

Application of Order-Disorder Concepts to Kinetics of Diffusionless Transitions in Solids

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FOLLOWING the procedure of Hijmans and de Boer,¹ any crystal lattice may be represented as a superposition of figure assemblies. If only nearest neighbor interactions are taken into account, the figure assemblies consist of $2/Z$ "bonds" (0-0) and of $(1-Z)$ "points" (0), Z being the coordination number. In diffusionless transformations of solids, every reaction center is capable of undergoing a transformation from the initial state A (○) to the final state B (●) by one of two processes. The first is a nucleation step; any isolated center has a certain probability of executing the transformation, which is characterized by a rate constant k_n . The second is a propagation mechanism; any center in state A adjacent to a center in state B is subject to an induced transformation by virtue of the strain energy existing at the interface of dissimilar phases. The rate constant for this process is designated as k_p . The over-all rate of conversion according to the law of mass action is thus $-dN/dt = k_n N_n + (k_n + k_p) N_p$, where N is the total number of centers in the configuration A , and where N_n and N_p represent the number of candidates available for the two types of transformations.

The reaction centers will be identified with the points of the figure assembly representation of the lattice. Then at any time t , let α_0 and α_1 represent the probabilities of finding members of the point figure assembly or units in the lattice in the configuration A or B ; let β_0 , β_1 , and β_2 represent the probabilities of finding members of the bond figure assemblies in the configurations AA , AB , or BB . If there are L -reaction centers in the lattice, then, in the figure assembly, $N_n = ZL\beta_0 + (1-Z)L\alpha_0$ and $N_p = ZL\beta_1$. To obtain the final formulation of the rate law it is necessary to express β_1 and β_0 as a function of α_0 . This can be done by assuming quasi-equilibrium conditions to prevail; the methodology of order-disorder theory¹ may then be utilized for this calculation. Upon carrying out the calculations one obtains ultimately the expression ($f \equiv \alpha_0$)

$$-\frac{1}{k_n} \frac{df}{dt} = f + \frac{k_p}{k_n} Z \left\{ \frac{-1 + [1 + 4(K-1)f(1-f)]^{1/2}}{2(K-1)} \right\}, \quad (1)$$

where K is regarded as an adjustable parameter, indicative of the tendency toward phase aggregation. Large values of K correspond to clustering of A or B units; small values of K represent an interdispersion of A and B units. Nonequilibrium conditions may be simulated by choosing large (small) K values when k_p/k_n is large (small), regardless of the K value which would apply if

the rate of equilibration kept pace with the rate of transformation.

Graphical integrations of (1) show that as K is decreased from large values towards unity, the conversion curve, σ_0 vs $k_n t$, changes from an exponential to a sigmoidal type; the sigmoidal form and the initial acceleratory period become more pronounced with increasing values of k_p/k_n . The conversion curves obtained from (1) thus correspond to the transformation curves commonly encountered in the literature.²

Some special cases are of interest. If $K=1$, Eq. (1) may be integrated to yield

$$k_n t = (1 + k_p Z/k_n)^{-1} \ln \{ [1 + (Zk_p/k_n)(1-f)]/f \} \quad (2)$$

an equation recently proposed by Burgers and Groen.³ Conversion curves according to (2) are also very reminiscent of those found in a publication by Johnson and Mehl.⁴ If K is large, then upon making suitable approximations, Eq. (1) can be integrated to obtain

$$[Zk_p/(K-1)]^{\dagger} t = C + \cos^{-1}(2f-1), \quad (3)$$

where C is an arbitrary constant, most conveniently evaluated from the value of t corresponding to $f = \frac{1}{2}$. The assumptions inherent in Eq. (3) fail to apply near $f=0$ or 1. Equation (3) duplicates the conversion curves for the white \rightarrow grey transformation of tin.³

It is hoped to publish a full account of this work at a later date.

¹ J. Hijmans and J. de Boer, *Physica* **21**, 471, 485, 499 (1955); **22**, 408 (1956).

² P. W. M. Jacobs and F. C. Tompkins in *Chemistry of the Solid State*, edited by W. E. Garner (Butterworths Scientific Publications, London, 1955), Chap. 7.

³ W. G. Burgers and L. J. Groen, *Discussions Faraday Soc.* **23**, 183 (1957).

⁴ W. A. Johnson and R. F. Mehl, *Trans. Am. Inst. Mining Met. Engrs.* **135**, 396 (1939).

Absolute Emission Intensity of Schumann-Runge Radiation from Shock Heated Oxygen†

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ABSOLUTE measurements have been made of the radiation from oxygen behind a moving normal shock wave which permit the determination of the oscillator strength for the Schumann-Runge bands.

Observations were made through a Pyrex section of a 17-ft, 1.5-in. diameter shock tube in a direction perpendicular to the tube axis. The radiation was focused on the entrance slit of a Bausch & Lomb grating monochromator. Ten percent of the entering radiation was reflected to a 6292 DuMont phototube which served as a monitor. The remainder of the light was dispersed by the grating and the desired wavelength focused at the exit slit. Here a mask and wedge mirror divided the

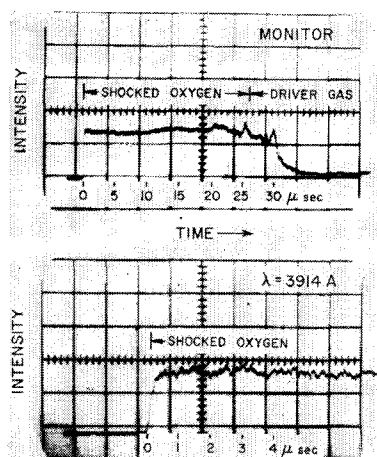


FIG. 1. Oscilloscope traces of radiation intensity as a function of time behind a moving shock wave in oxygen with temperature of 4100°K and $\rho/\rho_0 = 0.19$. The top trace is of the monitor signal with sweep speed of 5×10^{-6} sec/division; the bottom trace is of the monochromator channel at $\lambda = 3914 \text{ \AA}$ and sweep speed of 10^{-6} sec/division.

radiation into two bands 33 Å wide and 66 Å apart and directed the radiation in each band onto a 6292 photomultiplier. The three photomultiplier outputs were displayed and photographed on oscillograph screens. Simultaneous measurements of the initial oxygen pressure and temperature and the speed of the luminous front were used to determine the equilibrium conditions behind the shock wave.

Typical oscillograph records of the monitor and one of the monochromator channels are shown in Fig. 1. The constant level of the radiation intensity gives evidence of uniform conditions behind the shock front and that the boundary layer which is building up along the wall is probably not influencing the results. The absolute intensity is deduced by direct comparison with an NBS-calibrated tungsten lamp.

The results are shown in Fig. 2 for oxygen at 4100°K and densities of 0.19 and 0.022 of standard density ($\rho_0 = 1.44 \times 10^{-3} \text{ g/cm}^3$). The intensity per oxygen molecule is given in watts steradian⁻¹ micron⁻¹. The concentration of molecular oxygen was calculated assuming thermodynamic equilibrium. The data are in agreement with the λ^{-5} spectral dependence expected for Schumann-Runge emission.¹ Also spectra from oxygen at 6000°K that have been obtained show Schumann-Runge radiation.

The possibility of self-absorption by individual lines has been studied. Theoretical considerations indicate that the ratio of Doppler line width to line spacing should be ~ 0.5 and hence self-absorption is not important for emissivities of less than ~ 0.5 . Since the experimental emissivities vary from a high of only 0.05 to a low of 8×10^{-5} , self-absorption can be neglected. Furthermore there is no indication that either the density dependence or the spectral distribution is affected by self-absorption.

The emitted intensity in the normal direction from an optically thin layer can be expressed² as $I/(O_2)l = (1/6)fr_0\sigma T^4(hc/k\lambda T)^5 \exp(-E_0/kT)$ watts steradian⁻¹ micron⁻¹ molecule⁻¹, where (O_2) is the density of molecular oxygen, l is the thickness of the radiating layer,

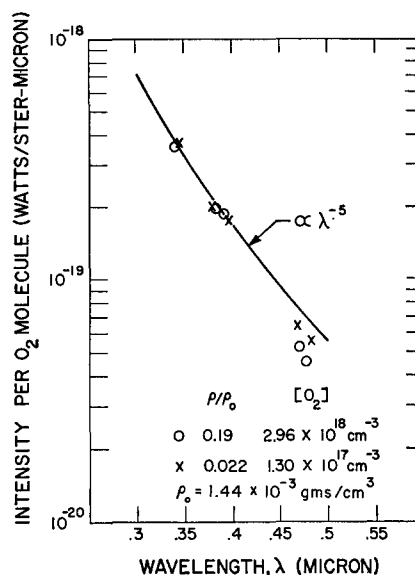


FIG. 2. Spectral intensity of radiation from oxygen at 4100°K.

f is the oscillator strength, $r_0 = 2.8 \times 10^{-13} \text{ cm}$ is the classical electron radius, $\sigma = 5.7 \times 10^{-12} \text{ watt cm}^{-2} \text{ deg}^{-4}$ is the Stefan-Boltzmann constant, T is the absolute temperature, $hc/k = 1.44 \text{ cm deg}$, λ is the wavelength of the radiation and E_0 is the energy of the ground vibration level of the excited electronic state ($50\,000 \text{ cm}^{-1}$).

Using this expression we obtain a value for the effective f number of 0.015. This is considerably smaller than the value of 0.16 measured for ground-state absorption.^{2,3} Since the emission occurs at a larger internuclear separation than the absorption this implies that the f number decreases with increasing nuclear separation.

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¹ Kivel, Mayer, and Bethe, *Ann. phys.* **2**, 57 (1957).

² Watanabe, Inn, and Zelikoff, *J. Chem. Phys.* **20**, 1969 (1952).

³ Watanabe, Zelikoff, and Inn, "Absorption coefficients of several atmospheric gases," *Geophysics Research Directorate—Air Research and Development Command, Cambridge, Massachusetts* (1953).

Measurement of Rate Constants of Fast Reactions in a Supersonic Nozzle*

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AERODYNAMICISTS engaged in the simulation of flight at high speeds are interested in the study of the supersonic flow fields of gas mixtures where one or more species are not in chemical equilibrium. For this reason a mixture of N_2 and a small amount of NO_2 was passed through a continuously operating Mach number 2 supersonic nozzle with an exit cross section of $2 \times 3 \text{ cm}$.