alyzed water to hydrogen, which was collected in a gasometer. No significant amounts of hydrogen were ever obtained. Experiments which will be described later have shown that no water is formed by the action of liquid ammonia on inulin at room temperatures.

Tyndall Effect in Liquid Ammonia Solutions of Inulin

Qualitative information regarding the relative size of the dissolved particles of inulin and the disaccharides in liquid ammonia was obtained with the use of a Tyndallmeter, constructed in the following manner.

The light source, a photo flood lamp, was mounted at one end of a wooden box, 110 cm. long and 10 × 10 cm. in cross section. A mirror at the other end reflected the light upward and at right angles to the incident beam, so that it passed lengthwise through the sealed tube containing the ammonia solution under examination. A lens between the mirror and the source was so adjusted that the light was brought to a focus about 3 cm. above the base of the ammonia tube. The intensity of the light was measured by photographic means. Neither the camera nor the meter was moved during the course of the experiments. The films and prints were uniformly exposed and developed.

Filtered liquid ammonia solutions of the sugars were prepared in the following manner. A long soft glass tube was constricted at the middle, and two small stopcocks sealed on as side tubes close to the constriction and on either side. A sintered Jena filter plate of finest porosity was ground into the constriction with emery and a solution of camphor in turpentine, and cemented in place with strong sodium silicate solution. Sugar, after thorough drying, was placed in one end of the tube (which was likewise carefully dried) and both ends of the tube sealed in a current of ammonia. Ammonia was distilled in to dissolve the specimen, the solution being forced through the filter by inverting the tube and cooling the empty half. It was immediately placed on the Tyndallmeter and photographed. (The concentration of the solutions was about 0.5%.) Solutions of sucrose and lactose were almost optically clear, but usually gave very slight Tyndall cones in spite of many filtrations, presumably because of material not retained by the filter. Solutions of inulin on the other hand gave very pronounced Tyndall cones, suggesting again the presence of colloidal particles.

Summary

Inulin, in liquid ammonia solution, behaves as a gelating colloid, and not as a difructose anhydride, as claimed by some investigators: since (1) it slowly precipitates on standing, forming a translucent gel; (2) it exhibits the Tyndall effect; and (3) it will not diffuse through a cellophane membrane, while sucrose does so readily.

STANFORD UNIV., CALIF. RECEIVED MAY 14, 1937

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 592]

Measurement of a Reaction Rate at Equilibrium by Means of a Radioactive Indicator. The Reaction between Arsenic Acid and Iodine

BY J. NORTON WILSON AND ROSCOE G. DICKINSON

In the study of chemical kinetics and equilibrium, it is customary to correlate the specific rates k_f and k_r for a pair of forward and reverse reactions with the corresponding equilibrium constant K, in accordance with the equation

$$k_f/k_r = K$$

In making empirical tests of this relation, however, the specific rates k_f and k_r are in general measured with the system considerably displaced from equilibrium in order that accurate values may be obtained more easily. Hence it is of interest to appreciate that such methods do not eliminate the possibility that k_f and k_r might actually change as equilibrium is approached, but in such a way as to keep the ratio k_f/k_r approximately constant. The use of radioactive indicators, which have become an important chemical tool, permits the measurement of rates at equilibrium and thus makes it possible to place the kinetic theory of equilibrium on a sounder experimental foundation.

In the present paper are described some experiments involving reactions on which previous rate[1] and equilibrium[2] measurements have been made by customary methods; these reactions are the oxidation of arsenious acid by iodine, and its reverse

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H^+ \qquad (1)$$

Experimental Procedure.—A radioactive arsenic with a half period of twenty-six hours is formed from ordinary arsenic by neutron capture.[3] To utilize this we exposed 15 to 20 g. of pure crystalline arsenic (Kahlbaum) for two to three days to a radon–beryllium source of neutrons whose initial strength was 200 to 300 millicuries; the exposure occurred in a large block of paraffin. The arsenic

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(1) J. R. Roebuck, *J. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905); W. C. Bray, *ibid.*, **9**, 578 (1905); H. A. Liebhafsky, *ibid.*, **35**, 1648 (1931).

(2) E. W. Washburn and E. K. Strachan, *ibid.*, **35**, 681 (1913).

(3) F. A. Paneth and J. W. J. Fay, *Nature*, **135**, 820 (1935).

was then burned to arsenious oxide in a stream of air and a weighed amount of oxide dissolved in a measured volume of 1 *N* standard sodium hydroxide solution, which was then diluted to the desired concentration. The reaction mixtures were then prepared from standard solutions of arsenic acid, hydrochloric acid, and the radioactive arsenite.

The mixtures so prepared were brought to thermostat temperature and a measured volume of standard potassium iodide at the same temperature was added. The mixtures were such that at equilibrium comparatively little free iodine should be present. The color due to free iodine developed immediately on the addition of the potassium iodide and became constant within a minute or two, indicating a rapid approach of equilibrium.

The solutions were kept at a temperature constant to within 0.1° for a measured period of from four to seventeen hours. During this period exchange of radioactive arsenic between the tri- and pentavalent states occurred presumably through reactions with iodide and iodine. The exchange was then quenched by dilution with water and addition of an excess of ammonium hydroxide sufficient to make the solution 0.6 *N* in the latter reagent. The arsenate was then immediately precipitated as magnesium ammonium arsenate by the addition of magnesium–ammonium nitrate solution. The precipitate was washed with 0.6 *N* ammonium hydroxide, filtered, dried, and ignited to magnesium pyroarsenate which was then ground to a fine powder.

A fixed weighed amount of the powder was placed in a shallow cylindrical depression 0.1 cm. deep and 5 cm. in diameter in a thick sheet of brass; the powder was pressed down to fill the depression fully and evenly. The brass sheet was then placed in a reproducible position under a quartz fiber electroscope and the activity of the arsenic measured. Separate fillings of the brass container gave results with a maximum deviation from the mean of about 3% of the net activity. The electroscope was calibrated for linearity of scale. Natural leak was measured frequently and corrected for.

About one-fifth of the original radioactive arsenite solution was oxidized to arsenate with sodium hypobromite and was then precipitated, ignited, and its activity measured just as with the exchange samples. All activities were corrected to the same time using the half period twenty-six hours.

In some preliminary experiments the usual reaction mixtures containing arsenate, radioactive arsenite, and hydrochloric acid were made up with the omission of iodide. Even after the solution was boiled for three hours, the subsequently precipitated arsenate exhibited no activity. This shows that any direct exchange between the tri- and pentavalent arsenic is negligibly slow, and that the method of separating the arsenate did not itself induce exchange. Incidentally, a similar lack of exchange in alkaline solution (~1 *N* sodium hydroxide) was also found after three hours of boiling.

Treatment of Results

In the experiments described here, the initial concentrations of trivalent and pentavalent arsenic were not significantly different from the equilibrium concentrations, and it is assumed that substantially all of the exchange occurred under equilibrium conditions; further justification for this is given below. We shall accordingly first obtain relations valid for the case where the initial solution is at chemical equilibrium.

Let α and β be the respective fractions (corrected for radioactive decay) of pentavalent and trivalent arsenic which are radioactive at any time t measured from the beginning of exchange; if initially only the trivalent arsenic is radioactive then at $t = 0$, $\beta = \beta_0$ and $\alpha = 0$. Let $(\mathrm{As^V})$ and $(\mathrm{As^{III}})$ be the total concentrations (at. wts. × vol.$^{-1}$) of arsenic in the respective valence states. The total concentration of radioactive arsenic (corrected for decay) is $\alpha(\mathrm{As^V}) + \beta(\mathrm{As^{III}})$; since this remains constant, it follows that

$$\alpha(\mathrm{As^V}) + \beta(\mathrm{As^{III}}) = \beta_0(\mathrm{As^{III}}) \tag{2}$$

Let R be the (constant) rate (atomic wts. × vol.$^{-1}$ × time^{-1}) at which arsenic passes from the trivalent to the pentavalent state or the reverse. Without reference to the orders of the reactions involved, the rate at which radioactive pentavalent arsenic is formed is given by the rate R at which trivalent arsenic passes to the pentavalent state multiplied by the fraction β of trivalent arsenic which is radioactive, *i. e.*, βR. Similarly the rate at which radioactive pentavalent arsenic disappears is αR. The net rate at which the concentration $\alpha(\mathrm{As^V})$ of pentavalent radioactive arsenic increases is the difference between these two terms, *i. e.*

$$(\mathrm{d}\alpha(\mathrm{As^V})/\mathrm{d}t) = (\beta - \alpha)R \tag{3}$$

Writing $(\mathrm{As}) = (\mathrm{As^{III}}) + (\mathrm{As^V})$, and substituting for β from (2), we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{R}{(\mathrm{As^V})}\left[\beta_0 - \frac{(\mathrm{As})}{(\mathrm{As^{III}})}\,\alpha\right] \tag{4}$$

Integrating, and inserting the condition $\alpha = 0$ at $t = 0$

$$R = -\frac{1}{t}\,\frac{(\mathrm{As^V})(\mathrm{As^{III}})}{(\mathrm{As})}\ln\left[1 - \frac{\alpha}{\beta_0}\,\frac{(\mathrm{As})}{(\mathrm{As^{III}})}\right] \tag{5}$$

Since α/β_0 as well as the other quantities on the right are measurable, R may be calculated for the particular solution used. In the present experiments the quantity α/β_0 has been taken as the ratio of the electroscopic activity of pyroarsenate from a solution which has exchanged for a time t to that of pyroarsenate from the original unexchanged arsenite.

On the assumption that a given arsenic atom passed from one valence state to another only through oxidation or reduction by iodine or iodide, the rate R may now be identified with the rate of the oxidation of arsenious acid by iodine or the equal rate of reduction of arsenic acid by iodide.

The results of such experiments are given in the table. Columns 2 to 6 give the empirical composition of the solutions as made up. The empirically measured rates are given in moles × liters^{-1} × min.$^{-1}$ in the column headed R.

MEASUREMENT OF THE RATE OF
OXIDATION AND REDUCTION AT EQUILIBRIUM AND THE CALCULATION OF SPECIFIC RATE CONSTANTS

	Formula weights per liter											
No.	H_3AsO_3	H_3AsO_4	HCl	NaCl	KI	$(I^-)_e$	$(I_3^-)_e$	Activity, α/β_0	Time t, min.	Rate R $\times 10^5$	Temp., °C.	$k \times 10^2$, corr.
1	0.120	0.119	0.130	0.121	0.0091	0.0091	2.5×10^{-7}	0.062	952	0.85	25.0	6
2	.114	.113	.236	.114	.0086	.0086	6.5×10^{-7}	.072	617	1.43	25.0	6.2
3	.107	.100	.196	.100	.0408	.0407	4.5×10^{-5}	.226	555	5.38	25.2	6.7
4	.105	.098	.107	.100	.100	.099	1.9×10^{-4}	.333	732	7.80	25.2	7.4
5	.125	.273	.098	.081	.100	.099	4.5×10^{-4}	.265	789	20.3	24.6	7.9
6	.125	.406	.098	.081	.100	.098	7.1×10^{-4}	.208	657	31.1	24.6	8.2
7	.125	.203	.098	.081	.100	.099	2.6×10^{-4}	.280	839	12.6	24.6	6.5
8	.125	.273	.163	.081	.100	.097	1.0×10^{-3}	.212	361	27.8	24.6	6.6
9	.107	.099	.196	.100	.0405	.0403	6.1×10^{-5}	.256	278	12.6	35.0	16.1
10	.105	.098	.107	.100	.100	.099	3.1×10^{-4}	.350	408	14.1	35.0	13.7
11	.151	.096	.079	.074	.0536	.0536	1.8×10^{-5}	.342	713	6.75	35.1	16.5
12	.151	.096	.237	.074	.0107	.0107	1.2×10^{-6}	.231	1001	2.78	35.1	11.3

In the columns headed $(I_3^-)_e$ and $(I^-)_e$ are given the concentrations of I^- and of I_3^- in the various solutions at equilibrium. These were calculated for the runs at 25° using the constant[2]

$$K = \frac{(H_3AsO_4)(H^+)^2(I^-)^3}{(H_3AsO_3)(I_3^-)} = 5.5 \times 10^{-2}$$

For the runs at 35° a value of K (3.8×10^{-2}) was estimated from that at 25°, and that at 0° (1.6×10^{-1}) measured by Roebuck.[1] Here (H_3AsO_4) and (H_3AsO_3) have been taken as (As^V) and (As^{III}), respectively, and (H^+) as the formal concentration of hydrochloric acid. This is adequate since $(I_3^-)_e$ was in all cases small and is needed only to calculate a small correction to $(I^-)_e$ and to show the small amount of reaction required to reach chemical equilibrium.

A more detailed analysis of the rate of exchange which considered the fact that I_3^- was initially absent rather than at its equilibrium concentration, led to an expression similar to (5) but with t replaced by $t - (1/a)(1 - e^{-at})$ where $a = R/(I_3^-)_e$. Because of the small values of $(I_3^-)_e$ in the experiments the use of this expression gives values of R differing by less than 1% from those given by equation (5).

The assumption that radioactive exchange occurred only through iodine-iodide reduction and oxidation may be tested by determining whether the rates of exchange depend on concentrations in the manner to be expected from Roebuck's kinetic studies. In order to do this, we have calculated specific rate constants for the reduction of As^V by placing $R = k(H_3AsO_4)(H^+)(I^-)_e$ the right-hand member being Roebuck's expression. As was done by Roebuck, we have taken $(H_3AsO_4) = (As^V)$ and (H^+) as the formal hydrochloric acid concentration. The values of k thus obtained are given in moles^{-2} × liters^2 × min.$^{-1}$ under k (corr.); a small temperature correction to 25° (or 35°) has been applied when the experiments were made at temperatures slightly different from these. At a given temperature the values of k show reasonably good constancy.

The assumptions may be further examined by comparing the absolute values of the constants with those of Roebuck.[1] As recalculated by Liebhafsky, Roebuck's measurements of this specific rate give the values 6.3×10^{-3} at 0° and 1.6×10^{-2} at 10° (units: moles^{-2} × liters^2 × min.$^{-1}$). If these be extrapolated to 25° using the Arrhenius equation, the value 0.057 is obtained in satisfactory agreement with the mean value 0.071 from the exchange measurements; extrapolated to 35°, Roebuck's values give 0.125 and the exchange measurements 0.154.[4] The Arrhenius heat of activation is calculated from Roebuck's measurements to be 14,300 cal. per mole; the exchange measurements give the value 14,100. It appears then that the radioactive exchange occurs mainly through the oxidation and reduction of the iodine, and that the kinetics of the oxidation and reduction at equilib-

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(4) In calculating the mean values of k the results of experiments 1 and 2 have been omitted because of the small precision of α/β_0; experiment 12 also has been omitted.

rium are the same as those remote from equilibrium.

The authors are indebted to the W. K. Kellogg Radiation Laboratory at this Institute for the preparation of neutron sources used in this investigation.

Summary

Radioactive trivalent arsenic does not exchange with non-radioactive pentavalent arsenic in dilute acid or alkaline solutions in the absence of other easily oxidizable or reducible substances. In the presence of iodine in acid solution, however, an exchange takes place at a measurable rate. On the assumption that the exchange occurs through the oxidation and reduction of the iodine, we have calculated the rates of oxidation and reduction at chemical equilibrium from measurements of rates of exchange in systems containing iodide ion and small amounts of free iodine. The rates of oxidation and reduction measured in this way are in agreement with the kinetic expressions shown by Roebuck to hold for the same reactions remote from equilibrium, and lead to specific rate constants which agree with those measured by him.

PASADENA, CALIF. RECEIVED APRIL 7, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Effect of Iodine on the Rate of Decomposition of Ethylene Oxide

BY R. FRANCIS FAULL AND G. K. ROLLEFSON

In a previous investigation on the effect of iodine on the decomposition rate of acetaldehyde and propionaldehyde,[1] it was found that the decomposition mechanism could be divided into two parallel sets of reactions. The rate-determining step of the first set was a simple bimolecular reaction which depended only on the square of the initial iodine concentration. The second set consisted of a series of reactions such that the rate was first order with respect to the aldehyde concentration and one-half order with respect to the initial iodine concentration. This second series of reactions was essentially the catalysis of the decomposition of the aldehydes by free radicals and iodine atoms. Because the thermal decomposition of ethylene oxide was known to be free from reaction chains induced by free radicals,[2,3] the iodine catalyzed decomposition of ethylene oxide offered an interesting possibility to test the steady state theory advanced in the earlier paper.

At temperatures above 350° the addition of small amounts of iodine is found to cause a marked catalysis in the decomposition of gaseous ethylene oxide. Some typical results at 392.5° are shown in Fig. 1. The pressure increase is plotted as the ordinate against time as the abscissa. It is evident that during the major portion of the reaction the rate is independent of the concentration of the ethylene oxide. This steady state condition is in accord with the theory already advanced.

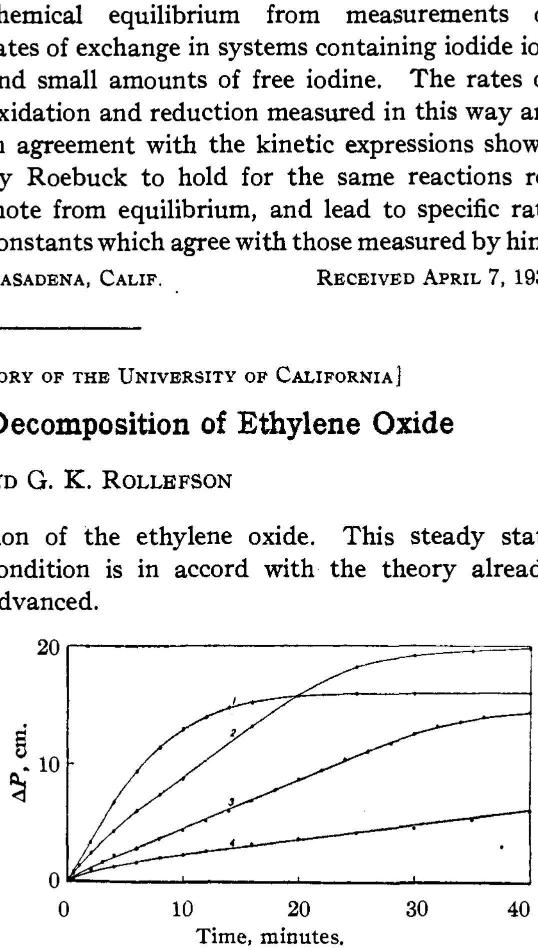

Fig. 1.—The curves show typical experiments at 392.5°. The initial concentrations are as follows:

Experiment	Ethylene oxide, cm.	Iodine, cm.
1	20.15	2.15
2	24.75	1.50
3	22.00	0.95
4	20.85	.65

The apparatus used and the experimental procedure were similar to that adopted in the aldehyde investigation. An analysis of the gaseous products was made using the methods of Leighton.[4-6] The results are summarized in Table I. The methane was identified by showing that combustion of the hydrocarbon gas left after the removal of carbon monoxide yielded two moles of water to one of carbon dioxide.

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[1] Rollefson and Faull, THIS JOURNAL, **59**, 625 (1937).

[2] Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935, p. 161.

[3] Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936).

[4] Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

[5] Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933).

[6] Blacet and MacDonald, *ibid.*, **6**, 334 (1934).