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Fred R. Whaley

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The Exchange of Energy Between Polyatomic Molecules and a Metallic Surface

FRED R. WHALEY,* *Department of Chemistry, Johns Hopkins University*

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Experimental evidence is given to show that fairly complicated molecules, on striking a hot surface, do not absorb energy in their vibrational degrees of freedom to any

appreciable extent. In regard to the energy interchange the molecules behave like hypothetical gases of six degrees of freedom, translational and rotational.

MOST of the work reported on energy exchanges between gases and solids deals with light monatomic or diatomic molecules. However, Rice and Byck¹ in attempting to decompose acetone and dimethyl mercury by impinging it on a platinum surface at 1600°C concluded that the "transfer of energy from a heated target to the internal degrees of freedom of an organic molecule is not 100 percent efficient." The purpose of this work is to show experimentally that, when fairly complicated molecules strike a hot surface, the efficiency of energy transfer from the solid surface to the vibrational degrees of freedom of the impinging molecule is very low and, within the limits of experimental error, possibly equal to zero.

The apparatus consisted essentially of a water-cooled, cylindrical chamber about 10 cm long and 4 cm in diameter, in which was suspended a platinum wire. With the aid of tungsten leads sealed through the glass, the wire could be heated electrically and its temperature calculated from its resistance. Allowance was made for the almost negligible resistance of the leads, and this correction was kept constant by keeping the leads at the temperature of solid CO₂ throughout all the readings. A bulb containing the substance being used and surrounded by a bath of alcohol and solid CO₂, was connected with the chamber. The pressure in the chamber could be measured by means of a McLeod gauge, so constructed that when pressure measurements were taken the pressure of the vapor in the capillary was only a fraction of the vapor pressure at room

temperature of the substance used. The chamber could be evacuated either rapidly through a wide tube or slowly through a capillary.

A calibration curve was obtained by evacuating the chamber to about 10⁻⁴ mm of Hg and plotting the energy input in the wire against the temperature of the wire. Due to varying conditions of the surface of the chamber, probably because of platinum and carbon deposited there, the calibration curves varied slightly from day to day. Curves obtained before and after a run agreed, however, so separate calibration curves were made with each run.

The run itself was made by keeping the substance in the chamber at a known pressure and again plotting energy input against temperature. At a given temperature the energy given up to the colliding molecules could at once be read from the graph. This was compared with the energy exchange calculated, assuming the gas to be a hypothetical gas of only six degrees of freedom, translational and rotational.

In this calculation the following equation derived by Langmuir² was used:

$$m = p(M/2\pi RT)^{1/2},$$

where m = grams striking surface per second per cm²; p = pressure; M = molecular weight; T = absolute temperature; R = gas constant. The mols per second hitting wire = mA/M where A is the area of the wire. The energy absorbed per second in watts is:

$$[4.185mA(T_2 - T_1)C_v]/M,$$

where $(T_2 - T_1)$ is temperature difference between wire and walls and C_v is the specific heat.

* Du Pont Fellow.

¹ F. O. Rice and H. Byck, *Proc. Roy. Soc. A* **132**, 50 (1931).

² I. Langmuir, *Phys. Rev.* **2**, 329 (1913).

Runs were made with chloroform, acetone, methyl alcohol, carbon tetrachloride and ethyl acetate. The substance was kept at constant pressure during a run by the constant-temperature bath and the slow pumping through the capillary. The pressure should be sufficiently low that the temperature distribution of the molecules colliding with the wire is equal to the distribution of molecules in temperature equilibrium with the walls. This means that the mean free path must be at least as great as the diameter of the wire, and preferably two or three times as great.

In the runs with methyl alcohol, carbon tetrachloride and ethyl acetate the pressure was sufficiently low, the highest being 0.047 mm for ethyl acetate. The mean free path was 0.034 cm. The diameter of the wire was 0.025 cm.

Let us designate the molecules about to strike the wire as *A* molecules. These had their last collision with other molecules, which we shall call *B* molecules, when they were at an average distance from the wire equal to Λ , the mean free path. The *A* molecules will have a temperature distribution equal to that of the main body of the gas, unless an appreciable fraction of the *B* molecules just came from the wire, hence having a temperature increment. That fraction is approximately the angle in radians subtended by the wire from a point at distance Λ , divided by 2π .

In the ethyl-acetate run this fraction is about 0.12, but the *A* molecules, colliding with *B* molecules coming from the wire, can at best receive a temperature increment of half the increment received by the *B* molecules. Since the efficiency of energy transfer on collision may not be perfect, the error due to this preheating of the *A* molecules is probably even less than the maximum error, which is $0.12/2 = 0.06$ or 6 percent. This is within the limits of experimental error. For methyl alcohol and carbon tetrachloride the error is even less. Figs. 3, 4 and 5 show the marked agreement between the observed energy changes and those calculated for a hypothetical gas of six degrees of freedom.

In the chloroform and acetone runs this error is about 13 percent, which is too high even allowing for inefficient energy exchanges between molecules *A* and *B*. This would tend to make the

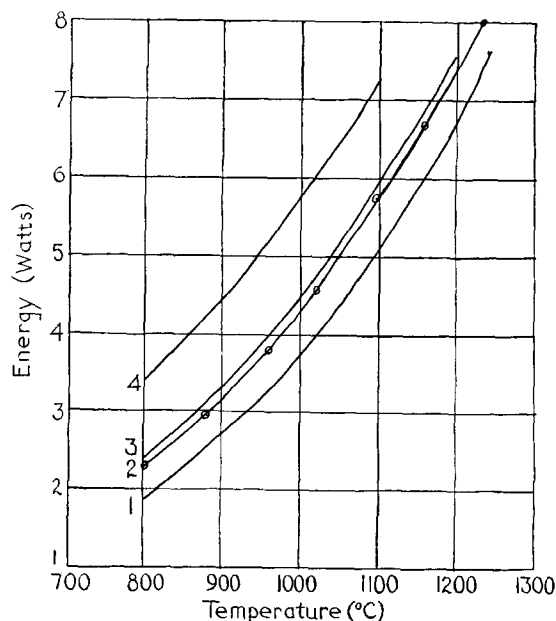


FIG. 1. Chloroform.

calculated energy exchange too high. Figs. 1 and 2 show a calculated value higher than the measured value.

In each graph, 1 is the calibration curve, 2 is the observed energy curve and 3 is the energy curve calculated on the basis of perfect efficiency in energy transfer to translational and rotational

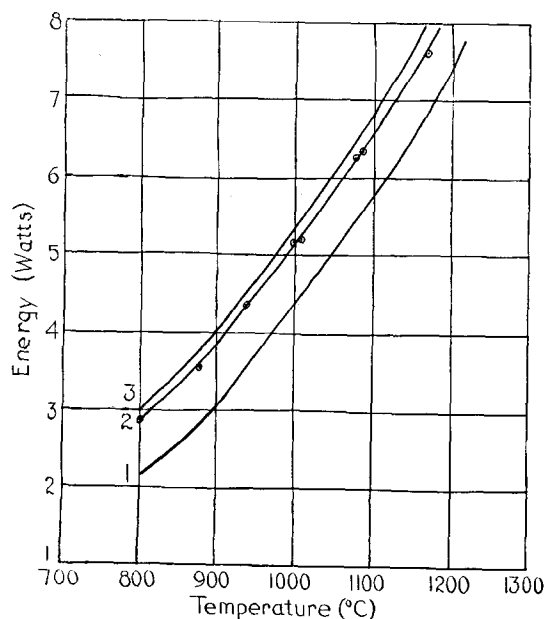


FIG. 2. Acetone.

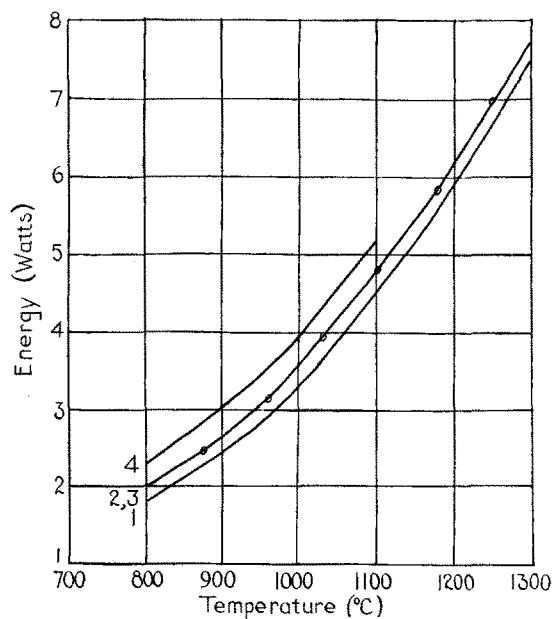


FIG. 3. Methyl alcohol.

degrees of freedom and no transfer of energy to the vibrational degrees of freedom. Curve 4 is calculated by assuming perfect efficiency of energy transfer to all degrees of freedom. (Specific heat values were calculated by Dr. D. H. Andrews and his students in this labora-

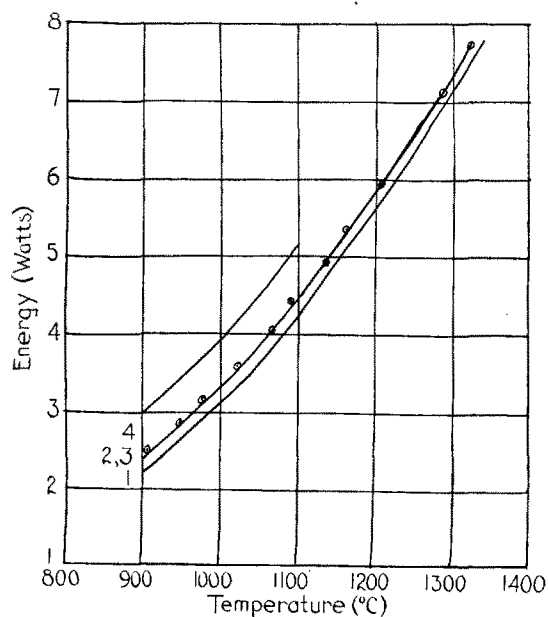


FIG. 4. Carbon tetrachloride.

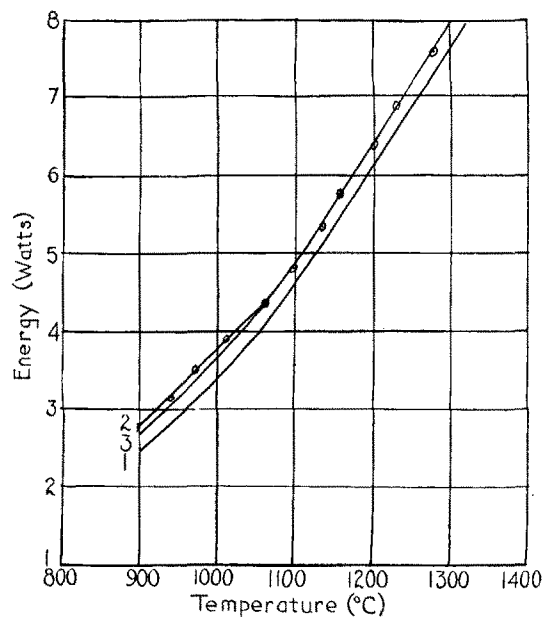


FIG. 5. Ethyl acetate.

tory from Raman data.) Experimental points on curve 2 are shown. Table I summarizes the conditions under which the experiments were carried out for each of the substances studied.

TABLE I.

Substance	Pressure (mm)	Δ at 0°C and one atm. (cm)	Δ at press. used (cm)	Ratio of Δ to wire diam.
CHCl_3	0.140	265×10^{-8}	0.014	0.56
CH_3COCH_3	0.146	258×10^{-8}	0.013	0.52
CH_3OH	0.0256	517×10^{-8}	0.153	6.10
CCl_4	0.0376	326×10^{-8}	0.066	2.64
$\text{CH}_3\text{COOC}_2\text{H}_5$	0.047	212×10^{-8}	0.034	1.36

DISCUSSION

Zener³ concludes from theoretical considerations that light molecules of light atoms colliding with each other exchange rotational quantum numbers freely, but that the transfer of vibrational energy may be difficult even in cases of exact resonance. Although in the work reported here one of the colliding bodies is platinum and not a "light molecule," the results seem to conform with Zener's conclusion.

³ C. Zener, Phys. Rev. 37, 556 (1931).

Herzfeld and Göppert Mayer⁴ showed from theoretical considerations that the time necessary for an organic molecule, adsorbed on a hot surface, to absorb energy in its vibrational degrees of freedom was longer than the collision time. The results reported here are in accord with that theory.

Van Wijk⁵ by optical methods shows that the accommodation coefficient for rotational energy in the case of H_2 is very small. Knudsen⁶ by

⁴ Herzfeld and Göppert Mayer, *Zeits. f. physik. Chemie Bodenstein Festband*, 669 (1931).

⁵ Van Wijk, *Zeits. f. Physik* 75, 584 (1932).

⁶ M. Knudsen, *Ann. d. Physik* 6, 129 (1930).

measuring radiometer pressures finds that the accommodation coefficient for the internal energy of H_2 can be equated to the accommodation coefficient for the translatory energy. The work of both these authors with H_2 seems to be contrary to the results reported here, but the latter deal with heavier and more complicated molecules.

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