

SpaceTime Yield and Reaction Rate

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expansion of the dipole moment of the pair of molecules $A \cdot B$ such as⁴

$$(\frac{d\alpha}{dq_i})_A \cdot (\frac{d\mu}{dq_k})_B \text{ and } (\frac{d\mu}{dq_i})_A \cdot (\frac{d\alpha}{dq_m})_B$$

with the q 's being the normal coordinates for all possible vibrations of the molecules A and B and with α and μ the polarizabilities and the dipole moments of both molecules. This new kind of molecular spectrum can only be observed in those cases where both components are sufficiently transparent in relative thick layers. However, in those cases this method of investigation permits the observation in absorption in the rock salt or LiF region of low frequencies which are difficult to investigate with the ordinary infrared absorption technique. In comparison with the Raman effect it permits observations on colored or photochemically unstable substances in small quantities.

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¹ J. Fahrenfort and J. A. A. Ketelaar, *J. Chem. Phys.* **22**, 1631 (1954).

² Coulon, Rosin, and Vodar, *Compt. rend.* **240**, 956 (1955).

³ J. A. A. Ketelaar and F. N. Hooge, *J. Chem. Phys.* **23**, 749 (1955).

⁴ J. Fahrenfort, thesis, University of Amsterdam, 1955; J. A. A. Ketelaar, *Rec. trav. chim.* (to be published).

Mobility and Quantum Yield of Charge Carriers in Crystal Violet*

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(Received May 16, 1955)

WHEN a small portion of an extensive crystal violet film well removed from one or both electrodes is illuminated, the observed increase of conductance is only a few percent of that expected if the same energy were uniformly distributed over the whole surface. Since the material is a good insulator and the mobility in the dark part of the film is low due to the large number of traps, the secondary effect of illumination of a small area is to cause the field across it to be greatly reduced by space-charge effects, and little change in conductance is seen.

This phenomenon is illustrated by the changes observed while a spot of light is being moved continuously across a cell as shown in Fig. 1A. The rise of conductance is slow until the spot approaches the far electrode and the resistance of the portion remaining unilluminated becomes comparable to that of the part already illuminated; then the voltage drop across the latter begins to rise sharply and there is apparently a burst of conduction.

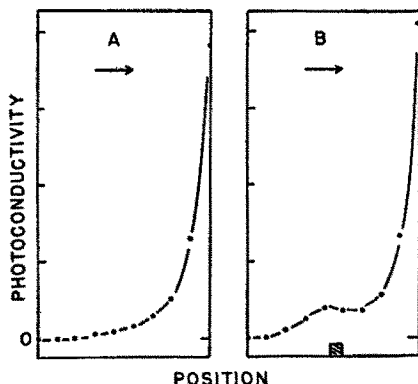


FIG. 1. Conductance in arbitrary units versus position of a light spot being traversed steadily across a cell 6 mm wide, at the rate of 0.17 mm/sec: A, without previous treatment; B, after having been illuminated in a narrow strip having the same relative position as the hatched block. The nominal field is 30 volts/cm.

Since the traversal required 35 seconds, the mobility of carriers in the dark region must be extremely low. This pattern is observed independently of the direction of traversal with respect to electrode polarity, the small asymmetry in detailed shape being consistent with the previous finding that electron conduction predominates.¹

In the experiment of Fig. 1B a narrow transverse zone parallel to the electrodes was illuminated for 30 seconds. Then a spot of light was traversed as before. The same pattern is seen except for a hump on one side of the illuminated area and a flattening at it. The flattening can be attributed to space-charge effects as before, but the hump is most probably due to optical re-excitation of carriers formed during the stationary illumination and trapped in the dark part of the film. The invoking of such a process is not inconsistent with earlier kinetic data for the early stages of illumination, although there is no evidence that they are important when the film is in the steady state in light.

In an earlier note² the writer estimated the quantum yield of charge carriers in pure crystal violet films to be ~ 0.1 based on measurements of the initial rate of rise of conductance in illumination, assuming the carriers to be in thermal equilibrium with the trapping levels, so that only the fraction $\exp(-0.38 \text{ eV}/kT)$ was free. This assumption is strongly suspect not only because of the evidence for optical re-excitation of trapped carriers, but also because studies on impure films having traps of various depths show rather constant initial rise rates. The preferred interpretation of the experiment seems rather to be that during its course a substantial fraction of the carriers was mobile, and that in consequence the quantum yield is more probably of approximate order $\exp(-0.38 \text{ eV}/kT)$ or about 10^{-6} .

This agrees with the conclusion reached for the very similar dye basic fuchsin, that the quantum yield was temperature dependent quite apart from considerations of mobility, with an activation energy of 0.38 eV.¹

* This work was supported by the Charles F. Kettering Foundation.

¹ R. C. Nelson, *J. Chem. Phys.* **22**, 885, 890, 892 (1954).

² R. C. Nelson, *J. Chem. Phys.* **19**, 798 (1951).

Space-Time Yield and Reaction Rate

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SPACE-TIME-YIELD, defined as quantity of product per unit volume per unit time, was recommended by Haber and Greenwood¹ and Rideal and Taylor² as a useful concept in the study of gaseous reactions in continuous flow systems. Recent applications of this concept for calculations of yields,^{3,4} catalyst activity evaluations,^{5,6} and correlation of relative reactivity of a molecular species with structural modifications^{4,7} within the molecule imply a direct proportionality to the rates of reaction. The present communication examines this concept in the light of the rate equations in flow systems. It is shown that space-time yield is a convenient criterion for estimating reaction order, and relative activities of chemical reactants or catalyst surfaces providing certain experimental requirements are fulfilled.

Good treatments of the problems relating to the establishment of rate equations in flow systems are found in the more recent works of Denbigh,⁸ Hulburt,⁹ and Harris.¹⁰ There are three main differences between static and flow systems as far as kinetic treatments are concerned. Reactions in flow systems generally take place under conditions of constant pressure. A volume effect, arising when there is a continuous change in the number of moles of reacting mixture must be considered in the definition of concentration terms. If lateral diffusion of the reactant molecules occurs, the concentration terms must also take this effect into account. In practice the diffusion effect can be made negligible by use of large flow rates, small reactor cross section, moderate temperatures and pressures. For the case of negligible lateral

diffusion, the integrated rate expressions¹⁰ for a first-order reaction are

$$k_1 = \frac{V_0}{V_r} \left[n \ln \left[\frac{N_A}{N_{A0} - \frac{1}{n} N_c} \right] - \frac{n-1}{n} \left(\frac{N_c}{N_{A0}} \right) \right] \quad (1)$$

where V_0 is the velocity of flow of entering mixture, V_r the reactor volume, n the moles of product per mole of reactant undergoing change, N_A , N_c the moles of reactant (A) and product (C) leaving the reaction zone, and N_{A0} the moles of reactant entering per second. If there is no volume change (i.e., $n=1$), and the conversion per pass is small (<10%), this expression simplifies to

$$k_1 = \frac{V_0}{V_r} \left(\frac{N_c}{N_{A0}} \right) \quad (2)$$

where it is readily seen that the concept of space-time-yield (moles product/unit time/unit reaction volume) is realized in the ratio (N_c/V_r) . Thus it follows that if the experiments are effected under conditions of constant input, contact time, temperature, and pressure, the space-time-yield (S.T.Y.) may be expressed in terms of the rate constant by

$$\text{S.T.Y.} = k_1(Q) \quad (3)$$

where $Q = (V_0/N_{A0})$, a constant for the given set of conditions. A direct proportionality thus exists between the space-time yield and the rate constant in the region where the conversions are a measure of the initial rate. From a consideration of the integrated rate expressions^{8,10} for the second-order reactions, an expression quite similar to (3) can be derived, where Q again is a parameter dependent only on the moles of reactants and velocity of flow entering the reaction zone.

A comparison of the space-time yields under comparable conditions in the region of small conversions for two similar processes is thus a direct comparison of the rate constants for the two reactions. Providing the operating conditions are comparable, and the processes are similar, the concept of space-time yield offers a ready means for estimating the order of reaction and comparing activities of catalyst surfaces or chemical reactants.

- ¹ F. Haber and F. C. Greenwood, *Z. Elektrochem.* **21**, 251 (1915).
- ² E. K. Rideal and H. S. Taylor, *Catalysis in Theory and Practice* (MacMillan and Company Ltd. London, 1919), p. 66.
- ³ H. H. Storch, *Advances in Catalysis* (Academic Press, Inc., New York, 1948), Volume II, pp. 132, 147.
- ⁴ G. J. Janz and R. E. Myers, *J. Am. Chem. Soc.* **75**, 1510 (1953).
- ⁵ Janz, Timpane, and McCulloch, *Ind. Eng. Chem.* **45**, 1343 (1953).
- ⁶ G. J. Janz and W. J. G. McCulloch, *J. Am. Chem. Soc.* (to be published).
- ⁷ G. J. Janz and S. C. Wait, Jr., *J. Am. Chem. Soc.* **76**, 6377 (1954).
- ⁸ G. Denbigh, *Trans. Faraday Soc.* **40**, 352 (1944).
- ⁹ H. M. Hulburt, *Ind. Eng. Chem.* **36**, 1012 (1944); **37**, 1063 (1945).
- ¹⁰ G. M. Harris, *J. Phys. & Colloid Chem.* **51**, 505 (1947).

Thermodynamic Properties of the System Methane-Carbon Monoxide at 90.67°K

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THE cell theory applied to solutions¹ predicts a *positive* excess free energy together with a volume *contraction* on mixing if the molecules are spherical and of equal radius, and if, moreover, ϵ_{12}^* is the geometric mean of ϵ_{11}^* and ϵ_{22}^* , where ϵ_{ij}^* is the maximum intermolecular potential energy of a pair ij . We report here briefly the results of experiments designed to test this prediction. These were carried out on the system methane-carbon monoxide since this both fulfils the theoretical requirements and also lends itself to accurate measurement.

The following properties of the condensed system have been measured: (1) the total vapor pressure; (2) the condensation pressure; (3) the volume change on mixing; (4) the virial coefficients of the gases.

All measurements were made at 90.67°K, the triple-point of methane, at which the vapor pressure of methane is 87.85 mm and

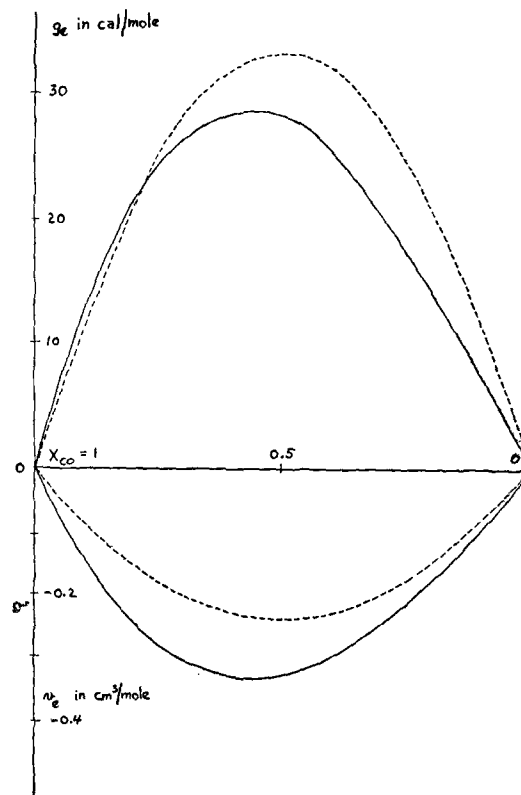


FIG. 1.

that of carbon monoxide 1895.9 mm. The essential results are shown graphically in Fig. 1, in which the excess free energy and the excess volume are plotted as a function of mole fraction. Not only are the predictions of the cell theory qualitatively confirmed, but the quantitative agreement between the observed values (solid curves) and calculated values (dotted curves) of these two excess functions is very satisfactory.

A detailed account of this work will be submitted for publication in the *Transactions of the Faraday Society*.

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¹ I. Prigogine and V. Mathot, *J. Chem. Phys.* **20**, 49 (1952); Prigogine, Bellemans, and Englert-Chwoles, *J. Chem. Phys.* (to be published).

Note on the Potential of the α -Pd/H₂ Electrode

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RECENT work of the authors¹ has shown that the open circuit potential difference of an α -Pd/H₂ electrode against a hydrogen (Pt/H₂) electrode both in the same sulfuric acid solution was about +0.050 v. Similar results were obtained by Hitzler and Knorr² and Stout.³ However, Aten and Zieren⁴ and Frumkin and Aladjalova⁵ obtained for the same apparent electrode system a zero potential difference. The following experiments were conducted at this laboratory which render these divergent results compatible.

In the first experiment, a palladium plate was plated with palladium black (from a PdCl₂ solution containing 1% lead