

the reaction as measured on a reduced and partly carburized synthetic-ammonia-type catalyst consisting initially of about 48 percent Fe_2C -Hägg and 52 percent α -iron. The curve is calculated for such a mixture, and the experimental points (circles) fit the curve fairly well up to just beyond the Curie point of Fe_2C -Hägg. The sample was kept at 470°C for 280 min., but the reaction was already complete after 150 min. After cooling, the sample was reheated and cooled (crosses represent average values) and found to be cementite plus a small amount of excess α -iron which had been present initially. A similar experiment was carried out with precipitated iron oxide containing 10 weight-percent copper and 0.32 weight-percent potassium (based on weight of iron), which consisted of about 48 percent hexagonal close-packed iron carbide, Fe_2C ,² and 52 percent α -iron after reduction and partial carburization. In this case, the reaction was complete after 60 min.

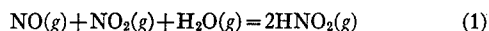
¹ Arnold and Read, *J. Chem. Soc.*, **65**, 788 (1895); Brill and Mark, *Zeits. f. physik. Chemie* **133**, 443 (1928); Hägg, *Zeits. f. Krist.*, **89**, 92 (1934); Jack, *Nature* **158**, 60 (1946); Lipson and Petch, *J. Iron Steel Inst.*, **142**, 95 (1940); Mittasch, Kuss, and Emert, *Zeits. f. anorg. allgem. Chemie* **170**, 193 (1928); Pingault, *Ann. Chim.*, **20**, 371 (1933); Schenck and Stenkhoff, *Zeits. f. anorg. allgem. Chemie* **161**, 287 (1927).

² Hofer, Cohn, and Peebles, *J. Am. Chem. Soc.*, **71**, 189 (1949).

Rate of the Rapid Gas Phase Reaction between NO , NO_2 , and H_2O

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FOLLOWING the successful application by Johnston and Yost¹ of the cathode-ray oscillograph to the study of the very rapid reaction between nitrogen dioxide and ozone, we have applied this technique to the following reaction, which



is also probably involved in the atmosphere immediately after a lightning stroke, and which had been reported² to be practically instantaneous. In a trapped non-equilibrium mixture of the reacting gases the concentration of nitrogen dioxide was followed by photographing the screen of an oscilloscope which registered the output voltage of a multiplier photo-tube exposed to a chopped beam of blue light emergent from the reaction cell.

In experiments on dilution with nitrogen of mixture of NO and NO_2 , such mixtures were found to attain equilibrium instantaneously (within the limits of observation of our apparatus). By using a constant large excess pressure of NO , namely 1 atm. throughout, the ratio between the concentrations of the molecular

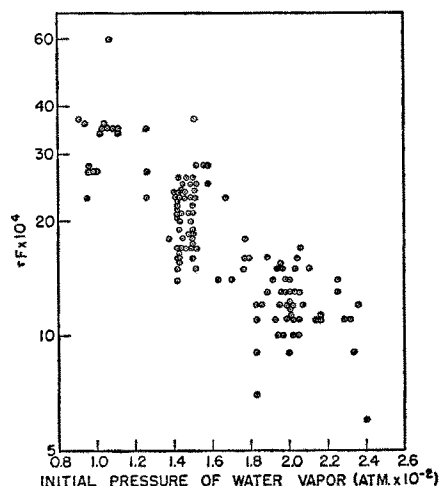


Fig. 1. Plot of τF of Eq. (3) against initial pressure of water vapor.

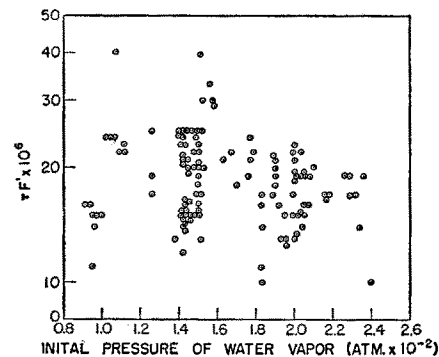


Fig. 2. Plot of $\tau F'$ against initial pressure of water vapor.

species NO and N_2O_3 was kept constant at 2.1. The initial partial pressure of nitrogen dioxide was varied from about 0.005 to 0.03 atm., and that of water vapor from about 0.09 to 0.025 atm. The molecular ratio of NO_2 to H_2O was varied between 0.34 and 2.5. One hundred and twenty-three separate runs were made, all at temperatures of from 23° to 25°C .

Calculations from thermodynamic data indicated that the reaction should reach an equilibrium with a substantial fraction of the reactants unconsumed, the equilibrium constant for reaction (1) being estimated as 1.65 atm.^{-1} . Eleven of our photographs provided data from which this constant could be estimated; the resulting values ranged from 0.92 to 3.1 atm.^{-1} , the log mean being 1.74, the median value 1.67.

Since the average age of the mixture in the light path at the instant of trapping was of the order of one centisecond, while the half-time of the reaction was in some cases as low as 1.4 centiseconds, it was considered more feasible to determine reaction rates on the basis of the rate of approach to equilibrium rather than on the "initial rate" approximation. The images on the photographic negatives were measured and relative displacement from position representing equilibrium were plotted on a logarithmic scale *vs.* time (linear scale). From such a plot an approximate half-time (i.e., time required for the system to proceed from any given state halfway to an equilibrium state) could be readily measured.

For a state of the system not too far from equilibrium, the general differential rate equation may be written

$$dx/kdt = Y[(a-x/2)(b-x/2) - x^2/K] \quad (2)$$

where x denotes P_{HNO_2} , a and b are initial values of P_{NO_2} and $P_{\text{H}_2\text{O}}$, respectively, k is the rate constant of reaction (1) and K the appropriate equilibrium constant, Y being a factor (possibly variable) to represent any catalytic or inhibitory influences affecting the rate. If the reaction is first order with respect to both NO_2 and H_2O , i.e., Y is constant, a plot of the type described should give a hyperbolic tangent curve having the asymptotic slope $-Fk/2$, where

$$F = [(a-b)^2 + 16ab/K]. \quad (3)$$

The half-time (τ) derived from this plot would then be inversely proportional to F ; i.e., the product τF should be constant. Figure 1 shows a test of this constancy, in which τF (on a logarithmic scale) is plotted against initial pressure of water vapor, showing a distinct trend in the sense of inverse variation; a comparable plot of τF *vs.* the initial pressure of NO_2 displays no such trend. On the assumption that this indicates a higher order for the reaction with respect to water vapor, the product $\tau F'$ was plotted (Fig. 2), where F' is the product of F with the calculated pressure of water vapor in the equilibrium state. Values of $\tau F'$ show no significant trend with concentration of either reactant, and scatter noticeably less than those of τF .

Based on the latter formulation, with $Y = b - x/2$, the rate constant k is estimated at $7.3 \times 10^4 \text{ atm.}^{-2} \text{ sec.}^{-1}$, or $\log k = 4.86$ with a probable error in the log of 0.09, corresponding to a factor of 1.2.

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¹ H. S. Johnston and D. M. Yost, *J. Chem. Phys.* **17**, 386 (1949).

² E. H. Melvin and O. R. Wulf, *J. Chem. Phys.* **3**, 755 (1935).

Vibration-Frequency Correlations in the Paraffin Hydrocarbons

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THERE have been several attempts fairly recently to account at least partially for the vibration spectra of the paraffin hydrocarbons.¹ Barriol and Chapelle² concluded that few of the 700 to 1100 cm^{-1} bands could be C—C chain vibrations, contrary to previous views. A study of deuteropolythene with polarized infra-red radiation³ disclosed that the 720 cm^{-1} band was due to a perpendicular CH_2 rocking mode. A recent normal coordinate analysis of *N*-paraffins⁴ supports the view that CH bending modes make the greater contribution to the spectra. That this is so would be expected from the number of coordinates to be allocated to C—C stretching (one), and CH bending (four), in the unit link of the primary hydrocarbon chain. In a recent paper,⁵ pairs of frequencies at 1145 and 1170 cm^{-1} and at 1200 and 1250 cm^{-1} are assigned to the vibrations of skeletons of systems *X*- CHMe_2 and *X*- CMe_3 , respectively, force constant calculations on systems with *X* of infinite mass being said to confirm these assignments.† It is felt that they are incorrect, and that further work on these lines will lead to confusion. There is a fairly constant pair of frequencies at about 1135, 1180 cm^{-1} in the *N*-paraffins, and a very close pair of fairly strong bands at about 1147, 1155 cm^{-1} in 3-methyl paraffins. Again, a pair at about 1200–1210 cm^{-1} and 1250–1260 cm^{-1} can be found in the *N*-paraffins; in the 3-methyl compounds a pair at about 1200, 1280 cm^{-1} becomes evident with a primary chain longer than eight carbon atoms, appearing to arise from a single band at 1250 cm^{-1} in the shorter chains. There is thus no evidence for the assignments of 1145, 1170 cm^{-1} and 1200, 1250 cm^{-1} to skeletal vibrations of *X*- CHMe_2 and *X*- CMe_3 respectively. The former pair appears more likely to be due to methyl rocking; in polyisobutene there is rather an indefinite maximum at 1160 cm^{-1} , and there is a band in this region in hydro-rubber; also in crepe rubber, and, more intense, in methyl rubber.⁶ The bands in the *N*-paraffins decrease in intensity with increasing chain-length. The region 1200–1300 cm^{-1} is the expected one for CH_2 bending parallel to the chain; in a long chain there is the one maximum at 1295 cm^{-1} and lower frequencies appear, first as shoulders to this band, as the chain-length decreases. The single strong sharp maximum in polyisobutene may perhaps be due to the CH_2 groups being non-adjacent in a chain with a preferred locked configuration.

The following argument should be considered. In a chain made up of *N* identical (repeated) units, if the vibrational displacement coordinates for any isolated link are Δ_1 to Δ_n , then the displacements in the chain are $\Delta_j e^{im\theta}$ ($j=1$ to n), for the *m*th unit ($m=1$ to *N*); $i^2=-1$ and θ is the phase difference between corresponding displacements in adjacent units. For stable (normal) vibrations, $0=\pi/N$. The secular equation for the vibrations can be reduced to order n^4 ,⁷ and the normal coordinates written

$$\eta_k = \left(\sum_{j=1}^n c_{kj} \Delta_j \right) e^{im\theta}$$

Clearly, the allowed fundamentals in a chain of *N* units will be made up of the frequencies characteristic of lengths corresponding to all factors of *N*, plus frequencies first found in the *N*-chain (equal in number to the number of primes from 1 to *N* which are

not factors of *N*, multiplied by the number of coordinates per chain-link, *n*). This argument is quite general. The exact result will never apply because of complications introduced with rotational isomerism. But it may be used to explain away the remarkable number of frequency-correlations found in the infra-red spectra of the paraffin hydrocarbons.

¹ The infra-red spectra are conveniently collected in the "Catalog of Infra-Red Spectrograms," American Petroleum Institute, Research Project 44. Raman frequencies are given by Kohlrausch, and there are other more recent data, e.g., reference 4.

² Barriol and Chapelle, *J. Phys. Radium* **8**, 8 (1947).

³ G. B. M. Sutherland and N. Sheppard, *Nature* (London) **160**, 739 (1947).

⁴ T. Simanouti and S. Mizushima, *J. Chem. Phys.* **17**, 1102 (1949).

⁵ G. B. M. Sutherland and D. M. Simpson, *Proc. Roy. Soc. A* **199**, 169 (1949).

† The author carried out a frequency-prediction for the system *X*- CMe_3 ($mX=\infty$), and found the following values: A_1 : 1105, 603, 199 cm^{-1} ; E : 1282, 425, and 310 cm^{-1} , with $k_{\text{C-C}}=4.65$, $f_{\text{C-C}}=0.45$, $\times 10^6$ dynes/cm. The characteristic frequencies for the system would be 1105 and 1282 cm^{-1} . This does not agree with Sutherland and Simpson (see reference 5).

⁶ H. W. Thompson and P. Torkington, *Proc. Roy. Soc. A* **184**, 3 (1945); *Trans. Faraday Soc.* **41**, 246 (1945).

⁷ E. Bartholome and E. Teller, *Zeits. f. Physik. Chemie* **B19**, 366 (1932); J. G. Kirkwood, *J. Chem. Phys.* **7**, 506 (1939); Whitcomb, Nielsen, and Thomas, *J. Chem. Phys.* **8**, 143 (1940).

Isothermal Rate of Solidification of Small Droplets of Mercury and Tin

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AGGREGATES of mercury droplets were prepared by agitating pure mercury and a 0.01 molar solution of stearic acid in white mineral or Cenco pump oil with a Waring blender. The mean volume, \bar{v} , of the droplets corresponded to a diameter of about 3.8 microns. After changing the medium of dispersion from oil to methyl cyclopentane (this had no detectable effect on the particle-size distribution) the solidification of aggregates of these droplets was followed dilatometrically.

In continuous cooling experiments (0.5°/min.) most of the droplets solidified between -98 and -102° . The progress of solidification with time was followed at four constant ($\pm 0.01^\circ$) temperatures in the range -98.5 to -100° .

After plotting the fraction solidified, *X*, against time, *t*, the slope dX/dt , was measured at various constant fractions of transformation between 0.30 and 0.45. If it is assumed that \bar{v} equals the root-mean-square volume of the droplets that have not solidified the nucleation frequency, I $\text{cm}^{-3} \text{sec}^{-1}$ can be written $I = dX/\bar{v}dt(1-X)$. The absolute value of $\log I$ may be in error by as much as 0.3 because of the assumption, but the dependence of $\log I$ upon temperature is not affected by it provided *I* at the various temperatures is measured for a constant fraction transformed.

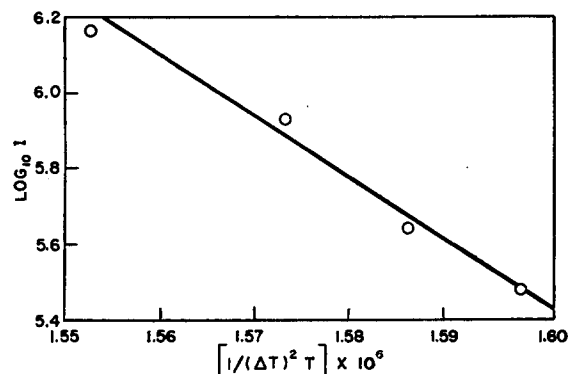


FIG. 1. $\log I$ vs. $1/(\Delta T)^2 T$ for aggregate of mercury droplets at 40 percent solidification.