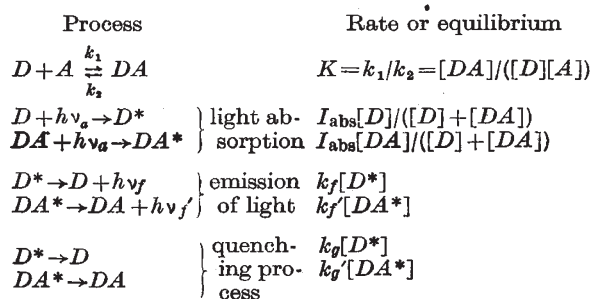


Fig. 1. Concentration effect of proton acceptors on the relative fluorescence intensity of β -naphthol in *n*-hexane (5×10^{-4} mole/l.): (1) butylacetate; (2) methylacetate; (3) ethyl-chloracetate

β -naphthyl methyl ether in the same order of magnitude. These observations show that the changes mentioned above of intensity of fluorescence are due to hydrogen-bond formation.

If the equilibrium of hydrogen-bond formation in the ground-state is not perturbed during excitation, then one may set up the following scheme for the process of fluorescence:



where D and A are respectively β -naphthol and a proton acceptor, and the other notations have the usual meaning.

On the basis of this scheme the following relation can easily be derived if one assumes, as in practice, that the extinctions of the wave-length of excitation of A and AD are equal:

$$\frac{f}{f_0} = \frac{1 + \alpha K[A]}{1 + K[A]} \quad (1)$$

where f_0 is the intensity of fluorescence of the pure β -naphthol solution, f is that of the system containing a certain proton acceptor, and α is the ratio of the quantum yields of fluorescence in the two cases.

If, on the other hand, a new and different equilibrium state for hydrogen-bond formation is realized during the life-time of the excited molecule, then a relation similar to (1) still holds, but in this case K is related to the excited molecule. Hence in this

Table 1
(in kcal./mol.)

	$\Delta F_{283}^{(f)}$	$\Delta F_{283}^{(a)}$	$\Delta F_{283}^{(f)} - \Delta F_{283}^{(a)}$
Dioxane	-1.6 ₈	-1.50	-0.1 ₈
Butyl acetate	-2.8 ₀	-1.80	-1.0 ₀
Methyl acetate	-2.4 ₈	-1.82	-0.6 ₈
Ethyl acetate	$\Delta F_{298}^{(f)}$ -2.0 ₄	$\Delta F_{298}^{(a)}$ -1.67	$\Delta F_{298}^{(f)} - \Delta F_{298}^{(a)}$ -0.3 ₇
Ethyl chloracetate	-1.8 ₈	-1.29	-0.5 ₈

case K obtained from the data of fluorescence intensity ($K^{(f)}$) may be different from that obtained from the absorption spectra ($K^{(a)}$), whereas if the equilibrium state is maintained, $K^{(a)}$ and $K^{(f)}$ must coincide.

Formula (1) agrees with the experimental observations very exactly. The K -values obtained from it, however, are different from those of $K^{(a)}$ obtained from the absorption spectra by the method of Rosenblatt².

The free energy of hydrogen-bond formation as calculated from $\log K^{(a)}$ and $\log K^{(f)}$ are tabulated in Table 1. Probable errors would be less than ± 0.05 . Thus, in all cases $|\Delta F^{(f)}|$ is greater than $|\Delta F^{(a)}|$, and we may conclude that the equilibrium shifts toward hydrogen-bond formation to some extent during the life-time of the excited molecule.

NOBORU MATAGA
YOZO KAIBE
MASAO KOIZUMI

Polytechnic Institute,
Osaka City University,
Osaka. Nov. 17.

¹ Nagakura, S., and Baba, H., *J. Amer. Chem. Soc.*, **74**, 5693 (1952).
Nagakura, S., *J. Chem. Soc. Japan*, **75**, 734 (1954).

² Rosenblatt, D. H., *J. Phys. Chem.*, **58**, 40 (1954).

An Early Electric Valve

ALTHOUGH the Edison effect was discovered some twenty years before the thermionic valve was patented, it is perhaps not generally known that the rectification of a current by an electric valve had taken place as early as 1863.

P. Riess, in a paper entitled "On the Electrification of the Magnetic Needle by the Secondary Currents of a Leyden Battery"¹, describes the repetition of some experiments carried out originally by M. Gaudin in which "an apparatus called the electric valve" was used. The valve consisted of a glass cylinder inside which were a brass disk 25 mm. in diameter and a separate platinum wire. The distance between the disk and the point of the wire was about 2 mm. When the cylinder was evacuated, a current was found to pass through it from the plate to the wire if the pressure was "not less than 2 lines or greater than 5 inches of mercury". From his experiments Riess formulated the rule: "By means of the electrical valve, and in any position, the secondary current of the Leyden jar deflects the magnetic needle in the direction of a current proceeding from the disk to the wire". This is tantamount to saying the current passes in one direction only, or that rectification has taken place.

D. B. MCNEILL

Physical Laboratory,
University,
Southampton.

¹ Riess, P., *Phil. Mag.*, **27**, 313 (1864); *Monats. Berl. Akad.* (Nov. 1863).

Relation of Radon to Non-active Air Contamination

Anderson, Mayneord and Turner¹ have directed attention to the variation of atmospheric radon content. It may be of interest to note that similar observations were made here during the four months, November-February, 1953-54. Samples were collected daily from air drawn through four-inch filter paper TFA-41. The activity of the papers was determined by inserting them directly into an ionization chamber with a vibrating-reed type amplifier