

non-specific activated diffusion. The data needed to test this hypothesis were available in papers by Edwards and Pickering<sup>3</sup>, and by Dewar<sup>4</sup>. Graham<sup>5</sup> first noted the large temperature coefficient of the diffusion process through rubber, and that the diffusion velocities had no connexion with the molecular weights.

Edwards and Pickering's data for the diffusion of hydrogen, helium and carbon dioxide through vulcanized rubber, and Taylor, Hermann and Kemp's data<sup>6</sup> for the diffusion of water through vulcanized rubber, give good straight lines when log (diffusion rate) is plotted against the reciprocal of the absolute temperature (*T*), with the exception of the data for carbon dioxide at temperatures of 80° and 100° C. Similarly Dewar's data (Fig. 1) for diffusion of hydrogen, helium, carbon monoxide, carbon dioxide and oxygen through pure para-rubber, give linear log (diffusion rate) vs 1/*T* curves. Energies of activation calculated from these curves for vulcanized and for para-rubber are given in the accompany table. They are very much larger for the pure para-rubber than for the vulcanized rubber.

VULCANIZED RUBBER			PARA RUBBER		
Gas	Energy (cal./mol.)	Author	Gas	Energy (cal./mol.)	Author
He	6,300	Edwards and Pickering	He	15,400	Dewar
H <sub>2</sub>	6,470	"	H <sub>2</sub>	19,000	"
	5,900	Daynes <sup>7</sup>			
CO <sub>2</sub>	7,580	Edwards and Pickering	CO <sub>2</sub>	19,100	"
H <sub>2</sub> O	2,780	Taylor, Hermann and Kemp	O <sub>2</sub>	16,300	"
			CO	19,000	"

The solubility of these gases in rubber varies only slightly with temperature<sup>8</sup>, so that no explanation save one involving activated diffusion can account for the velocity *increasing* exponentially with temperature.

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<sup>1</sup> *Alty, Phil. Mag.*, **15**, 1035 (1933).

<sup>2</sup> *Barrer, J. Chem. Soc.*, 378 (1934).

<sup>3</sup> *Edwards and Pickering, Sci. Papers. Bureau of Stds.*, **16**, 327 (1920).

<sup>4</sup> *Dewar, Proc. Roy. Inst.*, **21**, 813 (1914-16).

<sup>5</sup> *Graham, Phil. Mag.*, **32**, 401 (1866).

<sup>6</sup> *Taylor, Hermann and Kemp, Ind.-Eng. Chem.*, **28**, 1255 (1936).

<sup>7</sup> *Daynes, Proc. Roy. Soc., A*, **97**, 286 (1920).

<sup>8</sup> *Wroblewski, Wied. Ann.*, **8**, (1879).

### Nitric Oxide and Alkyl Ethers

THE reaction of dimethyl ether and nitric oxide has been investigated in some detail by Dr. P. F. Gay and myself<sup>1</sup>, and whatever the mechanism of the secondary reaction which follows the suppression of the main decomposition process may be, it seems to be quite clear that it cannot be the one represented by the equation,



since the ratio, (CO + CO<sub>2</sub>)/CH<sub>4</sub>, in the product is the same as when nitric oxide is absent from the system. What does happen is that the ratio CO<sub>2</sub>/CO

is greater when nitric oxide is present than when it is absent, and in the presence of nitric oxide the product contains very little free hydrogen. It seems likely, therefore, that the mechanism suggested by Dr. Gay and myself<sup>2</sup> explains the effect of the nitric oxide better than that put forward by Messrs. Thompson and Meissner in *NATURE*<sup>3</sup> of June 12.

I may point out that nitrous oxide is also certainly a product of the process, and it is interesting to note that ammonia, or an amine, is also formed. However, the significance of this observation will only be arrived at by quantitative study of an exacting character, which will be difficult.

As Dr. Gay and I have pointed out, the interaction of nitric oxide and the ethers is a particular instance of a common phenomenon involving the retardation or suppression of one process and the acceleration or initiation of another. Similar reactions have been studied in this laboratory.

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<sup>1</sup> *J. Faraday Soc.*, **33**, 768 (1937).

<sup>2</sup> *NATURE*, **133**, 546 (1936).

<sup>3</sup> *NATURE*, **139**, 1018 (1937).

### Structure and Resistance of Thin Metal Films

IT was proposed by Kramer<sup>1</sup> that a film below a certain 'transition temperature' is mainly amorphous, though containing some regions of normal metal, and that at the transition temperature the film is converted completely into the normal crystalline metal. The transition temperature was given by an empirical formula in terms of atomic volume, conductivity, and the number of free electrons per atom (*N*) in the normal metal. Structural changes have been shown to occur by different investigators<sup>2</sup>, and have been discussed by them and others<sup>3</sup>. It has not always been observed that the structural changes occur at a sharply defined critical temperature, and theories alternative to that of Kramer have been proposed.

It does not appear to have been remarked that the resistance-temperature curve shown by Cosslett<sup>4</sup> indicates a transition temperature at about 10° C. for indium. If we take for indium *N* = 3, then Kramer's formula indicates a transition temperature of 282° K., which is in excellent agreement with Cosslett's curve. Kramer takes *N* = 3 for aluminium, which would justify the use of *N* = 3 for indium, although Hume-Rothery prefers *N* = 1 in each case<sup>5</sup>. The transition temperature of 282° K. would not agree with the recent proposal of Fukuroi<sup>6</sup> that the 'recrystallisation' temperature is 0.4 multiplied by the melting point, since the melting point of indium is 428° K., and the zero-thickness transition temperature would be higher than 282° K.

On the other hand, this agreement with Kramer's theory may be fortuitous, since, setting *N* = 1 in his formula, we obtain for rubidium and caesium transition temperatures of 80° K. and 117° K. respectively. The work of Lovell<sup>7</sup> on rubidium covered the range 64°-90° K., and showed not only no transition point but a resistance-temperature curve with a positive slope, while caesium<sup>8</sup> showed similarly a positive slope, which would not be expected below the transition temperature.