

Experimental Determination of the Life-times of Atomic Resonance States

PREVIOUS experimental work on the measurement of the life-times of atomic energy states has been subject to error mainly due to the inaccuracy of vapour pressure data. A magnetic rotation method devised by Weingeroff¹ which eliminates the vapour pressure in the final expression for the life-time has apparently been overlooked. This method has recently been employed here² for the measurement of the life-times of certain atomic resonance states; a detailed account of the method will be given in a later paper; but it was felt that the following results would be of interest at the present time.

Atom	Transition	Wave-length	Life-time (sec.)
Na	3^2S-3^2P	5896, 5890 Å.	$1.61 \pm 0.06 \times 10^{-8}$
K	4^2S-4^2P	7699, 7665	$2.71 \pm 0.09 \times 10^{-8}$
Rb	5^2S-5^2P	7947, 7800	$2.81 \pm 0.09 \times 10^{-8}$
Tl	$6^2P_{3/2}-7^2S_{1/2}$	5350	$1.43 \pm 0.05 \times 10^{-8}$

Further work is progressing with the view of adapting the method to molecular transitions, and the results will be reported at a later date.

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¹ Weingeroff, M., *Z. Phys.*, **67**, 679 (1931).

² Stephenson, G., Ph.D. Thesis, University of London (1950).

Role of Capillary Condensation in Physical Adsorption

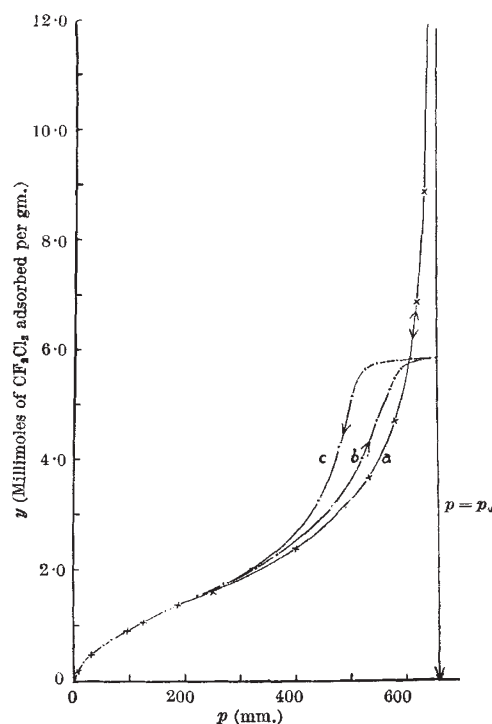
THE study of physical adsorption in the past decade has been dominated by the theory of multilayer formation put forward by Brunauer, Emmett and Teller^{1,2}. Despite quantitative limitations, the theory explains the sigmoid shape of isotherms obtained normally for adsorption on free surfaces. In the case of porous solids, it suggested that pore diameters furnish an upper limit (n) to the number of multilayers, and derived appropriate n -limited equations. Modified forms of these equations were later suggested by Brunauer, Deming, Deming and Teller³, by Anderson^{4,5}, and by Pickett⁶. The fundamental point of all of these equations is that a pore becomes filled by building up n layers of adsorbed molecules, thereby obviating the need for postulating capillary condensation.

It has become increasingly clear that capillary condensation cannot be dismissed as easily as this. Indeed, there is strong evidence that capillary condensation takes place in addition to multilayer formation. The point is one which can readily be tested. Suppose we compare isotherms for a loose powder with a surface of more than $100 \text{ m}^2/\text{gm}$. and for the same powder compressed to a plug of fairly low porosity. On the theory of multilayers, the plug would show progressively lower adsorption than the powder as relative pressure increases, since surface properties are unchanged, and the only difference is that n is restricted from infinity to a small finite value.

If, however, capillary condensation is possible, the reverse is true, since an increasing proportion of pores becomes filled by this process with increase of pressure. We thus expect the isotherm for the plug

to rise above the isotherm for the free powder, though, of course, at very high relative pressures the pore-space becomes completely filled, and adsorption on the loose powder, being unlimited, then becomes greater.

By a series of experiments along these lines we have decisively confirmed the importance of capillary condensation. A typical experiment is shown in the accompanying graph. Curve (a) is for adsorption of CF_2Cl_2 on Linde silica as a loose powder at -33.1°C . (saturation vapour pressure, $p_0 = 659 \text{ mm}$). By adsorption of nitrogen, the surface was found to be $300 \text{ m}^2/\text{gm}$. Desorption gave points on the same curve. Curves (b) and (c) are adsorption and desorption branches for the same powder compressed to a porosity of 0.506. At low pressures, neither multilayer formation nor condensation is important, so that both plug and powder give identical results within experimental errors. At higher pressures, adsorption on the plug takes place much more rapidly. Finally, a limit of $y = 5.84$ millimoles/gm. is approached.



Adsorption of CF_2Cl_2 at -33.1°C . on Linde silica: $\times-\times-$, loose powder; $-\cdot-\cdot-$, plug ($\epsilon = 0.506$)

The calculated limit, assuming the density of liquid CF_2Cl_2 at -33.1°C ., was $y = 5.72$. It is not likely that the difference is due to experimental errors, so that it is probably due either to a difference in density between adsorbate and bulk liquid, or to a reversible swelling of the plug during adsorption. On desorption, a well-marked hysteresis loop is observed, confirming that this is associated with capillary condensation. It may be noted that, about midway along the desorption branch, it became necessary to leave the sample overnight. No change took place in this time, indicating that the cause of the difference between the adsorption and desorption branches is certainly not due to slow rates of equilibration.