

## OPTICAL PUMPING AND MOLECULE FORMATION

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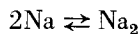
The autor shows that in an alkali metal vapour the rate of equilibrium between diatomic and mono-atomic molecules may be changed by space orientation of the spin of the valence electrons of the atoms.

We consider in a metal vapour dynamic equilibrium between atoms and diatomic molecules. For alkali-vapours such an equilibrium exists, the constant of equilibrium  $K(T)$  being temperature dependent.

Such equilibrium have been studied either by spectroscopic methods or by molecular beam methods; Lewis, *Z. Phys.*, **69**, 787 (1931). For example, for saturated sodium-vapour at a temperature of 327°C, about 98.6% of the vapour is in the atomic state, and 1.4% in the molecular state, the partial pressures being

$$p_{\text{Na}} = 3.65 \times 10^{-2} \text{ mm Hg and } p_{\text{Na}_2} = 5.42 \times 10^{-4} \text{ mm Hg.}$$

The reaction of equilibrium is



and the equation of equilibrium can be written:

$$p_m = K(T) p_a^2 \quad (1)$$

where  $p_a$  is the partial pressure of the atoms and  $p_m$  the partial pressure of the diatomic molecules.

The diatomic molecules are diamagnetic. The molecule has no magnetic momentum. The atoms of sodium (or other alkali) are paramagnetic, the magnetic momentum being the momentum associated to the spin of the unpaired valence-electron in a  $^2S_{1/2}$  state.

If two atoms with their spin pointing in the same direction are approaching each other the potential function of interaction is repulsive. No molecule can be formed. If two atoms with their spins in opposite directions are approaching each other, the potential function of interaction is attractive and both atoms can combine to form a molecule (a third partner is necessary to assure conservation of momentum. This can be a foreign gas molecule. Our conclusions are not affected by this).

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By optical pumping we are able to orient the atoms of the vapour, obliging most of them to point their spins in the same direction of space. If complete orientation could be performed all atoms approaching each other would no more be able to combine. No molecule would be formed.

We must conclude that the constant  $K(T)$  of equilibrium must depend upon the degree of atomic orientation.

Let us define a degree of orientation by

$$S = \frac{N_1 - N_2}{N_1 + N_2} \quad (2)$$

where  $N_1$  is the number of atoms with spin up and  $N_2$  the number of atoms with spin down (the axis of orientation is an arbitrary axis in space determined by the pumping light beam).

The total number of atoms is  $N = N_1 + N_2$  and we can write

$$N_1 = N \frac{1+S}{2} \quad \text{and} \quad N_2 = N \frac{1-S}{2}.$$

The corresponding partial pressures are

$$p_1 = p_a \frac{1+S}{2} \quad \text{and} \quad p_2 = p_a \frac{1-S}{2}.$$

Obviously equation [1] has to be changed to

$$p_m = K'(T) p_a^2 \quad (3)$$

where

$$K'(T) = K(T) (1-S^2) \quad (4)$$

For no orientation we find the normal rate of molecules  $K'(T) = K(T)$ , for complete orientation we find  $K'(T) = 0$  and  $p_m = 0$ .

Practically orientation rates corresponding to  $S = 0.9$  are easily obtained and give  $K'(T) = 0.36 K(T)$ .

The proportion of diatomic molecules in an optically oriented vapour should be substantially reduced.

Experiments to test these conclusions are in progress.