixth runs. The addition of water to the hydrogen–deuterium gas mixture had no apparent effect on the separation. Also, the deuterium was found to be concentrated in the steam. This was not the expected result since the lighter isotope usually reacts more rapidly than the heavier one. These facts can be explained if it is assumed that the separation was caused by isotope exchange between the hydrogen and steam. It is probable that the steam as first produced contained less deuterium than the reacting gas. However, the freshly reduced iron catalyzed rapid isotope exchange so that the deuterium concentrations in the two compounds changed toward the equilibrium values. At temperatures near 300° the exchange was nearly complete so that the observed separation factors varied only slightly. At temperatures near 200° the rate of exchange increased from run to run as more metallic iron became available due to the progressive reduction of the iron oxide. This caused the exchange to proceed progressively further toward equilibrium.

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(11) K. Hirota and J. Horiuchi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **30**, 151 (1936).

(12) A. Clark, *Ind. Eng. Chem.*, **45**, 1476 (1953).

(13) H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

(14) G. Okamoto, *J. Sci. Hokkaido Imp. Univ.*, [III] **2**, 115 (1938).

(15) M. Rome and C. F. Hiskey, THIS JOURNAL, **76**, 5207 (1954).

(16) J. Horiuchi and G. Okamoto, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **28**, 231 (1936).

A value of 1.59 at 301° is obtained by averaging the separation factors and temperatures in the higher temperature range. This is a little lower than 1.67, the value obtained by extrapolating the data of Suess[9] to this temperature. Since the steam formed near the exit of the reaction tube remained in contact with the iron only a very short time, complete equilibrium would be unlikely.

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KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Solubility and Entropy of Solution of Argon in Five Selected Non-polar Solvents

BY L. W. REEVES AND J. H. HILDEBRAND

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The solubility of argon in five non-polar solvents with different solubility parameters has been measured over a sufficient temperature range to yield reliable values of the entropy of solution. The results for solubility in mole % and entropy of solution at 1 atm. and 25° are as follows: $C_6F_{11}CF_3$, 0.4600, −1.5; $C_6H_{11}CH_3$, 0.1855, −0.9; CCl_4, 0.134, −0.5; $C_6H_5CH_3$, 0.1095, +0.4; CS_2, 0.0487, +1.8. For the entropy of dissolving argon at 1 atm. and 25° into its solutions at the same mole %, 0.0100, the respective figures are 6.1, 4.8, 4.7, 5.15 and 5.0. They vary much more widely when calculated to equal volume concentration. The variation of solubility with temperature depends mainly upon the dilution necessary to balance the effects of intermolecular forces.

It is becoming increasingly evident that the considerable success of regular solution theory in accounting for equilibrium relationships in non-electrolyte solutions results from the fact that discrepancies between the actual entropy of solution and our expressions for it are more or less balanced by corresponding discrepancies for the enthalpy of solution. Our predictions of isothermal solubility are therefore much more reliable than those of its temperature dependence. The solubility of bromine in f-heptane, that we reported recently,[1] serves as a striking example. It is evident that there is still much to be learned about entropy of solution, and the work hereinafter described is directed to that end. We select solutions of gases in liquids instead of liquids in liquids because mixing liquids is equivalent to vaporizing one pure component, expanding the vapor and then condensing into the solution, where unknown factors involved in the first and third steps may partly cancel and thus escape attention. An additional advantage is that one may work with very dilute solutions, where solute–solute interaction is practically absent, and Henry's law is closely obeyed.

We have used solvents with a wide range of intermolecular forces, and we plan to extend the project to include the gases hydrogen, nitrogen, argon, carbon tetrafluoride and sulfur hexafluoride, in order to cover a range of molecular mass and size. Data from these laboratories for hydrogen and deuterium[2] are in press. We are also obtaining figures for partial molal volumes of the solute gases.

Materials.—Linde "Standard Grade" argon was found by spectroscopic analysis to be 99.9% pure. Since the main impurity was air, whose solubility is not very different from that of argon, it seemed unnecessary to try to correct for its presence. The f-methylcyclohexane was from the stock purified by Glew and Reeves.[3] "Spectro-grade" methylcyclohexane was passed through silica gel dried for several days at 250°. "Reagent Grade" carbon disulfide and carbon tetrachloride were shaken with mercury after standing over P_2O_5. All solvents were distilled in a vacuum-jacketed 15-plate column at a reflux ratio of 15:1. The densities at 25° and boiling points of the treated solvents were as follows: toluene, 0.8623, 110.60 ± 0.01°; carbon tetrachloride, 1.5845, 76.52 ± 0.05°; methylcyclohexane, 0 76505, 100.9 ± 0.05°; carbon disulfide, 1.2558, 46.41 ± 0.05°; f-methylcyclohexane, 1.7878, 76.14°.

Procedure.—The apparatus was that of Cook and Hanson,[4] with a few modifications. The gas is measured repeatedly at various pressures in a 20-cc. buret, and then admitted to the thoroughly degassed solvent, confined over mercury. The whole apparatus is then rocked by a motor-driven cam. After shaking for about 5 minutes, the residual gas is admitted to a secondary buret of about 1-cc. capacity with a calibrated capillary, where its volume and pressure are measured. The process is repeated until the amount of residual gas does not change. Changes in barometric pressure often occur more rapidly than the equilibrium can follow, therefore a manostat was used, consisting of a 12-liter bulb mounted in a thermostat controlled to 0.001°.

The temperature control of the original apparatus was replaced by a contact thermometer and relay box. The gas handling system of Cook and Hanson was replaced by a conventional all glass system.

Results.—The results are given in Table I, expressed as mole fraction of gas, x_2 in the solution at 1 atm. and a series of temperatures.

The data in Table I are plotted in Fig. 1 as log x_2 *vs.* log T. The slopes of these (slightly curved) lines at 298.15°K. plotted on large scale, multiplied by the gas constant, R, give the entropies of solution shown in Table II together with the smoothed out values of x_2 at 25°. The figures for CCl_4 at 25° are extrapolated. They are to be directly determined later.

Lannung[5] measured the solubility of argon in two non-polar solvents, cyclohexane and in benzene. His values recalculated as mole fraction are included in Table II for 25°, and plotted over his range of temperature in Fig. 1. The scatter of the points is such as to prevent calculation of the entropy of solution with the desired accuracy.

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[2] M. W. Cook, D. N. Hanson and B. J. Alder, *ibid.*, in press.

[3] D. N. Glew and L. W. Reeves, THIS JOURNAL, **60**, 615 (1956).

[4] (a) M. W. Cook and D. N. Hanson, *Rev. Sci. Instr.*, in press; (b) University of California Radiation Laboratory—2459 report (1954).

[5] A. Lannung, THIS JOURNAL, **52**, 68 (1930).