Time, minutes	16	18	19
% Conversion	81.0	93.1	93.1

Ethyl maleate was treated in a similar manner with boron fluoride in carbon tetrachloride, with boron fluoride-ether complex alone and with dry hydrogen bromide added, and with hydrogen bromide in carbon tetrachloride. In every case less than 1% of the ester was isomerized. The analyses were carried out as before.[8]

Summary

It has been found that boron fluoride readily converts cis-stilbene to the trans-isomer.

(8) Price and Thorpe, THIS JOURNAL, **60**, 2839 (1938).

Many compounds have in common the ability to catalyze the Friedel–Crafts type of reaction, the polymerization of olefins, the condensation of olefins with aromatic compounds and the cis-trans-isomerization of olefins. It is suggested that the common factor in these reactions is the electron-deficient nature of the catalyst and that such catalysts may associate with the electrons of the carbon–carbon double bond to give an active intermediate common to each reaction.

URBANA, ILLINOIS   RECEIVED MARCH 31, 1939

NOTES

Note on the Leakage of Helium through Pyrex Glass at Room Temperature. III

BY G. P. BAXTER

Some years ago an experiment was begun to measure the rate of leakage of helium through Pyrex glass at room temperature.[1] A sealed globe (1044 ml.) filled with helium originally under slightly less than average atmospheric pressure in this locality, 75 cm., was occasionally compared in weight with a very similar sealed globe, containing argon under a pressure somewhat above atmospheric, 79 mm. Over a period of three and one-half years the rate of loss was about 1% per year.

Recently, after over eleven years, when a reweighing of the globe was undertaken, a small crack was discovered in the argon globe. Since the argon was originally at a pressure above atmospheric, mechanical loss of argon would diminish, not increase, the loss in weight of the helium globe. In spite of the crack the helium globe was found to have lost a total of 17.8 mg., in a little over eleven years (4128 days), or over 10% of the original helium or 109 cm.[3] The over-all rate for the total period is 0.053 mm.[3] per day per cm.[2] of Pyrex glass of average thickness 1.34 mm. This is a slightly lower rate than that calculated from the first year's experience, 0.059 mm.[3] per day per cm.[2] but the greater part of this difference is accounted for by the diminishing helium content of the globe.[2]

(1) Baxter, Starkweather and Ellestad, Science, **68**, 516 (1928); Baxter and Starkweather, ibid., **73**, 618 (1931).

(2) Original weight of helium = 0.171 g. Erroneously given in ref. 1 as 0.168 g.

In the following table are given the leakage constants (years^{-1}) assuming the rate to be proportional to the pressure, for periods from one year to over eleven years, the actual losses in weight, and the losses calculated from the average leakage constant for the first three periods.[3] From the leakage constant and loss in weight for the total period it seems probable that the argon counterpoise was losing in weight owing to the crack, although in the recent weighing, which was continued over several weeks, the helium globe was still diminishing in weight by comparison.

Years	K, years^{-1}	Actual loss in wt., mg.	Calcd. loss in wt., mg.
1	0.0102	1.73	1.78
1.5	.0106	2.71	2.66
3.5	.0106	6.23	6.15
Av.	.0105		
11.3	.0097	17.8	19.1

(3) For a discussion of the mechanism of the leakage of helium through glass, see Urry, THIS JOURNAL, **54**, 3887 (1932). Urry's experimental data are not inconsistent with the above.

T. JEFFERSON COOLIDGE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.   RECEIVED MARCH 18, 1939

Isotopes of Potassium in Phosphate Rocks and Soils

BY A. KEITH BREWER

Taylor and Urey[1] have shown recently that in the base exchange of potassium in zeolites "the heavier isotope is taken up more readily and is more difficult to replace." Since base exchange regularly occurs in nature, isotope abundance

(1) I. W. Taylor and H. C. Urey, J. Chem. Phys., **6**, 429 (1938).

measurements should furnish an entirely new method of studying the mixing of potassium in soils and rocks. In order to determine the extent to which an isotope effect can be expected in nature, the base exchange method of isotope separation was applied to greensand.

The technique employed in these experiments was essentially the same as that described by Taylor and Urey, except that the 100-ft. (30-meter) column was replaced by a 4-in. (10-cm.) filtration funnel. By using a short column of greensand the "single stage" isotope effect is obtained; large effects resulting from the accumulative action taking place in a long column are not to be expected. In these tests a dilute solution of sodium chloride was allowed to trickle slowly through the greensand. From time to time a small quantity of the filtrate was collected and the isotope abundance ratio measured in the usual way.[2] No appreciable change was observed in the isotope ratio of the first potassium coming through in the filtrate, the ratio being $K^{39}/K^{41} = 14.20$; this is not surprising since the potassium content was high. After a moderate amount of washing in which the quantity of sodium in the solution used was three or four times the initial potassium in the greensand, abundance ratios of the order of $K^{39}/K^{41} = 14.00$ were obtained. Continued washing to the point where only minute quantities of potassium remained in the filtrate reduced the ratio to $K^{39}/K^{41} = 13.60$. Small deviations between samples were observed due to the non-uniformity of the greensand. The results showed clearly that K^{41} is more firmly held in the zeolite structure than is K^{39}; in consequence, isotope effects of the type described by Taylor and Urey should be expected to occur in nature under conditions where base exchange processes are operative.

A wide variety of soils and phosphate rocks has been investigated for a possible isotope effect. The samples were ground and sifted to 100 mesh. No chemical treatment was needed. The results obtained are presented in Table I.

Ten typical high phosphorus rocks from various deposits were tested; the ratio was the same in each instance. The fossil bone and tooth were from the Mulberry deposit in Florida. The soils tested are described in Department Bulletin No. 1311 and Technical Bulletin No. 484, United States Department of Agriculture.

(2) A. Keith Brewer, Ind. Eng. Chem., 30, 893 (1938).

TABLE I

Soils	K_2O, %	Na_2O, %	K^{39}/K^{41}
Porto Rico red clay	..	..	14.20
Stockton clay	2.15	1.24	14.20
Susquehanna sub	0.76	0.02	14.20
W. Va. rottenstone	..	..	14.20
W. Va. diatomaceous earth	..	..	14.24
W. Va. red clay	2.00	0.50	14.20
Marshall clay 213	2.60	1.10	14.20
Cecil B	0.23	0.08	14.30
Norfolk loam	.40	.21	14.22
Las Vegas A	..	..	14.20
Chester A	2.02	.47	14.19
Chester B	1.55	.19	14.18
Frederick colloid	1.22	..	14.20
Fullerton colloid	1.28	..	14.20
Miami colloid B	2.85	1.11	14.30
Hagerstown colloid	2.84	0.45	14.23
Florida silt	..	..	14.18
Greensand	..	..	14.20
Wyomingite	..	..	14.25
Ocean water	..	..	14.20
Phosphate rocks	0.2 app.	..	14.20
Fossil tooth	Low	..	14.20
Fossil bone	Low	..	14.20
Hawaiian basalt	..	..	14.11
Bone (fresh)	..	..	13.90

In view of the results mentioned above, it is evident that a soil in which the potassium has been largely replaced by base exchange should have low isotope ratio. An example of this type of action is found in a sample of Hawaiian basalt which had been exposed to ocean water. Again it should be expected that a soil normally low in potash which is acquiring potassium from some abundant source should have a high isotope ratio. This effect is illustrated in the Cecil B soil, where the relative abundance of K^{39} is enhanced by the subsoil acquiring potash from the topsoil leachings. Bone and tooth fossil show the normal isotope ratio of 14.20, although the ratio for fresh bones averages 13.90. It is evident that the initial potassium in the bones has been entirely replaced during the long aging processes.

The fact that the potassium isotope ratio is so nearly constant, although base exchange is continuously taking place, indicates that mixing is likewise continuous. In virtue of the ease with which small deviations in the abundance ratio can be produced in the laboratory, it is surprising that the values are so uniform. While it cannot be stated with certainty, an analysis of the data indicates that actual deviations do occur which could be estimated readily with a mass spectrograph having ten-fold the sensitivity of the one in use.

The writer is especially indebted to Mr. Donald L. Reed for making the isotope extractions with greensand.

BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.   RECEIVED MARCH 31, 1939

Hydrogen Bonding by Negatively Substituted CH Groups. VI. Acetylenic Compounds[1]

BY M. J. COPLEY AND C. E. HOLLEY, JR.

In a series of articles[2-5] the solubilities of several gaseous halogenated methanes (of the types CH_3X, CH_2X_2, CHX_3 and CX_4) in a number of donor solvents were reported. The extremely high solubilities (or large negative deviations from Raoult's law) observed for the halo-forms were accounted for on the basis that complexes are formed through the bonding of the hydrogen of the haloform to an exposed pair of electrons on an oxygen or nitrogen atom present in the solvent. New evidence for the existence of complexes of this type was observed recently by Buswell, Rodebush and Roy[6] while studying the infrared absorption spectra of solutions in carbon tetrachloride of chloroform with an ether, a ketone, or an amine.

Since the presence of the highly electronegative halogen atoms on the carbon atom of a haloform activates the hydrogen and makes it available for coördination, it is logical to suspect that other strongly negative groups attached to a CH radical will lead to the same behavior on the part of the hydrogen. Among the compounds in which such CH groups occur are the acetylenes (1-alkynes), the derivatives of formic acid, the triarylmethanes, molecules containing an active methylene group, etc.

In Table I the mole fraction solubilities of acetylene at a partial pressure of one atmosphere are compared with the theoretical mole fractions calculated from Raoult's law. The observed mole

(1) Original manuscript received July 11, 1938.
(2) G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).
(3) Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).
(4) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666 (1938).
(5) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2714 (1938).
(6) Buswell, Rodebush and Roy, *ibid.*, **60**, 2528 (1938). See also Gordy, *ibid.*, **60**, 605 (1938).

fractions are calculated from data in the "International Critical Tables," Vol. III, p. 269, and in an article by James.[7] There exists a close parallelism between the observed order of solubilities and the order[3,4] observed for chloroform or monofluorodichloromethane in similar types of solvents. Solubilities are greatly in excess of those predicted by Raoult's law in the ethers, esters, and ketones; solubilities are much less than the theoretical in solvents containing an active hydrogen (ethyl alcohol and acetic acid) where the solvent molecules are already associated by means of the more stable O–H–O bonds; no enhancement of solubility is obtained in aromatic compounds when the donor atom is attached to the benzene
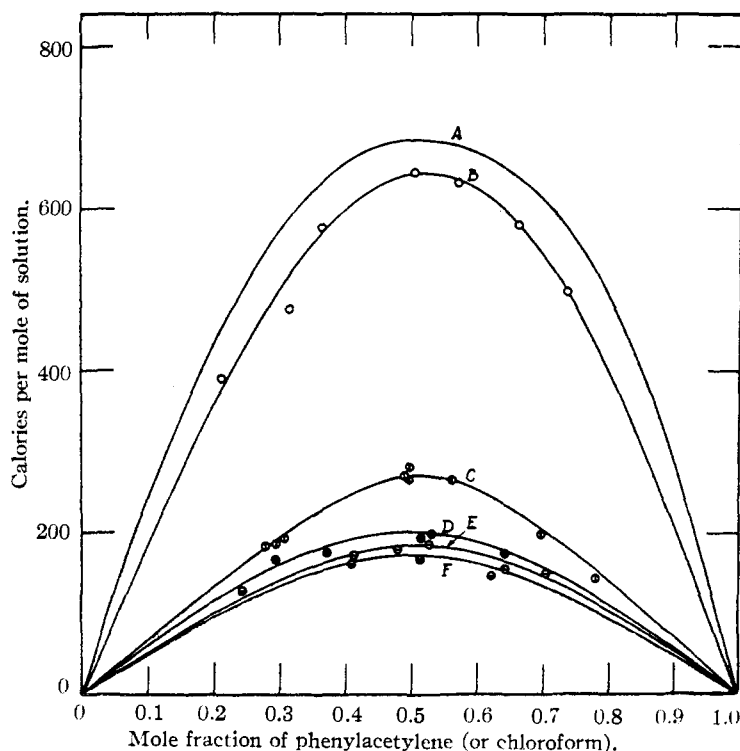

Fig. 1.—The heat evolved per mole of solution at 3° *versus* the mole fraction of phenylacetylene (or chloroform): A, chloroform and diethyl ether; B–F, phenylacetylene and, respectively, N,N-dimethylacetamide, diethyl ether, acetone, cyclohexylamine, methyl acetate.

ring; and normal or less than normal solubilities are found in compounds which do not contain a donor atom. The appreciably lower solubilities in formates than in acetates possibly are due to activity of the hydrogen of the acid residue of formates which leads to some intermolecular association. The solubilities[4] of monofluorodichloromethane are also appreciably lower in the N-disub-

(7) James, *Ind. Eng. Chem.*, **5**, 118 (1913).