

Thermal Diffusion in Single Crystals of Zinc

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Citation: [The Journal of Chemical Physics](#) **24**, 492 (1956); doi: 10.1063/1.1742532

View online: <http://dx.doi.org/10.1063/1.1742532>

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of C=O frequencies due to *intermolecular* interaction will vary with the angle between the OCN^+ dipoles, but not specifically the angle between C=O and N—H bonds as Krimm suggests.

Clearly the lack of correlation of C=O frequency with O·····N distance (in part due to intramolecular differences); the C=O shift in $\alpha \rightarrow \beta$ transitions without change in N—H stretching frequency;⁵ the large C=O shift relative to the NH shift on association; and the maximum C=O shift when OCN dipoles are colinear, show that the dipole-dipole interaction controls the interaction of *trans* CONH groups and must therefore make a greater contribution to the total interaction energy than the potentially weak hydrogen bonding.

Indeed it can be argued that, because of criterion (2) above, the amide NH will not form a hydrogen bond, and the sharpness of the N—H stretching absorption bands in secondary amides and polyamides,³ polypeptides,⁶ and ammonium halides,⁶ relative to the broad bands of hydrogen bonded OH groups may be significant.

This conclusion has a very important bearing on polypeptide structures since the hydrogen bond colinearity criterion may not be applicable.

Thanks are due to British Nylon Spinners, Ltd., for permission to publish this note.

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Thermal Diffusion in Single Crystals of Zinc*

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(Received November 17, 1955)

THERMAL diffusion measurements have been made in single crystals of zinc both perpendicular and parallel to the C-axis, using traces of Ti^{204} , Ag^{110} , and In^{114} impurities. The zinc was A. D. McKay's highest purity material. The crystals

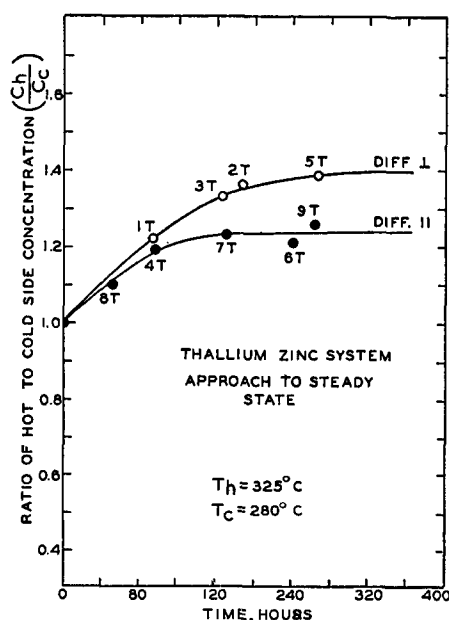


FIG. 1.

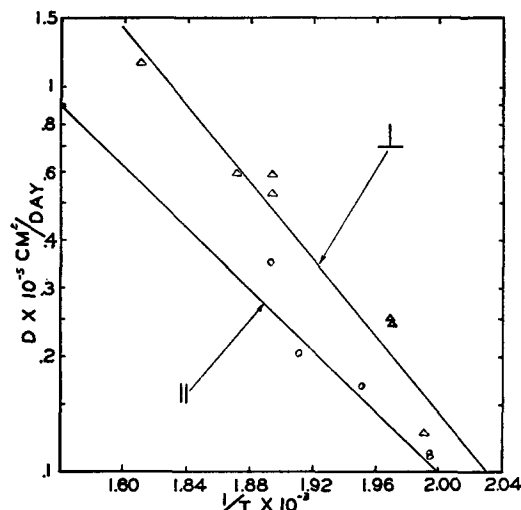


FIG. 2. Variation of diffusion coefficients with reciprocal temperature for thallium through zinc in both crystallographic directions.

were grown carrying trace amounts of the impurities and cleaned by standard methods along the appropriate axis into samples approximately 8 mm square and 3.5–4 mm thick. These were electropolished and placed between two copper rods each electrically wound and with a thermocouple bedded in the face of each. The whole system was then thoroughly insulated and a temperature gradient maintained across the crystal. The usual ΔT was 45°C. After a period of time, the crystal was removed and the concentration gradient measured by traversing with a collimating mechanism. This was repeated on a series of crystals run for different periods until the steady-state separation was reached. Figure 1 shows typical results. (All crystals were run through the traversing and counting system before being placed in the furnace to insure

TABLE I. The equilibrium concentration ratios and the separation factors (α).

System	$\Delta T = 45^\circ\text{C}$ Mean temperature	Concentration (h/c) Eq.	α
Indium-zinc			
Perpendicular	382.5°C	1.38	4.840
Silver-zinc			
Parallel	382.5°C	0.960	-0.622
Silver-zinc			
Perpendicular	382.5°C	0.976	-0.345
Silver-zinc			
Parallel	302.5°C	0.928	-0.970
Silver-zinc			
Perpendicular	302.5°C	0.945	-0.728
Thallium-zinc			
Parallel	302.5°C	1.24	2.85
Thallium-zinc			
Perpendicular	302.5°C	1.40	4.43

that the initial concentration was uniform.) The steady-state concentration ratios are shown in Table I. Of these, the thallium data are most reliable, as the collimation was best for this system, involving only beta radiation. The separation factors, α , are the usual thermal diffusion ratios defined, in this case, by the equation

$$\ln \frac{C_h}{C_c} = \alpha \ln \frac{T_h}{T_c} \quad (1)$$

An expression for α has been derived¹⁻³ involving the activation energies for motion

$$\alpha = \frac{q_2 - q_1}{RT} \quad (2)$$

Here, q_1 is the activation energy of the impurity, and q_2 the activation energy for zinc self-diffusion along the appropriate axis, which is available.⁴ Attempts were made to measure the activation energies for diffusion of thallium in zinc, using a sealed and evacuated furnace and burying the samples in copper turnings. In spite of our precautions, oxidation of the thallium led to rather irregular results and did not permit accurate calculation of the activation energies. From Eq. (2) and the measured values of α and q_2 , it is possible to calculate q_1 , which is the slope of a plot of $1/T$ vs $\ln D$ for thallium in zinc. In Fig. 2, the lines have the slope calculated in this manner, and the points are measured values of D . The results are at least not inconsistent.

F. R. Winter would like to acknowledge a fellowship from the Standard Oil Company in Ohio.

* This work was supported in part by the U. S. Atomic Energy Commission.

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Erratum: Isotopic Reaction Rates Between Methyl and Hydrogen

[*J. Chem. Phys.* **23**, 1505 (1955)]

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THE observed rate constants, k_{obs} , attributed to E. Whittle and E. W. R. Steacie (reference 4) were incorrectly deduced from their presented data. The relative values, however, remain unchanged. The observed rate constants are correctly listed in the table below, which should replace Table VI. E_0 is based on $E_c = 13.3$ kcal mole⁻¹.

TABLE VI. Calculated and observed rate constants for the eight isotopic reactions methyl + hydrogen.

Reaction	1	2	3	4	5	6	7	8
$A_{\text{calc}}^{400^\circ} \times 10^{-12}$	1.86	0.68	0.65	1.13	1.13	0.37	0.37	0.58
E_0 kcal mole ⁻¹	10.93	11.25	11.11	11.69	10.91	11.23	11.09	11.67
$k_{\text{calc}} \times 10^{-6}$	1.77	0.45	0.50	0.42	1.19	0.26	0.31	0.23
$k_{\text{obs}} \times 10^{-6}$ (cc, mole ⁻¹ sec ⁻¹)	1.56	0.55	0.23	0.33	1.26	0.54	0.31	0.43

The absolute value of $A_{\text{calc}}^{400^\circ}$ now corresponds closely to the observed value: taking the mean of the correct k_{obs} in conjunction with the observed $\bar{E} = 10.81$ kcal mole⁻¹ gives $\bar{A}_{\text{obs}}^{400^\circ} = 0.57 \cdot 10^{12}$, as compared with $\bar{A}_{\text{calc}}^{400^\circ} = 0.84 \cdot 10^{12}$. The approximate parallelism (Fig. 4) between the sequence of k_{calc} for constant E_0 , and k_{obs} , holds to exactly the same extent as before if $E_0 = 11.00$ kcal mole⁻¹. The ordinate of Fig. 4 now extends from 0.0–2.0 · 10⁶ cc mole⁻¹ sec⁻¹.

Thermal Decomposition of Nitrogen Dioxide*

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(Received November 15, 1955)

IN the course of investigating the oxidation of various gases by nitrogen dioxide it became necessary to study the decomposition of nitrogen dioxide at temperatures up to 1000°K. This reaction was investigated by Bodenstein¹ in the temperature range 592 to 656°K and for NO₂ pressures of the order of 200 mm of Hg. Under these conditions NO₂ decomposes to NO and O₂. The reaction rate is of second order with respect to NO₂ and the

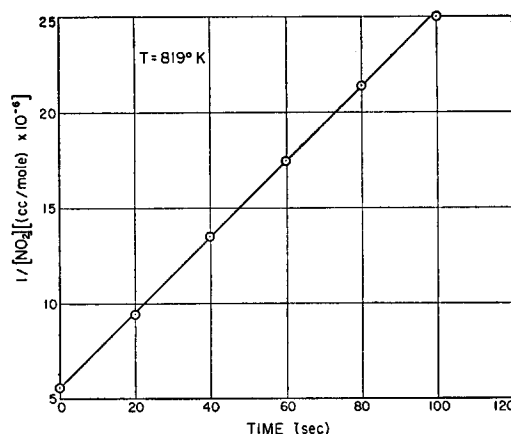


FIG. 1. Time variation of $1/(\text{NO}_2)$.

experimental activation energy is 26 to 27 kcal. No investigation has been reported to the effect of surface or of inert gases on the course of the reaction.

The present experimental measurements were carried out in a static system. The reaction vessel, a Vycor cylinder 52.3 cm in length and 3.5 cm in diameter, was housed in a tubular resistance furnace. The temperature of the reaction vessel was measured by means of chromel-alumel thermocouples attached to the outside of the reaction vessel. Nitrogen dioxide and inert gases were admitted to the reaction vessel through a short length of electrically heated tubing. The progress of the decomposition was determined indirectly by observing the change in optical density (near 4400 Å) with time of the reaction vessel contents.

The optical instrumentation consisted of an automobile-type tungsten lamp, a gelatin Kodak-Wratten filter 5-47 for selecting light of the desired wavelength, and an RCA 931A photomultiplier tube, operated by dry cells, for measuring the intensity of the transmitted light beam.

Experimentally, it was found that over the concentration range 0 to 10⁻⁷ mole/cc of NO₂ the transmission varied with concentration according to Beer's law. The absorption coefficient was found to be independent of temperature in the region of interest.

Measurements of the rate of reaction were carried out in the temperature range 630 to 1020°K and for NO₂ concentrations from 10⁻⁸ to 10⁻⁷ mole/cc. The order of the reaction with respect to NO₂ was determined by graphical analysis of the temporal variation of (NO₂), the concentration of NO₂. As shown in Fig. 1,

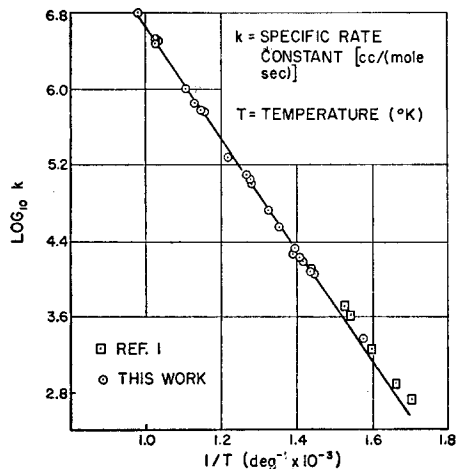


FIG. 2. Variation of specific rate constant with temperature.