librium with liquid at 25°. At about 40°, according to the same authors, the water film is less than one molecule deep, so it is safe to assume in the experiments made under the conditions of Expts. 25, 2, 7, 27 and 36, that there was a very small moisture content, less than a monomolecular layer. The above considerations emphasize our meager knowledge of the mechanism of gaseous reactions. The study of the oxidation of nitric oxide at lower pressures will be continued by means of a motion-picture camera in order to gain some insight in regard to the induction period.

Summary

1. Moisture catalyzes the reaction between nitric oxide and oxygen. The decrease in velocity with a paraffin surface has been interpreted as due to a decreased amount of moisture. Water vapor produces a maximum increase of speed of 50% over that in a paraffin-lined vessel.
2. Sulfur dioxide and the reaction product have practically no effect on the speed of reaction.
3. An induction period with a duration of ten seconds has been noted at initial partial pressures of the gases below about 14 mm. of mercury.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 181]

THE UNIMOLECULARITY OF THE INVERSION PROCESS

BY GEORGE SCATCHARD

RECEIVED MARCH 20, 1926 PUBLISHED SEPTEMBER 4, 1926

If the rate of a reaction be defined as that fraction of a reactant present in the system which reacts in unit time, this definition may be expressed mathematically as

$$R = \frac{-\mathrm{d}y/y}{\mathrm{d}t} = \frac{-\mathrm{d}\,ln\,y}{\mathrm{d}t} \tag{1}$$

in which R is the rate, t is the time and y is the quantity of the reactant in the system at the time t. Since y occurs in a ratio or in a logarithm, it may be expressed in any units—as mass, as moles or, corresponding to the quantity actually measured in most inversion experiments, as $\lambda - \lambda_\infty$, where λ is the optical rotation in a tube of any definite length, and the subscript ∞ refers to complete inversion. It is somewhat more convenient to work with another quantity, r, defined by the equation

$$r = 0.4343\,R = \frac{-\mathrm{d}\log y}{\mathrm{d}t} \tag{2}$$

It is customary, for unimolecular reactions, to assume that the rate as defined above is constant and to integrate Equations 1 or 2 to determine the numerical value of the rate. However, the very accurate measurements of Pennycuick[1] indicate that the rate of inversion of sucrose increases slightly during the course of the reaction. Therefore, the classical integrated expression should not be applied to these measurements, and Equation 2 cannot be integrated unless r be known as a function of t.

The rate at any time may be obtained by determining the slope of a smooth curve through the points obtained by plotting $-\log y$ against t. The accuracy of this method may be very considerably increased by plotting $-At - \log y$ against t, in which case r is A plus the slope of the curve. A is most conveniently chosen as $(-\log y)/t$ for the last measurement. For Pennycuick's measurements in the more dilute solutions the time interval is so large that even this method is less accurate than the precision of the experimental work warrants. In such a case $-At - \log y$ may be plotted against $\sqrt{t}$, and the slope of the curve so obtained divided by $2\sqrt{t}$ added to A to give r [since $\mathrm{d}x/\mathrm{d}t = (\mathrm{d}x/\mathrm{d}\sqrt{t})(\mathrm{d}\sqrt{t}/\mathrm{d}t) = (\mathrm{d}x/\mathrm{d}\sqrt{t})/(2\sqrt{t})$].

TABLE I

CHANGE OF REACTION RATE WITH FRACTION INVERTED

	0.02 *N* HCl[a]	0.099 *N* HCl	0.507 *N* HCl	0.905 *N* HCl
	40°	35°	35°	35°
k =	0.000605	0.001629	0.01045	0.02301
Fraction inverted	r/k	r/k	r/k	r/k
0.05	0.982	0.974	0.962	....
.10	.989	.978	.967	0.966
.20	.995	.984	.971	.969
.30	.998	.987	.975	.972
.40	1.000	.990	.978	.973
.50	1.000	.995	.981	.974
.60	1.000	.999	.983	.976
.70	1.000	1.000	.985	.979
.80	1.000	1.000	.986	.980
.90	1.000	1.000	.988	(0.978)

[a] In each case the concentration of sucrose is 171 g. per liter.

In Table I are given the rates obtained by applying this method to the measurements of Pennycuick divided by appropriate constants, k, for certain fractions of sucrose inverted. With 0.92 *N* acid the rate is constant within 0.1% after the sucrose is 35% inverted; with 0.099 *N* acid a constant value is not reached until 60% is inverted; the rate with 0.507 *N* acid increases continually; and the rate with 0.905 *N* acid passes through a maximum at 80% inversion. This last phenomenon is probably due to a small error in the determination of the rotation at complete inversion caused by side reactions in the presence of the strong acid. The rates in 0.907 *N* acid after 80% inversion are enclosed in parentheses, and are disregarded in the discussion that follows.

Table II contains the same ratios as Table I, but for definite time in-

---

[1] Pennycuick, THIS JOURNAL, **48**, 6 (1926).

TABLE II

CHANGE OF REACTION RATE WITH TIME

Time, minutes	0.02 *N* HCl r/k	0.099 *N* HCl r/k	0.507 *N* HCl r/k	0.905 *N* HCl r/k	Eq. 3 r/k
5	....	0.969	0.967	0.971	0.971
10	....	.973	.971	.973	.973
20	0.974	.975	.976	.976	.975
30	.978	.978	.981	.980	.978
40	.982	.981	.983	(0.978)	.980
60	.987	.984	.986	(0.976)	.984
80	.989	.986	.986	....	.987
100	.992	.988	.988		.989
150	.994	.992	....		.993
200	.996	.996			.996
300	.999	1.000			.998
400 to end	1.000	1.000			1.000

tervals after the start of the reaction. The last column contains the ratio calculated by the equation

$$r = k(1 - 0.03\,e^{-0.01t}) \tag{3}$$

The form of Equation 3 and the values of the numerical constants were obtained empirically from the results for the two solutions more dilute in acid, for which the values of k must be the final values of r. Then Equation 3 was used to determine k for the two more concentrated solutions. The agreement is very good. The maximum deviation of the measured rates from those calculated is 0.4%, and the average deviation is 0.13%. A comparison of the two tables shows clearly that the rate is a function, not of the fraction inverted, but of the time.

Combining Equations 2 and 3, we may integrate between the time limits 0 and t, or between t_1 and t_2, to obtain

$$\log \frac{y_0}{y} = k[t - 3(1 - e^{-0.01t})] = kt\left[1 - \frac{3}{t}(1 - e^{-0.01t})\right] \tag{4}$$

$$\log \frac{y_1}{y_2} = k[t_2 - t_1 - 3(e^{-0.01t_1} - \epsilon^{-0.01t_2})]$$

$$= k(t_2 - t_1)\left[1 - \frac{3}{t_2 - t_1}(e^{-0.01t_1} - e^{-0.01t_2})\right] \tag{5}$$

These expressions divided by t or by (t_2-t_1) correspond to the classical "specific reaction rate" or "velocity constant." Equation 4 may be compared with the experimental measurements independently of the graphic determination of the slopes. The mean deviations of the average "constants" from those computed by Equation 4 are for the four series: 0.5, 0.3, 1.2 and 0.8%, but the deviations for very short time intervals indicate a constant time error. If the average values be corrected by subtracting from the times the quantities: 0.2, 0.0, 0.1, 0.05 minutes, the mean deviations become: 0.3, 0.3, 0.4, 0.4%, without any trend with time. For the first two series the mean deviation of the individual measurements from their averages is 0.2 and 0.5%, so the agreement with the theory is as good as could be expected, and the time correction does not attribute an unreasonable error to the determination of the time of a reaction started by pouring one solution into another and stopped by pouring through a cooling coil.

From the nature of the change in rate it is possible to draw several conclusions as to the cause of the change. In the graphical method the start of the reaction is treated as any other point on the curve, and any error in the initial rotation or in the time of starting the reaction is completely eliminated after the first few measurements. For the same reason a constant time error, due to the reaction continuing a little during the cooling, would also be without effect. The time error indicated by the integrated Equation 4 is discussed above. There can be no significant error in the final rotation, except for the values enclosed in parentheses, for such an error would give a more rapid change toward the end of the reaction. Lack of thermal equilibrium because of heat produced or absorbed during the reaction would give a larger effect for the more rapid reactions and is therefore excluded.

The increase in rate cannot be caused by a change in the environment as the concentration of sucrose decreases and that of inert sugar increases, for such a change would persist throughout the reaction and would be nearly independent of the acid concentration. Table I shows clearly that the change in reaction rate fulfils neither of these criteria.

Equation 3 may be explained by the attainment of equilibrium in a process originally somewhat displaced from equilibrium for which the rate of attaining equilibrium is proportional to the displacement. This is more clearly shown in the differential form

$$dr/dt = 0.01\ (k - r) \qquad (6)$$

Two causes for such a change suggest themselves. The temperature of the solution might be lower than that of the thermostat at the start of the reaction. This explanation would demand that the temperature be 0.2–0.3° too low after 40 minutes in the thermostat, and that five hours be required to attain thermal equilibrium. It is, therefore, highly improbable. The mixing of the solutions might not be quite complete at the start, and true homogeneity might be attained only by diffusion. Five hours does not appear too long for this process, and it seems very probable that pouring the solutions from one flask to another does not result in absolutely complete mixing. It may be concluded that Equations 3 to 6 are characteristic of the technique of Pennycuick but not of the inversion process, and that the rates of inversion do not change more than a few tenths of a per cent. during the course of the reaction. The most probable values of the rates are the *k*'s given in Table I, even for the cases where the measured rates never attain these values.

In the paper of Pennycuick the results are expressed by the classical "reaction velocity," which may be shown from Equations 3 and 4 to change more uniformly than the rate, and the conclusion is reached that the change is due to increasing activity coefficients of the hydrogen ion and of the sucrose. It has been shown above that the present more precise treatment makes these conclusions untenable. The evidence for the increase in the hydrogen-ion activity appears sound, but these results indicate that there must be some compensating tendency to diminish the rate. It is much less certain that the activity coefficient of the sucrose increases during the inversion. The point of view of Pennycuick's paper is very similar to that presented by Moran and Lewis[2] except that other factors considered in the earlier paper are not discussed in the more recent one. This point of view has been criticized in detail in earlier papers.[3]

Summary

The precise measurements by Pennycuick of the rate of inversion of sucrose have been treated by a mathematical method more accurate than any hitherto applied to reaction rates. The rates have been determined graphically and an equation has been derived relating the change of rate to the time of reaction. From the nature of the change in rate it is shown that several possible experimental errors give no disturbance, and that the change cannot be due to a change in the environment but is most probably due to slightly inefficient mixing. It is concluded that in homogeneous solutions the rates of inversion are constants within a few parts per thousand, and the most probable values of these rates are given.

Cambridge, Massachusetts

[Contribution from the Chemistry Laboratory of the University of California]

SOME THERMODYNAMIC PROPERTIES OF ELECTROLYTES IN ACETIC ACID AND IN LIQUID AMMONIA

By T. J. Webb[1]

Received May 12, 1926 Published September 4, 1926

The freezing-point lowerings and other colligative properties of non-aqueous solvents, interpreted on the basis of ideal-solution relationships, led to the idea that electrolytes exist in a large number of non-aqueous solvents as simple molecules in equilibrium with associated molecules and with a small number of the ions of the electrolyte. At different concentrations, variations in the value of the colligative properties from that demanded by the laws of ideal solutions, were attributed to a shift in the equilibrium between ions, simple molecules and polymerized molecules. That such equilibria exist and that variations in the number of each molecu-

---

[2] Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922).

[3] Scatchard, This Journal, **43**, 2387, 2406 (1921); **45**, 1580 (1923).

[1] National Research Fellow.