TABLE I

Compound	Phosphoryl frequency (cm.$^{-1}$)	Shift (cm.$^{-1}$)
$POCl_3$	1300^a	. .
$(POCl_3)_2 \cdot TiCl_4$	1205	95
$POCl_3 \cdot TiCl_4$	1205	95
$(POCl_3)_2 \cdot SnCl_4$	1215	85
	1300, 1285^b	
$POBr_3$	1270	. .
$(POBr_3)_2 \cdot TiBr_4$	1185	85
$(POBr_3)_2 \cdot FeBr_2$	1220	50
Ph_3PO	1180	. .
$(Ph_3PO)_2 \cdot SnCl_4$	1125	55
$(Ph_3PO)_2 \cdot SnBr_4$	1125	55
$(Ph_3PO)_2 \cdot TiCl_4$	1130	50
$(Ph_3PO)_2 \cdot FeBr_2$	1125	55

[a] Thin film of liquid. [b] Partially resolved doublet.

maximum on the high frequency side. The shoulder maximum is more pronounced and resolved in $POCl_3 \cdot TiCl_4$ and $TiCl_4 \cdot 2POCl_3$ (which have identical spectra) and this is also true for the spectrum of $SnCl_4 \cdot 2POCl_3$. The most notable feature of this tin(IV) chloride compound is a strong doublet at the expected free $POCl_3$ phosphoryl frequency. The area under this doublet is approximately two-thirds that of the shifted band. In consideration of the similarity in shape and position between the shifted component of the PO band in $SnCl_4 \cdot 2POCl_3$ and that of the shifted band in $POCl_3 \cdot TiCl_4$ it must be concluded that a substantial proportion of the $POCl_3$ groups are indeed bonded to the tin in the $SnCl_4$ compound. The unchanged component may represent the absorption of a portion of the $POCl_3$ molecules in the crystal that are temporarily not bonded but nevertheless remain localized due to other crystal forces. The instability of this compound already has been mentioned and dissociation may well be prevalent within the crystal at temperatures 35° below its m.p., the temperature at which the spectrum was obtained.

The shifted PO bands of the $SnBr_4$ and $TiBr_4$ compounds of Ph_3PO do not reveal much fine structure, but those of the $SnCl_4$ and $FeBr_2$ compounds are clearly resolved into three submaxima. The frequencies given in Table I refer to that of the maximum in the proposed PO absorption band when more than one peak is detectable in the band envelope. There are two very strong absorption bands in the spectrum of Ph_3PO in the 1200 to 1100 cm.$^{-1}$ region and both are shifted to relatively the same extent.

In preliminary studies, we have found that the addition compounds of aluminum chloride with thionyl chloride[19] and benzoyl chloride[20] also show thionyl and carbonyl bands shifted to lower frequency by about 115 and 45 cm.$^{-1}$, respectively. This may be compared with the shift to higher frequency that nitrosyl chloride undergoes on complex formation with aluminum chloride. This complex is undoubtedly of the structure $NO^+ \cdot AlCl_4^-$ and the nitrosyl frequency in this solid compound is 2236 cm.$^{-1}$ compared with the NO frequency of 1800 cm.$^{-1}$ in pure nitrosyl chloride.[21]

Acknowledgment.—This work was supported in part by the Office of Naval Research.

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CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Exchange of Oxygen between Phosphoric Acid and Water[1]

BY BERNARD KEISCH,[2] JOSEPH W. KENNEDY[3] AND ARTHUR C. WAHL

RECEIVED MAY 10, 1958

The kinetics of the exchange of isotopic oxygen between phosphoric acid and water has been studied. The rate of exchange increases rapidly with the phosphoric acid concentration, the half-time of exchange at 100° decreasing from 250 hour at 5.9 *f* H_3PO_4 to 0.20 hour at 18.3 *f* H_3PO_4. The observed rate may be expressed as a function of the H_2O and H_3PO_4 activities a_w and a_1, respectively, in the following manner: rate $= k_1a_1a_w + k_2a_1^2 + k_3a_1^3/a_w$. The first term is of primary importance at the lower phosphoric acid concentrations, and the second term is the important one at the higher concentrations. The third term contributes appreciably (~10%) only in the most concentrated solutions. The proposed mechanism involves direct replacement of oxygen in H_3PO_4 (first term) and the reversible formation and hydrolysis of $H_4P_2O_7$ and $H_5P_3O_{10}$ (second and third terms). Support for exchange *via* reversible formation and hydrolysis of $H_4P_2O_7$ is given by the equivalence of the exchange rate and the rate of $H_4P_2O_7$ hydrolysis in the concentrated solutions. The activation energy measured at various concentrations of phosphoric acid decreases from 26.5 kcal./mole at 8.8 *f* H_3PO_4 to 19.7 kcal./mole at 17.8 *f* H_3PO_4.

The exchange of oxygen between water and phosphoric acid or its salts has been studied qualitatively by a number of workers.[4-8] Some of the results are contradictory. This paper describes a detailed study of the kinetics of the reaction

$$H_2O^* + H_3PO_4 = H_2O + H_3PO_4^*$$

We have measured the rate of the exchange as a function of the acid concentration and also the rate of hydrolysis of pyrophosphoric acid in concentrated phosphoric acid solutions. We have at-

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(2) Phillips Petroleum Fellow, 1955–1957.

(3) Deceased, May 5, 1957.

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(6) E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940).

(7) E. R. S. Winter and H. V. A. Briscoe, *ibid.*, 631 (1942).

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tempted to provide a rate law and a reasonable mechanism consistent with the data.

Experimental

Materials and Apparatus.—The oxygen tracer used was in the form of water containing about 1.5% O^{18} supplied by the Stuart Oxygen Company.

All materials were reagent grade chemicals and were used without further purification.

Phosphoric acid solutions of concentration greater than 85 weight % H_3PO_4 were prepared by the addition of calculated amounts of phosphorus pentoxide to 85 weight % acid to give nominal concentrations of 96–100% H_3PO_4. The mixtures were heated in a closed vessel on a steam-bath for at least a week to attain equilibrium among the various phosphoric acid species and water. It was shown that additional heating had no measurable effect on the exchange rate.

Isotope ratios were measured on a Consolidated-Nier Model 21-201 Isotope Ratio Mass Spectrometer. Experiments above 70° were controlled to ±0.2° in a bath of molten "Hydrofol Tinfat 50," a solidified fish oil obtained from Archer–Daniels–Midland Company of Cleveland, Ohio. Experiments below 70° were controlled to ±0.1° in a water-bath of usual design.

Analyses.—Isotopic analyses were performed on the oxygen obtained by electrolysis of the acid solutions between bright platinum electrodes in an evacuated bulb. It was found that the oxygen produced came from the water only.

The concentrations of phosphoric acid were determined either by density (employing data from the "International Critical Tables")[9] or by accurate dilutions of the solutions whose concentration had been determined by density. Density measurements were made at room temperature with a pycnometer. Concentrations were corrected for density change with temperature.

The water concentration in the more concentrated phosphoric acid solutions was determined by isotopic dilution. Water enriched in O^{18} was added, and the mixture electrolyzed before appreciable exchange took place.

Procedures.—For reaction solutions less than 85 weight % phosphoric acid, an accurate dilution of acid of known concentration was made using O^{18}-enriched water. For solutions of greater than 85 weight % phosphoric acid, an approximate dilution with O^{18}-enriched water was made of the nominal 96–100 weight % H_3PO_4, and the concentration determined after the exchange was complete.

The reaction solution was contained in an electrolysis vessel which was inverted so that the solution was not in contact with the electrodes. The vessel was placed in a constant temperature bath and removed at intervals, the reaction quenched by cooling and electrolysis carried out for isotopic analysis. Negligible exchange occurred during the interval the solution was out of the bath. Isotopic analysis was also performed before heating (zero time) and after about ten half-times ("infinite" time).

The rate of the reaction leading to randomization of oxygen isotopes is given by the expression

$$\text{Rate} = \frac{(\text{A})(\text{B})}{(\text{A}) + (\text{B})} \times \frac{\ln (1 - F)}{t} \qquad (2)$$

in which (A) is the molar concentration of oxygen atoms in one reactant (*i.e.*, the water), (B) is the molar concentration of oxygen atoms in the other reactant (*i.e.*, the acid), t is the time, and F is the fraction exchange as defined by the expression

$$F = \frac{\%O_0^{18} - \%O_t^{18}}{\%O_0^{18} - \%O_\infty^{18}} \qquad (3)$$

The symbols $\% O_0^{18}$, $\% O_t^{18}$ and $\% O_\infty^{18}$ refer to the per cent. O^{18} in one form at time zero, time t and "infinite" time, respectively.

One minus the fraction exchange was plotted against time as shown in Fig. 1. The rate was calculated by the "half-time" method.

Experimental Results

Concentration of Water in Concentrated Phosphoric Acid Solutions.—Huhti and Gartaganis,[10] by means of paper chromatography, characterized the equilibrium composition of concentrated phosphoric acid solutions from 68.8 to 86.3 weight % phosphoric pentoxide. (The lower limit is equivalent to about 72.4 weight % H_3PO_4, or about 17.5 f H_3PO_4.) They found that even at nominal concentrations below 100% orthophosphoric acid, there were measurable amounts of pyrophosphoric acid present and, hence, more water present than the nominal concentration. Since the rate calculated from a measured half-time depends on the actual water concentration, this was experimentally determined by isotopic dilution analysis. Equilibration of the solutions before analysis was carried out for one week at 100°. The results are shown in Table I. Also shown for comparison are values calculated from the data of Huhti and Gartaganis.[10] They equilibrated for 15 minutes at 350°.

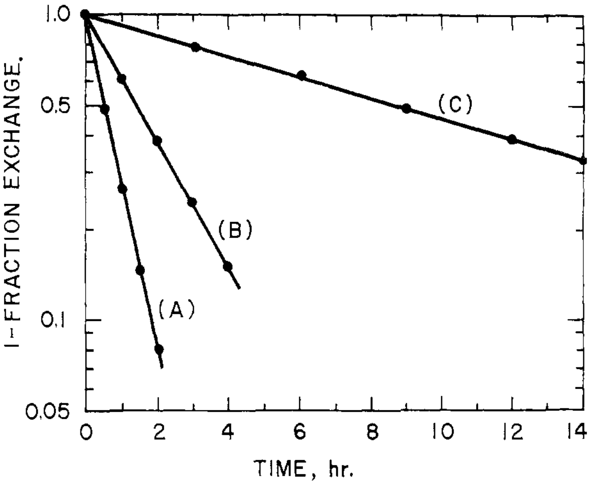

Fig. 1.—Typical exchange curves at 100°: curve A, 17.84 f H_3PO_4; curve B, 16.78 f H_3PO_4; curve C, 14.02 f H_3PO_4.

TABLE I

WATER IN CONCENTRATED H_3PO_4 SOLUTIONS AT 100°

Nominal wt. H_3PO_4	(H_3PO_4), f	(H_2O), f	(H_2O), M (this work)	(H_2O), M (Ref. 10)[a]
82.9	13.60	15.30	15.35	15.30
91.1	15.91	8.40	8.42	8.40
95.3	17.11	4.75	4.78	4.75
97.1	17.70	3.00	3.11	3.10
97.5	17.84	2.60	2.80	2.84
98.1	18.02	2.00	2.53	2.45
98.9	18.31	1.18	1.88	1.90
99.3	18.45	0.75	1.63	1.65
99.8	18.63	0.15	1.28	1.30

[a] Equilibrated at 350°.

The agreement between the values obtained from equilibration at the two temperatures is very good and, at first sight, suggests that the heat of hydrolysis of pyrophosphoric acid must be close to zero. However, in view of the relatively rapid hydrolysis of pyrophosphoric acid (to be discussed), it is more reasonable to assume that as the solutions at 350° cooled the hydrolysis equilibrium shifted, so that both sets of values are characteristic of conditions at 100°. Our solutions were quenched

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[9] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., p. 61.

[10] A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

rapidly in Dry Ice–acetone mixtures to minimize the shift.

Dependence of Rate of Exchange at 100° on the H_3PO_4 Concentration.—Table II shows the results obtained at 100° for the exchange reaction over the concentration range from 5.9 to 18.35 *f* H_3PO_4.

TABLE II

RATE OF EXCHANGE AT 100°

(H_3PO_4), *f*	(H_2O), *M*	Half-time, hr.	Rate × 10^4, g. atom/l. sec.
5.9	37.3	250[a]	0.111
8.9	29.8	88.7	.352
11.11	22.80	41.0[a]	.711
12.55	18.60	21.9[a]	1.25
12.80	17.80	16.5	1.54
13.4	16.4	13.7	1.75
13.64	15.02	12.65[a]	1.81
14.02	13.75	9.05	2.36
15.60	9.20	3.43	4.50
16.34	6.90	2.05	5.85
16.78	5.65	1.46	6.88
16.97	5.15	1.33	6.93
17.18	4.45	1.07	7.51
17.60[b]	3.37	0.702	8.81
17.76[b]	2.98	.550	10.0
17.84[b]	2.81	.550	9.47
18.02[b]	2.45	.417	11.0
18.20[b]	2.11	.337[a]	12.9
18.28[b]	1.98	.307	12.1
18.35[b]	1.45	.204	13.4

[a] Average of duplicate runs. [b] Molarity differs from formality due to formation of $H_4P_2O_7$.

Activation Energies.—Rates of exchange at four H_3PO_4 concentrations were measured at various temperatures and the results are shown in Table III. Activation energies as measured by the slopes of log *R* *vs.* 1/*T* plots are given in Table IV.

TABLE III

EXCHANGE RATE AT VARIOUS TEMPERATURES [(g. atom/l. sec.) × 10^4]

(H_3PO_4), *f*	25°	40°	60°	80°	90°	100°	110°
8.8	....	....	....	...	0.141	0.341[a]	0.78
12.2	....	....	0.0286	0.221	0.511	1.14[a]	2.62
15.1	....	0.0137	.106	0.672	1.59	3.45[a]	8.65
17.8	0.0148	0.070	.462	2.05	4.53	9.47	..

[a] Taken from smooth curve in Fig. 2.

TABLE IV

ACTIVATION ENERGIES

(H_3PO_4), *f*	$E_{act.}$, kcal./mole
8.8	26.5
12.2	24.0
15.1	23.1
17.8	19.7

Miscellaneous Exchange Rate Measurements.—Addition of KH_2PO_4 had no measurable effect on the exchange rate at 100° in 12.68 *f* H_3PO_4. In the absence of KH_2PO_4 the rate measured was 1.43×10^{-4} g. atom/sec.; in the presence of KH_2PO_4 (0.14 or 0.3 *f*) the rate measured was 1.41×10^{-4} g. atom/sec.

The presence of $HClO_4$ (0.9 *f*) in 13.4 *f* H_3PO_4 increased the rate at 100° from 1.75×10^{-4} to 2.07×10^{-4} g. atom/sec. This small increase in rate (~20%) is less than half the increase in rate caused by increasing the H_3PO_4 concentration by 0.9 *f*.

The presence of ~0.03 g. of finely divided TiO_2 in 10.5 ml. of 18.2 *f* H_3PO_4 increased the rate at 60° from 5.54×10^{-5} to 6.76×10^{-5} g. atom/sec.

Rate of $H_4P_2O_7$ Hydrolysis in Concentrated Phosphoric Acid.—A possible path for oxygen exchange is the reversible formation and hydrolysis of pyrophosphoric acid (and also, possibly higher polymeric phosphoric acids)

$$2H_3PO_4 \underset{k'}{\overset{k''}{\rightleftarrows}} H_4P_2O_7 + H_2O \qquad (4)$$

To test directly this possibility the hydrolysis rate was measured at 25 and 60°. (Rate measurements were attempted at 100°, but the rate was too large to be measured by our technique.)

For the 25° experiment, 100.3 nominal weight % H_3PO_4 was diluted to 98.0 nominal weight %, and the disappearance of water was followed by isotopic dilution analysis. The measured water concentration decreased from 2.95 *M* at time zero to 2.74 *M* after 10 hours, to 2.72 *M* after 20 hours, to 2.64 *M* after 29 hours, to 2.61 *M* after 47 hours and to 2.36 *M* at equilibrium.

For the 60° experiment 100.7 nominal weight % H_3PO_4 was diluted to 98.5 nominal weight %. The measured water concentration decreased from 2.80 *M* at time zero, to 2.65 *M* after 20 minutes, to 2.42 *M* after 60 minutes, to 2.32 *M* after 95 minutes and to 2.15 *M* at equilibrium.

It should be mentioned that the measured water concentration at time zero was about 7% less than the value calculated from the amount of water and the amount and composition of the phosphoric acid that were mixed. This discrepancy appears to be due to an induced reaction on mixing since further decreases in the water concentration occurs only slowly.

For interpretation of the hydrolysis data, rate expression (5) was assumed

$$-\frac{dc_w}{dt} = k'c_wc_2 - k''c_1^2 \qquad (5)$$

in which c_w, c_1 and c_2 are the concentrations of water, H_3PO_4, and $H_4P_2O_7$, respectively. Assuming c_1 to be constant, a condition closely approximated in the experiments, integration of equation 5 gives

$$\frac{1}{c_w^\infty + c_2^\infty} \ln \frac{(c_w^0 - c_w^\infty)(c_2 + c_w^\infty)}{(c_2^0 + c_w^\infty)(c_2 - c_2^\infty)} = k't \qquad (6)$$

in which the superscript 0 and ∞ refer to the initial and equilibrium conditions, respectively.

Values of k', 1.5×10^{-6} l. mole^{-1} sec.$^{-1}$ at 25° and 8×10^{-5} l. mole^{-1} sec.$^{-1}$ at 60°, were obtained from the slopes of the straight lines resulting from plots of

$$\log \frac{c_2 + c_w^\infty}{c_2 - c_2^\infty} \; vs. \; t$$

For comparison with the isotopic exchange rates the hydrolysis rate constants were multiplied by the product of the equilibrium concentrations of water and phosphoric acid under conditions for which exchange data were available. It was assumed k' did not change appreciably with composition of the concentrated solutions. The comparison is given in Table V.

TABLE V

COMPARISON OF RATES OF $H_4P_2O_7$ HYDROLYSIS AND H_2O-H_3PO_4 EXCHANGE

Conditions	Hydrolysis rate, mole/l. sec.	Exchange rate, g. atom/l. sec.
25°, 18.0 f H_3PO_4	1.5×10^{-6}	1.9×10^{-6}
60°, 17.8 f H_3PO_4	5×10^{-5}	4.6×10^{-5}

Discussion

It has been shown that in concentrated phosphoric acid solutions the rate of oxygen exchange between water and phosphoric acid and the rate of pyrophosphoric acid hydrolysis are nearly equal. The rate expression for the exchange reaction must contain, therefore, a term proportional to a_1^2/γ^*, in which a_1 is the activity of H_3PO_4 and γ^* is the activity coefficient of the transition state ($H_6P_2O_8$). This term must be of primary importance in concentrated solutions.

In addition, it seems unlikely that activities of $H_2PO_4^-$ or H^+ are involved in the rate expression because addition of KH_2PO_4 had no measurable effect on the rate and the presence of the strong acid $HClO_4$ had only a small effect, less than an equal-molar increase in the H_3PO_4 concentration.

Since a_1^2 falls off with decreasing phosphoric acid concentration more rapidly than does the exchange rate (see Fig. 2), either γ^* must decrease more than an order of magnitude with decreasing phosphoric acid concentration or the rate expression must contain other terms. (See appendix for activity values.) Although it is plausible for a large change in γ^* to occur as the medium is changed from nearly pure H_3PO_4 to an aqueous solution of H_3PO_4, it seems desirable to formulate a rate expression without an unknown variable. Therefore, additional terms involving the activity of H_2O (a_w) as well as the activity of H_3PO_4 (a_1) were tried. The resulting expression, which fits the data well, is

$$\text{Rate} = k_1a_1a_w + k_2a_1^2 + k_3a_1^3/a_w \qquad (7)$$

In the above expression, as shown in Fig. 2, the first term is important at the lower phosphoric acid concentrations, and the second term is important at the higher concentrations. The third term makes an appreciable contribution only above 18 f H_3PO_4 where the second term levels out and the exchange rate continues to rise. (The values of the rate constants depend on the reference point chosen for evaluation of the H_3PO_4 activity (a_1). A consistent set of values for the activities and rate constants is given in the appendix.)

It is for the high phosphoric acid concentrations that the exchange data are least reliable because the experimental procedure of mixing ~100 nominal weight % H_3PO_4 with water enriched in O^{18} resulted in exchange mixtures with excesses of $H_4P_2O_7$ and H_2O. The rapid net hydrolysis reaction that occurred did not in itself affect the exchange measurements since it resulted in no change in the isotopic composition of the water, by which the progress of the exchange was followed. Excessive concentrations of H_2O and $H_4P_2O_7$ would affect calculations of exchange rates from half-times and, possibly, the exchange rate itself (say by changing the activity of H_3PO_4). Both of these effects are believed to be small because the hydrolysis was nearly complete during the first half-time of exchange, and for the runs in concentrated solutions exchange points were not measured during this time. (The zero-time point (measured before heating) was above the linear exchange lines indicating the initial rate of exchange was somewhat larger.)

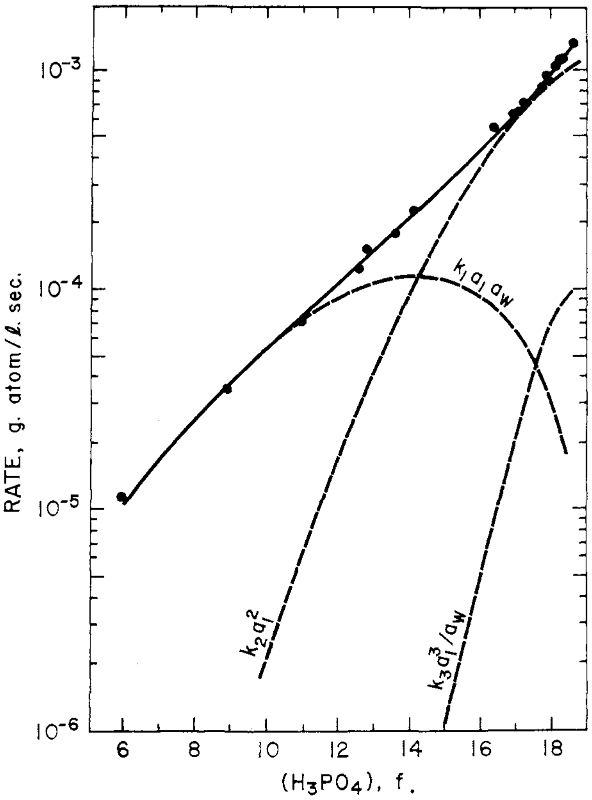

Fig. 2.—Exchange rate at 100° *vs.* phosphoric acid concentration. Points are experimental; solid curve represents equation 7; dashed curves show contributions of components of equation 7.

The form of the rate expression (equation 7) is consistent with exchange occurring *via* three paths, direct oxygen exchange between water and H_3PO_4 (first term), reversible formation and hydrolysis of $H_4P_2O_7$ (second term) and reversible formation and hydrolysis of $H_5P_3O_{10}$ (third term). For this interpretation it is assumed that the activity coefficients of the transition states for the three paths do not vary with phosphoric acid concentration, at least in the ranges in which the terms make important contributions.

The decrease in activation energy with increasing phosphoric acid concentration (Table IV) also suggests a change in mechanism with concentration.

Other empirical rate expressions which give fair fits of the exchange data are

$$\text{Rate} = k_4c_1^2/c_w \qquad (8)$$

$$\text{Rate} = k_5(a_1/a_w)^{1/2} \qquad (9)$$

$$\log\text{(Rate)} = 0.62\,(-H_0) + k_6 \qquad (10)$$

H_0 is the Hammett acidity function,[11] values for which were obtained by extrapolation of the data of

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[11] L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935).

Gel'bshstein, *et al.*[12] None of these rate expressions account for the observation that the rate of exchange and the rate of $H_4P_2O_7$ hydrolysis are nearly equal in concentrated phosphoric acid solution.

Appendix

The activity of water in phosphoric acid solutions at 100° was calculated from vapor pressure data.[13,14] The activity of H_3PO_4 was calculated from the water activity by the usual method[15] modified to include three components because of the presence of appreciable amounts of $H_4P_2O_7$ in the concentrated solutions. The modified relationship is

$$\ln \frac{a_1}{a_1'} = \int_{N_w'}^{N_w} \frac{(2N_w + N_1 - 1)}{(2N_w + N_1 - 2)} \, d \ln a_w \qquad (11)$$

in which a and N refer to activity and mole fraction, respectively, the subscripts 1 and w denote the quantities for H_3PO_4 and H_2O, respectively, and the primes denote the quantities at the selected reference point $N_1 = 0.05$. The integration was performed graphically. Table VI gives the results.

TABLE VI

ACTIVITIES AT 100°

(H_3PO_4),	a_w [a]	a_1 [b]
6.0	0.770	0.355
8.0	.625	1.09
10.0	.480	2.75
12.0	.315	7.70
14.0	.158	20.1
15.0	.102	29.3
16.0	.061	40.8
17.0	.0360	51.0
17.5	.0230	57.8
18.0	.0135	63.0
18.5	.00667	67.0

[a] Water is the standard state. [b] Relative values; a_1' (at $N_1 = 0.05$) arbitrarily taken as 0.05.

The values at 100° of the constants appearing in the various rate expressions are

$k_1 = 3.8\ (10^{-5})$ g. atom/l. sec.
$k_2 = 2.4\ (10^{-7})$ g. atom/l. sec.
$k_3 = 4.5\ (10^{-12})$ g. atom/l. sec.
$k_4 = 1.4\ (10^{-5})$ sec.$^{-1}$
$k_5 = 2.1\ (10^{-5})$ g. atom/l. sec.
$k_6 = -5.33$

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[12] A. I. Gel'bshstein, G. G. Shcheglova and M. I. Temkin, *Akad. Nauk Doklady, SSSR*, **107**, 108 (1956).

[13] "Phosphorus, Properties of the Element and Its Compounds," TVA, Chem. Eng. Rep. No. 8, Wilson Dam, Alabama, 1950, p. 45.

[14] M. M. Striplin, Jr., *Ind. Eng. Chem.*, **33**, 910 (1941).

[15] I. M. Klotz, "Chemical Thermodynamics," Prentice-Hall, Inc., New York, N. Y., 1950, p. 296.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA RADIATION LABORATORY]

The Heats of Formation at 25° of the Crystalline Hydrides and Deuterides and Aqueous Hydroxides of Lithium, Sodium and Potassium[1]

BY STUART R. GUNN AND LEROY G. GREEN

RECEIVED SEPTEMBER 19, 1957

The heats of reaction with water have been measured at 25° for lithium, sodium and potassium and for their hydrides and deuterides. The values determined, in kcal./mole, are: $M(c) + 1001\ H_2O(l) = MOH\cdot 1000H_2O + {}^1/_2H_2(g)$, $\Delta H^0_{Li} = -53.142 \pm 0.019$, $\Delta H^0_{Na} = -44.069 \pm 0.006$, $\Delta H^0_K = -46.900 \pm 0.010$; $MH(c) + 1001H_2O(l) = MOH\cdot 1000H_2O + H_2(g)$, $\Delta H^0_{Li} = -31.476 \pm 0.018$, $\Delta H^0_{Na} = -30.582 \pm 0.019$, $\Delta H^0_K = -33.081 \pm 0.005$; $MD(c) + 1001H_2O(l) = MOH\cdot 1000H_2O + HD(g)$, $\Delta H^0_{Li} = -31.321 \pm 0.007$, $\Delta H^0_{Na} = 30.693 \pm 0.004$, $\Delta H^0_K = -33.625 \pm 0.004$. The thermochemical crystal energies are calculated and compared with electrostatic crystal energies.

There are few data in the literature concerning the heats of formation of the isotopic metal hydrides. The only calorimetric values are those for uranium hydride, deuteride and tritide, determined by Abraham and Flotow.[2] Sollers and Crenshaw have investigated the dissociation pressures of the hydrides and deuterides of sodium and potassium.[3,4] For both of the elements, the dissociation pressure of the deuteride is greater than that of the hydride, and the heats of formation calculated from the temperature coefficients in the vicinity of 300° are, in kcal./mole, NaH, −14.44; NaD, −15.80; KH, −14.15; KD, −14.45. Tronstad and Wergeland[5] report that the dissociation pressure of LiH is greater than that of LiD.

The purpose of this investigation was to secure accurate thermochemical values of the heats of formation of the crystalline alkali metal hydrides and deuterides in order that the effect of isotopic substitution upon the lattice energy might be compared with the difference in electrostatic energy resulting from the changed lattice spacing. The procedure consisted of measurement of the heats of reaction of the metals, hydrides and deuterides with water, the heat of formation of the hydrides and deuterides then being calculated from the difference in the heats of reaction. From the heats of hydrolysis of the metals, the heats of formation of the aqueous hydroxides, and consequently also of the aqueous metal ions, were determined with a precision considerably greater than previously has been reported.

Experimental

The Calorimeter.—The calorimeter used in this work is described in greater detail elsewhere.[6] It consists of a gold-

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] B. M. Abraham and H. E. Flotow, THIS JOURNAL, **77**, 1446 (1955).

[3] E. F. Sollers and J. L. Crenshaw, *ibid.*, **59**, 2724 (1937).

[4] E. F. Sollers and J. L. Crenshaw, *ibid.*, **59**, 2015 (1937).

[5] L. Tronstad and H. Wergeland, *Kgl. Norske. Videnskab. Selskab. Forh.*, **10**, No. 10, 36 (1937).

[6] S. R. Gunn, *Rev. Sci. Instruments*, **29**, 377 (1958).