Sorption Hysteresis and the Vapor Pressure of Concave Surfaces

BY LEONARD H. COHAN

Introduction

Ever since hysteresis was established as a definite phenomenon in adsorption, most investigators have associated it with capillary condensation. The mechanism involved has never been clearly explained although many theories, three of which are mentioned below, have been formulated. Zsigmondy[1] and later Patrick[2] proposed the most generally accepted hypothesis: namely, that incomplete wetting during adsorption causes a higher equilibrium vapor pressure. Kraemer[3] and later McBain[4] have suggested that the pores of the sorbent are ink-bottle shaped, so that the vapor pressure during adsorption is determined by condensation in the large diameter of the bottle, while the pressure at which desorption occurs corresponds to the narrow neck. Finally, Foster[5] suggested that hysteresis is due to delay in forming a meniscus in the capillaries of the sorbent.

The following analysis is a more nearly quantitative consideration of Foster's suggestion. However, these ideas are not intended to supplant the theory of Patrick and Zsigmondy, but only to supplement this theory in order to explain certain experimental facts which otherwise would be very puzzling.

Discussion

Let us calculate the vapor pressure of an annular film, r, of liquid covering the inside of a cylindrical capillary of radius, r_c, and length, l. As shown in the cross-sectional view, Fig. 1, the radius, r, of the cylindrical film is less than r_c. However, for a very thin film (for example a monomolecular film) r and r_c may be considered equal. If we transport a small volume of liquid, $\mathrm{d}v = 2\pi r l \mathrm{d}r$, from a large body of liquid to the capillary, the decrease in surface is $2\pi l \mathrm{d}r$ and the change in surface energy is $-2\pi l\sigma \mathrm{d}r$. Equating this to the change of free energy accompanying the isothermal transfer of the above amount of liquid, we have

$$\Delta F = n(F_r - F_0) = -2\pi l\sigma \mathrm{d}r$$

where F_0 is the free energy of the bulk liquid, F_r that of the annular film, n the number of moles transferred, and σ the surface tension.

$$n = \mathrm{d}v/\text{molal volume} = 2\pi r l \mathrm{d}r/V$$
$$F_r - F_0 = RT\ln P_r/P_0$$

where P_0 and P_r are the vapor pressures of the bulk liquid and the film, respectively. Therefore, $RT \ln P_r/P_0 = -2\pi l\sigma \mathrm{d}r(V/2\pi{}^{r}l\mathrm{d}r)$, or

$$P_r = P_0e - \sigma V/rRT \qquad \text{(I)}$$

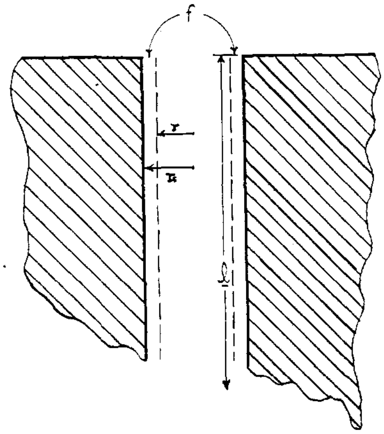

Fig. 1.

Thus given a capillary with open ends and radius r the walls of which are covered with only a thin film of liquid, condensation will take place at the pressure P_r.[6] However, the pressure, P_D, at which evaporation will occur must be calculated from the classical Kelvin equation

$$P_D = P_{r'} = P_0 - 2\sigma V/r'RT \qquad \text{(II)}$$

which differs from I only in the numerical factor 2. P_0, and V are as in I, while r' is the radius of curvature of the meniscus of the liquid (see Fig. 2). Now r' is greater than r_c unless perfect wetting (zero contact angle) is obtained, in which

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[1] R. Zsigmondy, *Z. anorg. Chem.*, **71**, 356–377 (1911); W. Bachmann, *ibid.*, **73**, 125–172 (1912); R. Zsigmondy, W. Bachmann and E. F. Stevenson, *ibid.*, **75**, 189–197 (1912); J. S. Anderson, *Z. physik. Chem.*, **88**, 191–228 (1914); J. S. Anderson, Inaugural Dissertation, Göttingen (1914).

[2] W. A. Patrick and J. McGavack, THIS JOURNAL, **42**, 946–978 (1920).

[3] E. O. Kraemer, "A Treatise on Physical Chemistry," edited by H. S. Taylor, D. Van Nostrand Co., New York, 1931, Chap. XX, p. 1661.

[4] J. W. McBain, THIS JOURNAL, **57**, 699–700 (1935).

[5] A. G. Foster, *Trans. Faraday Soc.*, **28**, 645–657 (1932); A. G. Foster, *Proc. Roy. Soc.* (London), **A146**, 129–140 (1934).

[6] Since the capillary is open at both ends, a meniscus cannot form during adsorption; hence, the equilibrium pressure, P_r, corresponds to a cylindrical curvature. Furthermore, when the pressure P_r is reached the capillary fills completely since P_r, the vapor pressure of the outermost annular ring, is greater than that of any ring farther away from the walls of the capillary. Obviously, when the desorption is begun from any pressure $\geq P_r$, a meniscus will be present and the equilibrium pressure, P_D, will be determined by the spherical curvature of this meniscus.

case $r' = r_c = r$. In this latter event P_r the adsorption pressure, and P_D the desorption pressure are related by the simple formula

$$P_r^2 = P_0P_{\mathrm{D}} \text{ or } P_{\mathrm{A}}^2 = P_0P_{\mathrm{D}} \qquad \text{(III)}$$

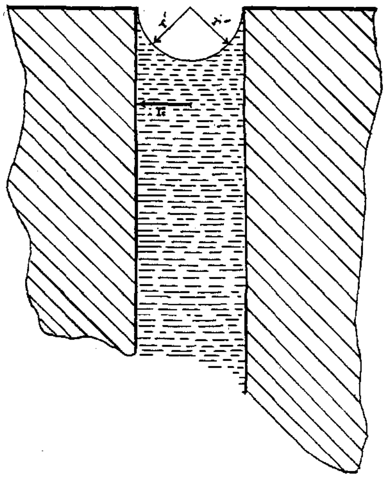

Fig. 2.

We must remember that in deriving equations I and II it has been assumed that V and σ are independent of r_c. As the experimental work of Patrick and Shereshefsky[7] and Shereshefsky and Steckler[8] indicates, this probably is not the case; and thus equations I, II, and III must be considered as first approximations. Furthermore, since the variation of σ and V depends on the sorbate used, the amount and even the presence of hysteresis in a given gel may well depend on the sorbate involved.

We may, however, draw from the above some conclusions as to the behavior of actual sorbent systems. (1) Hysteresis in systems consisting chiefly of open capillaries must be expected even when complete wetting has been realized. (2) If wetting is complete

$$P^2_{\mathrm{A}} = P_0P_{\mathrm{D}}$$

as a first approximation[9] in the case of open cylindrical capillaries.

For crevices with plane sides

$$P_{\mathrm{A}} = P_0$$

(3) For closed tapering capillaries a meniscus forms at very low pressures; hence for all pressures

$$P_{\mathrm{A}} = P_D$$

Thus perfect wetting eliminates hysteresis for a closed tapering capillary; however, even for open or non-tapering cylindrical capillaries there should be no hysteresis provided that at only one point the capillary has a diameter not larger than four times the thickness of the chemically adsorbed film.

If the latter condition is fulfilled

$$r = r'/2 \text{ (see Figs. 1 and 2)}$$

Thus the difference between equations I and II disappears and condensation and evaporation should take place reversibly.

(4) A direct inference from the above is that hysteresis may occur in the same gel with a small molecule and not with larger molecules. This is an interesting explanation of the puzzling results obtained by Pidgeon[10] with water and silica gel. In this system hysteresis occurs although with the identical gel other sorbates, such as ethyl alcohol and benzene, show no hysteresis when all permanent gases have been eliminated.

(5) Finally, in the presence of incomplete wetting—which is chiefly caused by impurities and permanent gases—hysteresis always should occur. Hysteresis of this type should extend over the entire isotherm, and one would also expect to observe some tendency for drift. This is in sharp distinction to the perfectly reproducible, *limited* hysteresis to be expected according to equation III in the absence of impurities and permanent gases. The isotherm must be closed at the high pressure end since from equation III P_{A} becomes equal to P_{D} as P_0 is approached. Further it must be reversible at the lower end—even when no chemical adsorption occurs—because the conditions of (3) above must always be fulfilled for the smallest capillaries.

The above prediction is borne out admirably by previous experiments. An examination of the available literature indicates that 94% of the experiments which resulted in unlimited hysteresis were carried out with systems containing permanent gas at a pressure of 10^{-2} mm. or higher. Of those experiments done with pressures below 10^{-2} mm., 94.5% reported limited hysteresis.[11]

Several experiments are suggested by the above theory as a further test of its validity. For example, it should be of interest to measure the isotherms for both adsorption and desorption on a

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[7] J. L. Shereshefsky, THIS JOURNAL, **50**, 2966–2985 (1928).

[8] J. L. Shereshefsky and S. Steckler, *J. Chem. Phys.*, **4**, 108–115 (1936).

[9] Since the experimental values for vapor pressure lowering[7,8] are larger than those calculated from equation II, equation III should underestimate the difference between P_{D} and P_{A}. The amount of underestimation should increase as r_c decreases.

[10] L. M. Pidgeon, *Can. J. Research*, **12**, 41–56 (1935).

[11] If the pressure dividing line is lowered to 5×10^{-4} mm., the above percentages are raised to 100% in both cases.

number of very fine quartz capillaries, prepared by the method of Patrick and Shereshesky.[7] The theory predicts that hysteresis should occur to a degree approximating that indicated by equation III. The larger the capillaries the more exact should equation III become. Of course, such an artificial system if closely examined would show discontinuities in both adsorption and desorption. However, in connection with experimental reports of discontinuous isotherms it is of interest to note that if capillaries could be obtained with a slight taper, say, from $r = a$ to $r = 2a$, discontinuities should disappear in the desorption but not in the adsorption isotherm. For the latter, the theory would still predict discontinuities since as soon as the pressure reaches $P_0e^{-\sigma V/aRT}$ the capillary will become blocked at the point $r = a$ and a meniscus will form. The vapor pressure will then be supersaturated with respect to a spherical surface of radius up to $2a$; hence, the entire capillary will fill. Another experiment, suggested by Prof. J. C. W. Frazer of the John Hopkins University Chemistry Department, is the measurement of the sorption isotherm on two parallel optically plane plates. The plates should be adjustable so that their distance apart could be varied. Such experiments as these present considerable but not insurmountable experimental difficulties. However, they would be of great value not only in testing the views expressed in this paper but also in interpreting sorption phenomena in general.

The author wishes to thank Professor J. C. W. Frazer of the Johns Hopkins University for his interest and helpful criticism.

Summary

1. The vapor pressure in equilibrium with the interior of a cylindrical shell of liquid is $P_r = P_0e^{-\sigma V/rRT}$ where r is the internal radius.

2. The above equation is used to show that in certain sorption systems hysteresis must be expected.

3. In the light of these new considerations an explanation of various experimental results is given.

4. Experiments to further test the views presented are suggested.

BALTIMORE, MD. RECEIVED NOVEMBER 23, 1937

[COMMUNICATION NO. 61 OF THE PHYSICAL CHEMISTRY DEPARTMENT, J. PILSUDSKI UNIVERSITY]

The Influence of Small Percentages of Certain Metals on the Solution Rate of Cadmium

BY M. CENTNERSZWER AND F. GONET[1]

The theory of local elements, published in 1830 by de la Rive, with the aim of explaining the fact that chemically pure zinc dissolves much more slowly in acids than zinc containing "admixtures" of foreign metals (*e. g.*, copper, lead, iron), postulates that the "foreign" metal particles form small "local elements" with the zinc particles. The latter become the anode, whereas the admixture forms the cathode, from which the hydrogen is evolved.[2]

In 1902, Palmaer formulated an equation by the aid of which it was thought possible to estimate quantitatively the rate of solution of metals containing certain admixed metals.[3] In the case of zinc, containing a small percentage of lead, Palmaer's equation takes the form

$$\rho = 0.217K/C\,(A + 2 \log C_{\mathrm{H}^+} - \log C_{\mathrm{Zn}^{++}})$$

where ρ is the reaction velocity, K the specific electrical conductivity of the solution, A the acting e. m. f. of the local element, C_{H^+} and $C_{\mathrm{Zn}^{++}}$ the concentration of the hydrogen and zinc ions in solution. The equation was proved experimentally by Ericson-Aurén and Palmaer, who found it to agree well with the experimental results.[4] Above all they showed that the influence of admixtures on the solution rate of zinc is the greater the smaller the hydrogen overvoltage on the positive metals (compare this with M. Centnerszwer and Is. Sachs[5]).

In 1914 Centnerszwer and Sachs[6] investigated

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(1) Kościuszko Foundation Scholar.

(2) De la Rive, *Ann. chim. phys.*, **43**, 425 (1830).

(3) T. Ericson-Aurén and Wh. Palmaer, *Z. physik. Chem.*, **39**, 1 (1902).

(4) T. Ericson-Aurén and Wh. Palmaer, *Z. anorg. allgem. Chem.*, **18**, 83 (1898); **27**, 209 (1901); *Z. physik. Chem.*, **39**, 1 (1902); **45**, 182 (1903); **56**, 689 (1906); Wh. Palmaer, "The Corrosion of Metals," Vol. 1, Handlingar 93, Stockholm, 1929; Vol. 11, Handlingar 108, Stockholm, 1931.

(5) M. Centnerszwer and Is. Sachs, *Z. physik. Chem.*, **87**, 692 (1914).

(6) M. Centnerszwer and Is. Sachs, *ibid.*, **89**, 213 (1914).