Summary

Measurements with temperature variation have been made for the sorption of carbon monoxide on supported copper and on massive and supported platinum. The results are qualitatively similar to like measurements of hydrogen on massive and supported metals and show that the presence of a secondary sorptive force is probably a general characteristic of metallic sorbents.

This factor, apparently solution, manifests itself only to a small extent with supported sorbents where the metal is largely exposed as surface. With massive metals and carbon monoxide the secondary action is over three times as great in the case of platinum, and about ten times as great in the case of copper, when compared with their respective supported forms.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Chemical Separation of the Isotopes of Hydrogen by the Addition of Metals and Compounds of Metals to Water, Acids and Bases. I. Relative Efficiencies of Specific Reactions. The Effects of Certain Factors other than Temperature[1]

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The possibility of obtaining separation of isotopes of hydrogen by displacement reactions of metals with acids was suggested by Washburn and Urey.[2] The first experimental results on displacement reactions were reported independently by L. and A. Farkas[3] and by ourselves.[4] Horiuti and Szabo[5] confirmed our own value of 2.5 for the separation coefficient in the Na–H_2O reaction, in experiments in which they introduced water vapor onto metallic sodium. More extensive observations at 90° have been reported by Hughes, Ingold and Wilson,[6] whose data differ somewhat from our own. Recently, Reyerson, Johnson and Bemmels[7] have reported qualitative data on the isotope separation which results when calcium carbide is treated with water.

The present paper describes quantitative investigations of the reactions of lithium, sodium, potassium, calcium, calcium carbide and aluminum carbide with water; magnesium, granulated and mossy zinc, c. p. and commercial iron, manga-nese, aluminum and ferrous sulfide with sulfuric acid; and aluminum with sodium hydroxide. In a following paper[8] the results of an investigation of temperature coefficients of the separation factors in several of the reactions are presented.

In both this and the following paper the specific gravity of pure D_2O at 27° is taken to be d^{27}_{27} = 1.10768[9] and that of pure protium water with the normal oxygen isotope ratio d^{27}_{27} = 0.999982.[10] Account is also taken of the slight non-additivity of H_2O and D_2O volumes reported by Luten.[11] This makes the equation for the specific gravity of a D_2O–H_2O mixture, in terms of the absolute mole fraction of D

$$S_{27^\circ} = 0.999982 + 0.10770 \, N_D - 0.0012 \, N_H N_D \quad (1)$$

While equation (1) is set up for 27°, it is applicable with high accuracy for moderate concentrations of D for the whole temperature range between 25 and 30°.

Experimental Description

(a) **The Reaction System.**—A diagram of an improved form[12] of the reaction system is shown in Fig. 1.

At the beginning of each run a weighed quantity (400–800 g.) of water, acid or base, with an enriched D content, was placed in the reaction vessel A, and a weighed quantity of the solid reagent (in small pieces) was placed in C.

(1) Except for slight modification for newer values of oxygen isotope abnormality in the electrolyte and in air and for the densities of pure D_2O and pure protium oxide, the values in this paper were presented before the Division of Physical and Inorganic Chemistry at the Cleveland Meeting of the American Chemical Society (September, 1934) and the Symposium on Deuterium, held with the Pittsburgh Meeting of the American Association for the Advancement of Science (December, 1934). Original manuscript received September 19, 1941.

(2) E. W. Washburn and H. C. Urey, *Proc. Natl. Acad. Sci. U. S.*, **18**, 496 (1932).

(3) L. Farkas and A. Farkas, *Nature*, **133**, 139 (1934).

(4) C. O. Davis and H. L. Johnston, THIS JOURNAL, **56**, 492 (1934).

(5) J. Horiuti and A. L. Szabo, *Nature*, **133**, 327 (1934).

(6) E. D. Hughes, C. K. Ingold and C. L. Wilson, *ibid.*, **133**, 291 (1934); *J. Chem. Soc.*, 493 (1934).

(7) L. H. Reyerson, O. Johnson and C. Bemmels, THIS JOURNAL, **61**, 1594 (1939).

(8) H. L. Johnston and W. H. Hall, manuscript in preparation.

(9) H. L. Johnston, THIS JOURNAL, **61**, 878 (1939).

(10) H. L. Johnston, *ibid.*, **57**, 484 (1935).

(11) D. B. Luten, *Phys. Rev.*, **45**, 161 (1934).

(12) This is actually a diagram of the reaction system used by Johnston and Hall.[8] In the original design the reaction flask was not thermostatted but was either exposed to air, or sprayed with a continuous stream of tap water (*cf. seq.*). The semi-automatic levelling bulbs (H, H) and calibrated flowmeters (J, J) were not included in the original design.
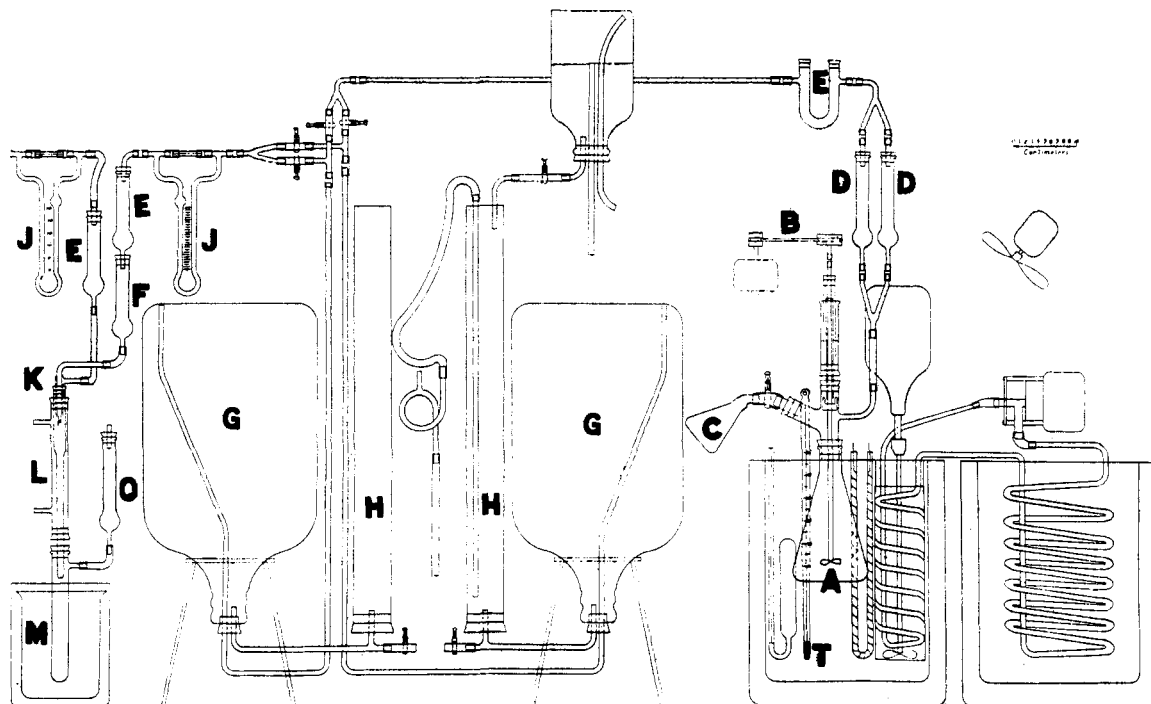
Fig. 1.—Reaction system: A, reaction vessel; B, stirrer; C, reagent flask; D,D,O, weighed $CaCl_2$ drying tubes; E,E,E, unweighed $CaCl_2$ drying tubes; F, sand trap; G, gas storage carboys; H,H, water levelling tubes to control pressure heads in the carboys; J,J, calibrated flowmeters; K, Pyrex oxyhydrogen torch; L, Pyrex condenser; M, ice-jacketed receiver; T, thermostat.

During the run the solid reagent was added slowly to the rapidly stirred liquid in the reaction vessel, and the evolved gas was: (1) dried, (2) collected over water (hydrogen sulfide and acetylene were collected over mercury), (3) redried and (4) burned in an excess of dry, tank oxygen.

Runs were permitted to go to completion (i. e., until all of the weighed solid reagent had reacted). Twenty-four to sixty grams of combustion water was formed in each run and, since the reagents were added slowly for the faster reactions, the duration of each run was from twelve to forty-eight hours.

Full gravimetric data were taken (cf. Table III) and isotopic analyses were carried out for: (1) the initial water, acid or base and (2) the water formed by combustion. In a few instances densities were taken on water from the residual solution but these were not essential since the change in the deuterium concentration in the reaction flask can be determined more accurately from the mass and the D concentration of the water produced by combustion of the evolved gas than by a direct measurement. Correction was applied for the gas that remained in the reaction vessel or other portions of the reaction system.

(b) **Densimetric Analyses with the Buoyancy Balance.** —Analyses were based on the specific gravities of purified water samples and were made by the "free submerged float" method,[13] in which the temperature of the water sample is varied until the density matches that of a cali-

brated glass float. This is a method which we have used extensively in this Laboratory with excellent results.[4,8,10,14]

The 1.5-cc. Pyrex float was calibrated at frequent intervals against purified samples of Columbus tap water, and the calibration points were graphed against time. When first made the float came to equilibrium in pure normal water at $26.773°$ but the calibration temperature rose steadily over a period of several months. We attribute this to gradual solution of the outer surface of the float.[15]

Flotation temperatures of samples analyzed, relative to normal water, are considered reliable to within ±0.001 to $0.002°$ (2 to 5 γ in density). The densities of normal water between 25 and 30° were taken from the "International Critical Tables."[16] In computing the density differences correction was applied for the thermal expansion of the Pyrex float.[17]

It has been our experience that the limiting factor in the accuracy attainable with the buoyancy balance is ordinarily the purification of water samples for analysis. In this work we repeated the purification of samples until constant density (to within 1 p. p. m.) was obtained.

(13) T. W. Richards and G. W. Harris, THIS JOURNAL, **38**, 1000 (1916); G. N. Lewis and R. T. Macdonald, J. Chem. Phys., **1**, 341 (1933).

(14) (a) R. D. Snow and H. L. Johnston, Science, **80**, 210 (1934); (b) W. H. Hall and H. L. Johnston, THIS JOURNAL, **57**, 1515 (1935); (c) ibid., **58**, 1920 (1936). A more detailed description of our procedures in densimetric analyses will be published in the Journal of the Ohio Academy of Science.

(15) There appears to be some relation between this behavior and the dimensions of the float. Earlier calibrations of an 8-cc. Pyrex float showed little change in a period of several weeks.

(16) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1927, Vol. III, p. 25.

(17) R. M. Buffington, THIS JOURNAL, **48**, 2305 (1926).

Table I is an illustration for a particularly troublesome sample, for which the density changed by about 8 p. p. m. in the second and third processings.

TABLE I

PURIFICATION RECORD OF A TROUBLESOME SAMPLE

Processings	1	2	3	4	5
Flotation temp. (Beckmann), °C.	3.695	3.675	3.664	3.663	3.664

(c) **Reagents.**—The deuterium-rich water used in this investigation was prepared by ourselves out of old electrolyte from electrolytic hydrogen cells of the Capital City Products Co. of Columbus. Water distilled from this electrolyte was further electrolyzed between nickel or iron electrodes in potassium hydroxide solution to a volume fraction of approximately $1/16$, which resulted in water whose hydrogen content was approximately 0.5% in D. The alkaline solution was neutralized with excess carbon dioxide and the water distilled away from the sodium bicarbonate in a copper still and redistilled in Pyrex. While the O^{18} abnormality must have amounted to about 9 p. p. m. on the density of the water at the end of the electrolyses,[10] the carbon dioxide treatment must have nearly or completely removed this abnormality.[14c] We have therefore taken the initial water in the several runs as normal in its oxygen isotope ratio.

The acid solution was prepared by adding Baker and Adamson C. P. fuming sulfuric acid to a weighed amount of deuterium-rich water. A sufficient amount was prepared at one time to serve for all of the runs with metals. Its concentration was found, by titration with standard base, to be 6.983 equivalents per 1000 g. of acid. Its deuterium content was 0.400 atomic % of hydrogen. The latter was determined: (1) by a direct density measurement on a middle fraction of water distilled from the sulfuric acid solution and (2) by deuterium analysis on the original water and computation of the amount of dilution by normal hydrogen from the fuming sulfuric acid. The two analyses agreed to within 1 p. p. m. on the measured and computed densities.

A second quantity of acid was prepared in a similar manner for the ferrous sulfide run.

The **basic solution** was prepared with C. P. sodium hydroxide, in a similar manner. The strength of the solution was 3.340 equivalents per 1000 g. of base.

The oxygen used in the combustions was from a commercial cylinder and had been prepared from air by the Linde process. Its oxygen isotope composition, relative to air, was determined by comparison of densities of two water samples—one prepared by combustion of tank hydrogen in an excess of the tank oxygen, the other by combustion of the same tank hydrogen in air. The combustions were brought about in the burner K. This manner of combustion will, in itself, have produced no change in the isotopic composition of either the hydrogen or the oxygen.[14c] The two water samples agreed in density to within 0.5 p. p. m. Our combustion samples must, therefore, have possessed the same oxygen abnormality as oxygen in air. We have accordingly applied a correction of −6.5 p. p. m.[14c,18] to densities of *combustion waters only*.

(18) M. Dole, *J. Chem. Phys.*, **4**, 268 (1936). See also Table VI of the recent paper by Swartout and Dole, THIS JOURNAL, **61**, 2025 (1939).

Coleman and Bell standard laboratory quality sodium and potassium were employed. Thick slices of the outer surface were cut away, in an atmosphere of nitrogen, and the metals cut into small pellets. The lithium was a reputedly pure metal supplied by A. D. Mackay of New York. The calcium metal was in the form of thick, silvery chips and was packaged, without analysis, for a local supply house.

Two C. P. samples of zinc were employed. The granular zinc was a J. T. Baker product and bore an analysis on the label which showed only 0.024% of total impurity, of which 0.02% was Pb. The mossy sample was Baker and Adamson's C. P. mossy zinc with an analysis on the label which showed 0.05% Pb and 0.002% of other impurities.

Also two samples of iron were employed. One was a 99.8% pure sample, from J. T. Baker, while the other was from a stock supply of "commercial iron filings" and contained 10 to 15% of impurities, principally carbon.

The aluminum was a granular C. P. product of Coleman and Bell and the magnesium was purchased from a local supply house as "A1 turnings for Grignard reagent." Manganese, calcium carbide, aluminum carbide and ferrous sulfide were stock chemicals of unknown origin and purity. The three last, in particular, may have contained considerable impurity.

(d) **Temperatures.**—No effort was made to thermostat the reactions. However, most of the runs were carried out at room temperature, which usually varied between 25 and 30° during the period of the experiments, and can be directly compared. The other reactions were carried out by spraying hot water from the laboratory pipes (55–60°) onto the wall of the reaction flask in order to accelerate otherwise sluggish rates. This was done in both of the runs with aluminum in acid; in the second lithium run, in which lithium was added to an already strong solution of lithium sulfate; in both runs with granular zinc and in both runs with C. P. iron. Cold tap water was sprayed onto the reaction vessel during the runs with sodium and with potassium in order to maintain the reaction mixtures close to room temperature.

Because the reactions were run relatively slowly, the temperatures of the reaction mixtures can seldom have differed by as much as 5° from the wall of the flask.

Because of the extreme slowness with which aluminum reacted with the acid a small quantity of mercury was added to promote the reaction. For the same reason copper strips were added to the reaction vessel in Run 11, with granular zinc.

Experimental Data

(a) **Sample Data and Calculations for a Typical Run.**—Table II contains the data obtained in a typical run (magnesium with sulfuric acid).

The separation coefficient, α, is defined by the equation

$$d \ln H = \alpha d \ln D \qquad (2)$$

with the symbols H and D used to represent the H_2O and D_2O equivalents of the quantities of

TABLE II

SAMPLE DATA AND CALCULATIONS

Run 18, 42.50 g. of Mg added to an excess of 6.983 N H_2SO_4.

	Initial acid	Combustion H_2O	Residue in reaction flask
Weight, g.	958.27	31.35 (obs.)[19]	995.57[25]
Water equivalent, g.	690.48	31.49 (calcd.)[20]	
ΔT of flotation, °C.	1.500	0.917[22]	
Specific gravity	1.0004081	1.0002470	
Mole fraction of D	0.004001	0.002467	
Wt. fraction of D[23]	.004446	.002742	
Quantity of D (as D_2O)	3.06987	.08635	2.98352[24]
Quantity of H (as H_2O)	687.41013[21]	31.40365[20]	656.00648[24]

$$a = \frac{\log\,(656.00648/687.41013)}{\log\,(2.98352/3.06987)} = 1.640$$

H and D, respectively, in the acid solution. The equation is integrated between initial and final amounts.

The good agreement between the observed[19] and calculated[20] weights of combustion water, and likewise the check on the gravimetric data through the observed and calculated weights of residue,[25] are good evidence against any significant amount of reduction by the reaction[26]

$$Mg + 2H_2SO_4 = Mg^{++} + SO_4^- + 2H_2O + SO_2 \quad (3)$$
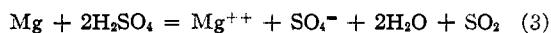
Failure to observe an odor of sulfur dioxide in the slow streams of excess oxygen from the burner is further confirmation of this.

(b) Complete Tabulation for All Fifteen Reactions in Water of Approximate 0.5% D Content.—Complete tabulations of the essential experimental data for all runs in the fifteen reactions investigated, together with the values of a, are given in Table III. Except as noted, calculations were carried out in the same manner

(19) The sum of: 29.55 g. collected in M (Fig. 1); 1.25 g. collected in O (no ice was on hand when this run was made); and 0.55 g. computed as the H_2O equivalent of an approximate 800 cc. of unburned H_2 left in the apparatus at the end of the run.

(20) Calculated from the weight of metal reacted.

(21) Corrected by 0.65 g. for loss of 1.31 g. of vapor to drying tube D.

(22) Corrected by 0.023° for the O^{18} abnormality of the tank oxygen.

(23) Wt. fractions were computed with the molecular weight values: $H_2O = 18.0156$, $D_2O = 20.0283$.

(24) Computed by difference between entries in the "Initial Acid" and "Combustion H_2O" columns.

(25) This weighing was taken as a check on the gravimetric data. It compares with the calculated value 996.06. The latter makes allowance for the 1.31-g. vapor loss to the drying tube D (ref. 21) and for the 3.60 g. of H_2 (0.25% in D) represented by the 31.35 g. of H_2O collected.

(26) The good gravimetric check on the weight of residue is significant in ruling out this reaction since SO_2 is 32 times as heavy as the equivalent amount of hydrogen. For example, in the run recorded in Table II, 100% reaction by (3) rather than by displacement would have liberated $32 \times 3.60 = 115.2$ g. of SO_2, a weight difference of 112.6 g., and 1% reaction by (3) would have therefore, introduced an error of +1.13 g. in the computed weight of residue. The observed discrepancy is only 0.5 g. and is within limits of error.

as illustrated by the run recorded in Table II. Temperatures were approximately 30°, with the exception of certain runs in which the reaction flask was heated to about 55°. These runs were referred to previously.

Run 1 is the preliminary run with sodium, previously reported.[4] Its value of α has been recomputed with corrections made for oxygen isotope abnormality in both the combustion water and the initial water and for the improved H/D ratio in ordinary water.

Comparisons[25] of the weight of residue found in the reaction vessel with that calculated from the initial weighings and the quantity of hydrogen (or hydrogen bearing gas) evolved are not included in the table. With few exceptions[27] calculated and observed weighings of residue agreed to within a few tenths of a gram. This can be considered to be within experimental limits of error. However, the observed amount of *combustion water* was usually *less* than the calculated weight. In some instances this was due to known accidental losses of hydrogen while the apparatus was allowed to run overnight, or to impurities in certain of the reagents (commercial iron, aluminum carbide and possibly calcium carbide, calcium and ferrous sulfide as examples). However, it can easily be shown that even relatively large errors in the *amounts* of combustion water, should they exist, do not affect the values of α significantly.

The precision with which α may be determined depends primarily on the precision with which compositions of Initial Water and of Combustion Water are determined. It can be shown, simply, that any percentage error in either of these compositions will influence α in the same proportion.

(27) Among the reactions that evolve H_2 (Runs 1 to 26 inclusive) only Runs 9, 10 and 13 showed disagreements in the gravimetric data amounting to more than 1 g. The average disagreement in this group (Runs 9, 10 and 13 not included) was ±0.4 g. In Run 13 the disagreement was 2.9 g. and for the combined K runs it was 11 g. The 11-g. disagreement in the gravimetric data for the K runs may be due in part to the presence of K_2O, which would not have been distinguished from 2K in the titrations of residue. We also encountered experimental difficulties resulting from explosions of small pieces of potassium in the reaction vessel, that caused some losses of material and weakened the validity of any gravimetric comparison. It can easily be shown, however, that the experimental values of α cannot have been influenced by these difficulties by more than a few hundredths of a unit.

The gravimetric check was less accurate with the residues from runs 27–32 inclusive. With CaC_2 the average disagreement was 3 g.; with Al_4C_3, 1 g.; and with FeS, 10 g. With CaC_2 and Al_4C_3 the disagreements may be accounted for by not unreasonable losses of hydrocarbon gases from the stirrer or gas train. It is possible that soluble impurities in the FeS may have been responsible, in whole or in part, for the relatively large discrepancy in the observed and calculated weight of residue in that reaction.

TABLE III

GRAVIMETRIC AND DENSITY DATA, AND VALUES OF THE ISOTOPIC SEPARATION FACTOR, FOR ALL RUNS WITH APPROXI-
MATE 0.5% D CONTENT IN THE INITIAL WATER[28]

Run	Reaction	Amounts, grams Metal[29] (or compound)	Initial liquid	Relative flotation temps., °C. Combustion water[30]	Initial water	Combustion water[32]	α
1	Na + H₂O	150.0	389.2	57.3	0.532	0.156	2.6
2	Na + H₂O	369.9[31]	849.67[31]	42.62	1.666[31]	.616	2.55
3	Na + H₂O	....	.....	52.94	....	.627	2.59
4	Na + H₂O	....	.....	47.21	....	.638	2.66
5	Li + H₂O	58.3[31]	810.17[31]	44.73	1.699[31]	.922	1.84
6	Li + H₂O	....	.....	31.04	....	.930	1.86
7	Ca + H₂O	120.79	641.80	54.28	1.521	1.082	1.41
8	Ca + H₂O	119.26	700.72	53.60	1.521	1.090	1.40
9	K + H₂O	391[31]	568.56[31]	31.53	1.705[31]	1.206	1.42
10	K + H₂O	....	.....	32.02	....	1.190	1.46
11	Zn (gran.) + H₂SO₄	127.90	840.80	34.33	1.500	0.269	4.89
12	Zn (gran.) + H₂SO₄	129.53	815.10	35.69	1.500	.247	5.24
13	Zn (mossy) + H₂SO₄	132.92	889.40	36.62	1.500	.199	6.19
14	Zn (mossy) + H₂SO₄	100.17	843.30	27.62	1.500	.200	6.12
15	Al + H₂SO₄	36.03	806.09	36.03	1.500	.303	4.45
16	Al + H₂SO₄	30.21	818.19	30.21	1.500	.295	4.52
17	Mg + H₂SO₄	36.78	792.48	25.80	1.500	.903	1.65
18	Mg + H₂SO₄	42.50	958.27	31.35	1.500	.917	1.64
19	Fe (c. p.) + H₂SO₄	101.27	587.94	32.67	1.500	.185	6.60
20	Fe (c. p.) + H₂SO₄	101.36	692.97	32.65	1.500	.188	6.48
21	Fe (Comm) + H₂SO₄	103.27	822.63	29.26	1.500	.215	5.81
22	Fe (Comm) + H₂SO₄	101.27	672.20	30.03	1.500	.228	5.56
23	Mn + H₂SO₄	102.67	580.90	33.57	1.500	.366	3.81
24	Mn + H₂SO₄	102.96	487.41	33.73	1.500	.360	3.89
25	Al + NaOH	30.20	570.60	30.20	1.669	.301	5.07
26	Al + NaOH	54.09	510.74	29.40	1.669	.308	4.87
27	CaC₂ + H₂O	117.57	550.94	24.31	1.728	.772	2.21
28	CaC₂ + H₂O	213.83	453.91	43.80	1.728	.732	2.36
29	Al₄C₃ + H₂O	123.35	488.00	27.40	1.728	.691	2.46
30	Al₄C₃ + H₂O	118.87	496.76	29.92	1.728	.705	2.42
31	FeS + H₂SO₄	183.31	674.09	32.90	1.690	.603	2.46
32	FeS + H₂SO₄	179.96	586.61	37.53	1.690	.609	2.46

(28) Acid and basic concentrations of solutions used were as follows: Runs 11–24, 3.492 moles of H₂SO₄ per 1000 g. of acid; Runs 25–26, 3.340 moles of NaOH per 100 g. of base; Runs 31–32, 3.487 moles of H₂SO₄ per 1000 g. of acid.

(29) The amounts of Na, Li and K used in runs with the alkali metals were determined by titrations of the alkaline solutions left in the reaction vessel. Except for K, which may have been contaminated with K₂O, these calculations agree well with those based on the amounts of combustion water collected as well as with those based on the weights of residues in the reaction flask.

(30) The values recorded in this column for runs with the alkali metals, *commercial* iron, and the compounds CaC₂, Al₄C₃ and FeS are the observed weights of combustion water (with corrections applied for water collected in the drying tube O and for the water equivalent of unburned gas in the apparatus). Values for all other runs were computed from the weights of reacted metal.

(31) Runs 2, 3 and 4 with Na form a single series which were carried out by adding successive portions of metal to an original 849.7 g. of water, and collecting three successive fractions of combustion water. The residue was weighed and titrated only after all 367.9 g. of Na had been added. In computing α's we have calculated the amounts of H and of D present in the reaction vessel after removal of each of the three fractions of combustion water, by subtracting from

If we take the ΔT's of flotation to be reliable to within about 0.004° (equivalent to 1 p. p. m. in density) in the present group of runs, this would amount to about $\pm 2\%$ in the precision of the values for α, for the majority of runs. This corresponds pretty closely to the reproducibilities observed in the experimental α's. Other factors, including inaccuracies in temperatures for certain of the runs, may increase the limits of error to $\pm$ about 5% for purposes of comparison with other work.

the original amounts the quantities of H and D collected in the receiver (corrected for losses to the CaCl₂ tubes and for H₂ in the apparatus). Each α is therefore an individual value at the mean alkalinity of each of the three successive runs—not a cumulative value. Runs 5 and 6, with Li, and 9 and 10, with K, were carried out in a similar manner except for the fact that only two fractions of combustion water were taken.

Hughes, Ingold and Wilson[6] criticized the accuracy of our preliminary determination[4] of α for the Na–H$_2$O reaction (Run 1 of Table III) on the grounds that it was somewhat sensitive to the choice of the H/D ratio in ordinary water. Due to improvements in the determination of the latter ratio, which is now known to within relatively close limits,[10,32] and to three-fold increase in the deuterium concentration of the starting water, the inaccuracy from this source cannot exceed 1 or 2% in the least favorable runs reported in the present paper (Run 1 not included).

(c) **Reaction at High Concentration of Deuterium.**—A. and L. Farkas[3] have published results for displacement reactions with water and acid 25 mole % in deuterium. For calcium they obtained a value for α (1.5) close to our own with 0.5% D. But with sodium, zinc and aluminum, respectively, their values of α were only about one-half of ours.

To check whether or not these results were due to a real dependence on the deuterium composition we carried out a single careful run with sodium in water of approximately 30 mole % deuterium. The reaction was carried out in the same manner as for the 0.5% D runs except that a smaller reaction vessel was employed and that no cooling water was used. Although special care was taken to add the sodium slowly the (undetermined) temperature of the reaction mixture must have been somewhat above that of the previous, water-cooled sodium runs. Specific gravities of the initial water and of the combustion

TABLE IV

DATA ON REACTION OF Na WITH WATER 31.083 MOLE % IN D (56.12 G. OF Na ADDED TO 116.21 G. OF INITIAL WATER)

	Amounts, grams	Sp. gravity, $d^{26}{}_{26}$	Composition, wt. per cent. of D
Initial water	115.70[43]	1.03372	33.396
Combustion water	20.64 (obs.)[43]	1.01780	17.893
Final residue water	95.06[35]		36.761[35]

$\alpha = 2.473$.

(32) Tronstad, Nordhagen and Brun, *Nature*, **135**, 515 (1935); Tronstad and Brun, *Trans. Faraday Soc.*, **34**, 766 (1938); Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 403 (1936); *ibid.*, **13**, 419 (1938); Hall and Jones, THIS JOURNAL, **58**, 1915 (1936); Gabbard and Dole, *ibid.*, **59**, 181 (1937); Swartout and Dole, *ibid.*, **61**, 2025 (1939).
(33) This includes a correction of 0.51 g. for 1.02 g. of water vaporized during the run.
(34) This compares with a calculated value of 22.4 on the basis of 56.1 g. of Na, assumed pure.
(35) Computed from the data for initial and combustion waters. The computed and observed values of total residue in the reaction flask agree well for this run. Thus, the computed value of the residue is 169.01 g. while the observed value was 168.90 g.

water were made by pycnometer, in an approximate 11-cc. pycnometer of special design. The significant data of this run are entered in Table IV, together with the value of α.

Aside from the possible influence of a small temperature coefficient in the separation efficiency the value of α obtained from this run should be reliable to the four figures recorded. It is seen that the results do not agree with those of A. and L. Farkas with 25% heavy water ($\alpha = 1.2$, which corresponds to only 13% of the separation efficiency observed by ourselves) but agree well with our own results in water of 0.5% D.

We made no check of the Farkas values for zinc and aluminum in acid of high D content.

Discussion of Results

It is apparent that the displacement reactions, and the reactions with the carbides and with ferrous sulfide, bring about isotopic separations that are properly characterized by definite coefficients (α's) that are relatively insensitive to experimental conditions other than temperature[8] and the purity of reagents. The values of these coefficients lie on both sides of the equilibrium α for the exchange equilibrium between gaseous and liquid phases, which is close to 3.0 at 30°.[36] From this it is apparent that differences in reaction *rates* contribute to the separation.

There appear to be definite, though small, increases in α with increase in alkalinity of the reaction mixture for the alkali metal–water reactions. This conclusion is based on trends observed in series of runs with sodium (Runs 2–4), lithium (Runs 5–6) and potassium (Runs 9–10). The trends are within error limits but seem too often repeated to be fortuitous. There is nothing to distinguish between pH and ionic strength as cause for the trends, but the point of greatest significance appears to be that neither of these factors has more than a barely significant influence on α. For example, in the series of runs with sodium the sodium hydroxide concentration varied from 0 at the initiation of the runs to 28.3 M at their conclusion. Average sodium hydroxide molalities for the three successive runs were 3.07, 11.1 and 22.2, respectively. Yet α changed by only 0.1 unit.

We confirm the observations of Ingold and coworkers regarding the relatively large influence of impurities in the reacting metals. The α's

(36) L. and A. Farkas, *Trans. Faraday Soc.*, **30**, 1071 (1934).

in Runs 21 and 22, with impure iron, are almost a full unit below those in Runs 19 and 20, with pure iron. The α's in our Runs 23 and 24, with impure manganese, are lower than the value obtained by the extrapolation of Johnston and Hall's data,[8] who used pure manganese, by about the same amount. Accidental entrance of mercury into the reaction vessel during Runs 14 (Zn, H_2-SO_4) and 26 (Al, NaOH) do not appear to have influenced the α's beyond the limits of experimental accuracy, but the mercury may not have become intimately mixed with the metals.

The order of the α's, among the displacement reactions, at 30° is: Ca, K, Mg, Li, Na, Al, Mn (pure[8]), Zn, Fe. This follows the order found by Hughes, Ingold and Wilson, at 90°: Li, Ca, K, Mg, Na, Al, Fe, Mn, Zn, except for the positions of Li and of Fe. Extrapolation of the curves of Johnston and Hall[8] to higher temperatures would give the order Zn, Mn, Fe at 90°, which is the reverse of the order reported by Hughes, Ingold and Wilson.

It is interesting to observe that the α's for the three metathetic reactions (CaC_2, H_2O; Al_4C_3, H_2O; FeS, H_2SO_4) are nearly identical.

There have been direct comparisons of heterogeneous reaction velocities with H_2O and D_2O, respectively, for the Al_4C_3–H_2O reaction. Urey and Price[37] reported the very high value of 23 for the ratio of reaction rates at 80°. This is ten times higher than our measured α at 30°. However, Barrer,[38] who used a more careful procedure obtained a reaction velocity ratio of 3.9 at 0°.

One of us has taken some preliminary data on reaction rates of aluminum with 4.5 N sulfuric acid, at 50°, as a function of the H/D ratio in the aqueous acid.

The results of these experiments are shown in graphical form in Fig. 2, where the rates are shown relative to the rate with ordinary 4.5 N sulfuric acid taken as unity. Each point on this graph is the average of two independent rate determinations with the same lot of acid. It is apparent that the reaction rate is linear with the D concentration, to within the limits of error, and that extrapolation to 100% D gives a reaction rate of about half that with acid 100% in H. This does not compare very accurately with the α of 4.5 found by us in the Al–H_2SO_4 reaction. However, the conditions of reaction may not have

been comparable, due to the presence of mercury in runs (15–16). Probably, both in this comparison and in that with aluminum carbide, the agreements obtained are as close as could be expected under the conditions of experiment. Investigations on reactions more suitably chosen for this comparison are in progress in this Laboratory.
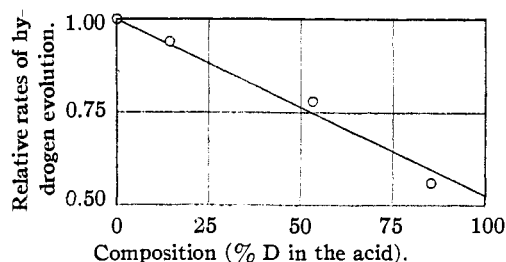

Fig. 2.—Relative velocities of the dissolution of aluminum in 4.5 N sulfuric acid, at 50°, as a function of the H/D ratio in the acid.

We accept the suggestion of Horiuti and Szabo[5] that the α's of displacement reactions are not necessarily the ratios of reaction velocities in pure H and pure D media, respectively, since the character of the reaction mechanism may lead to rates that are not strictly proportional to the relative numbers of H and D atoms. However, we fail to perceive the validity of their argument that the α for sodium cannot be the ratio of reaction rates since they obtained the same degree of isotopic separation in the reaction of water vapor with *excess* sodium as we had obtained in the reaction with excess liquid water. In view of our observation that α remains constant, within error limits, between 0.5 and 30% heavy water, it appears that the relative reactivities of OH and OD linkages remain the same when OH and OD are in the same molecule (*i. e.*, HDO) as when they exist in different molecules (*i. e.*, H_2O and D_2O).

To us, it seems of greater significance to stress the observation that Horiuti and Szabo obtained nearly the same α's[39] with *water vapor* as we obtained with *liquid water*, since the reaction with water vapor is clearly a molecular, as distinct from an ionic, mechanism. This implies that the reaction of the alkali metals with *liquid water* occurs by a molecular mechanism—a conclusion reached by Hughes, Ingold and Wilson by other reasoning, and previously suggested by Polanyi, who pic-

(37) H. C. Urey and D. Price, *J. Chem. Phys.*, **2**, 300 (1934).
(38) R. M. Barrer, *Trans. Faraday Soc.*, **32**, 486 (1936).

(39) Horiuti and Szabo did not compute α's for their four runs (two with sodium in excess and two with water vapor in excess) but tabulate data which we have used to compute their α's. The four runs yield an average α of about 2.2, with extremes of about 2.0 and 2.4, respectively.

tures[6] "the attachment of water molecules through their oxygen atoms to the metallic surface, and the subsequent elimination of hydrogen from two bound molecules in accordance with the (bond activation) mechanism of Horiuti and Szabo."

A fuller discussion of mechanisms will be left to the following paper.[8]

Summary

Quantitative data were secured on the extent of isotopic separation which occurs in the following respective reactions which liberate hydrogen or gaseous hydrides: Li, Na, K, Ca, CaC_2 and Al_4C with water; Mg, Zn, Fe, Mn, Al and FeS with aqueous sulfuric acid; and aluminum with aqueous sodium hydroxide. With a few exceptions the runs were made at or near room temperature. The hydrogen and hydrides were burned in a flame, with a slight excess of tank oxygen, and the water of combustion carefully purified and analyzed for its hydrogen isotope proportions by the free submerged float method. Correction was applied for the O^{18} abnormality of the tank oxygen, which was separately determined.

The data were quite reproducible, for a given set of reagents, and confirm the applicability of the quantitative relationship $d \ln [H] = \alpha d \ln [D]$, in which [H] and [D] are instantaneous values of the amounts of protium and deuterium, respectively, in the liquid phase, and α is the "isotopic separation factor," different for each reaction. The form of this relationship is identical with that which pertains to the isotopic separations by electrolysis.

A discussion of regularities observed in the results, and their bearing on some phases of the reaction mechanism is included.

COLUMBUS, OHIO   RECEIVED AUGUST 13, 1942

Iodine Monochloride. IV. The System Potassium Chloride–Iodine Monochloride[1]

BY JACOB CORNOG AND ELDON E. BAUER[2]

This paper describes a series of studies in which existing vapor pressure data of iodine monochloride have been extended, the system potassium chloride–iodine monochloride has been formulated, and earlier work with the polyhalides potassium dichloroiodide, $KCl\cdot ICl$ or $KICl_2$, and potassium dibromoiodide, $KBr\cdot IBr$ or $KIBr_2$, has been reviewed.

1. **The Vapor Pressure of Iodine Monochloride.**—The vapor pressure of iodine monochloride was measured by Cornog and Karges,[3] who used the static method of Smith and Menzies[4] for measurements within the temperature range 35 to 70°. A modified form of the dynamic method of Pearce and Snow[5] was used to measure all of the vapor pressure data included in this paper. The vapor pressure of iodine monochloride was measured between the temperatures −15 and 50°. This served both to validate the method and to extend existing data. The iodine monochloride used in these measurements froze at 27.3°. Measurements were made in a thermostat in which temperatures were constant within ±0.02°. Vapor pressure measurements were reproducible within ±0.1 mm. at

low pressures and ±0.3 mm. at higher pressures. The vapor pressure data for iodine monochloride are shown in Table I and are graphically represented in Fig. 1.

TABLE I

VAPOR PRESSURE OF SOLID AND LIQUID IODINE MONO-CHLORIDE

1 Temp., °C.	2 V. p. liq. ICl, mm.	3 V. p. solid ICl, mm.	4 V. p. liq. ICl by Cornog and Karges, mm.
− 15		1.2	
− 10		2.0	
− 5		3.1	
0		4.6	
5		6.8	
10	12	9.9	
15	16.3	14.3	
20	21.9	20.4	
25	29.3	28.3	
27.3	33.2	33.2	
30	38.4		
35	50.2		48.0
40	64.4		62.5
45	84.5		81.0
50	107.1		103.6

Each value in columns 2 and 3, Table I, is the average of from two to six observations. Comparison of the values shown in columns 2 and 4, Table I, shows reasonable agreement between current and previous observations. In the course of these experiments considerable time and ef-

(1) A summary of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Department of Chemistry, in the Graduate College of the State University of Iowa, May, 1942.

(2) Present address, Eastman Kodak Co., Rochester, N. Y.

(3) Cornog and Karges, THIS JOURNAL, **54**, 1882 (1932).

(4) Smith and Menzies, ibid., **32**, 1427 (1910).

(5) Pearce and Snow, J. Phys. Chem., **31**, 231 (1927).