

# Influence of Surface Forces on Flow of Fluids Through Capillary Systems

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## Introductory Remarks by Chairman

The science of physics started and developed its laws by measuring and mathematically correlating phenomena in the world of normal dimensions. What these normal dimensions are is evident from the choice as most suitable measuring units of the cm, the gram and the second. From this base, physics has extended its realm both ways to tremendously large and exceedingly small dimensions. During this process, it soon became evident that most laws of the normal dimensions are of a statistical and approximate nature and that they represent special solutions for the particular dimensions of more general laws. While the search for the latter is still going on and since human activity cannot be stopped until the most general laws have been discovered and special solutions found for each world of different dimensions, it is useful and proper to find by experiment the laws ruling the areas of particular dimensions or sets of dimensions. Such experimental search will, of course, be guided by the knowledge of the searcher of either or both the laws governing areas of larger and of smaller dimensions than those of the particular area of interest. One such area has been called by Wolfgang Ostwald "The World of Neglected Dimensions". It is the world of colloid chemistry characterized by a range of dimension from the size of large molecules to the wavelength of light just visible to the human eye. There is no valid a priori reason why the laws governing the world of colloidal dimensions should not be derivable in their simplest and most useful form from proper experimentation within the realm of these dimensions.

Nor is there a good reason why the relationship between these laws with those of the macro-world, on one hand, and the atomic world, on the other, should not be fully explored and evaluated. Dr. Flood deserves special commendation for clearly defining the areas dominated by molecular and mass phenomena, respectively, in flow through capillary systems and for presenting a simple equation that correlates micro-pore flow rates with relevant adsorption isotherms.

● **FLUID FLOW** mechanisms may be classified broadly into two categories: (a) Mechanisms which are essentially mechanical in nature, the flow depending on the bulk properties of the fluids concerned and upon the mechanical forces exerted upon the fluid bodies. (b) Mechanisms which are essentially molecular in character, the flow depending largely on the thermal motion of the individual molecules, the molecular weight, the collision cross-section, the mean free path, etc., rather than upon the density, pressure, viscosity, etc., of the fluid in bulk.

The Bernoulli flow of the inviscid liquid of classical hydrodynamics may be taken as an example of the first category. In this type of flow, pressure potential is converted into velocity potential and vice versa. The flow thus resembles the motion of a frictionless pendulum, potential energy of fluid masses being converted into kinetic energy of mass motion and vice versa. This type of flow involves no loss of energy, no loss of

net potential. While all ordinary fluid flow involves some loss of potential due to friction and/or entropy production, nevertheless the ideal Bernoulli type of flow is approximated quite well in the case of the flow of large masses of water at fairly high net velocities in pipes of large diameter. Another example of "mechanical" flow is that of the viscous flow of nearly incompressible liquids where the flow is controlled by viscosity and hydrostatic pressure gradients.<sup>1</sup>

Molecular flow is exhibited in such phenomena as "tagged molecule" self diffusion and generally by the interdiffusion of components where concentration gradients exist.

The mechanism of gaseous flow in small pipes and channels is more or less intermediate between the purely mechanical and the purely molecular flow mechanisms.

Usually in the case of "mechanical" flow, work is done to initiate the flow and work must be done continuously to maintain the flow, but little or no change in entropy of the fluid is involved. In the case of molecular flow mechanisms, the flow is accompanied by considerable entropy changes of the fluid and may involve little or no energy change and little or no net performance of work

That the flow mechanism and even the direction of flow depends not only on the fluids concerned, not only on the thermodynamic potential differences that may be involved but also on the nature of the flow path may be illustrated by considering the flow between two equal volumes of an ideal gas where the pressures and temperatures of the two volumes differ. Let  $p_1$ ,  $t_1$ ,  $n_1$ , and  $p_2$ ,  $t_2$ ,  $n_2$  be the pressures, temperatures, and concentrations of the two gases in the two volumes. We shall suppose that  $T_1 > T_2$  and that  $p_1$  lies between  $p_2$  and  $\sqrt{\frac{T_1}{T_2}} \cdot p_2$ , and hence that  $n_1$  lies between  $n_2$  and  $\sqrt{\frac{T_2}{T_1}} \cdot n_2$ , thus  $p_1 > p_2$ , and  $n_1 < n_2$ .

In this case if the two reservoirs are connected by means of a pipe whose diameter is small compared with the mean free path of the gas, the flow will be toward the first reservoir, that is, in the direction of decreasing concentration but in the direction of increasing pressure, i. e., the gas flows toward the higher pressure and the higher temperature. If, however, the diameter of the pipe is large compared with the mean free path, the body forces will prevail and the flow is toward the lower pressure. In the former case the net flow is determined by the statistics of the individual molecules while in the latter case by the net forces acting on small volumes or laminae of the fluid which contain many molecules. The latter is, of course, mainly a viscous or laminar flow with slip, the slip being modified by the temperature gradient. The relevant equations (1) are:

1. Molecular effusion through a hole of area  $A$  into a vacuum  $Q_m = A \left( \frac{M}{2 \pi R T} \right)^{1/2} p$
2. Effusion through a long circular capillary of radius  $r$ . The mean free path much greater than  $r$   $Q_m = - \frac{8}{3} r^3 \left( \frac{\pi M}{2 R} \right)^{1/2} \frac{d}{dz} \left( \frac{p}{\sqrt{T}} \right)$
3. Maxwell's equation for laminar flow with slip and thermal creep  $Q_m = - \frac{\pi r^4}{8 \eta} \frac{M}{R T} p \frac{dp}{dz} - \frac{\pi r^3}{2} \left( \frac{\pi M}{2 R T} \right)^{1/2} \left( \frac{2-f}{f} \right) \frac{dp}{dz} + \frac{3}{4} r^2 \frac{\eta}{T} \frac{dT}{dz}$   
 $Q_m =$  flow rate gr/sec, other quantities in c. g. s. units.

When the connecting pipe is of relative large diameter, and the mean flow velocity high there will usually be a contribution of the Bernoulli flow type, i. e., the kinetic energy of the flowing mass may be appreciable.<sup>1</sup>

Evidently the flow of gas through a pipe may be either largely mechanical or hydrodynamic in character or largely molecular or diffusive in character or of mixed character depending on the dimensions of the pipe, the mean free path, etc. In the case of liquids where the "mean free path" or mean "amplitude of vibration" is usually considerably less than a molecular diameter, the flow through pipes or capillary passages whose diameters are greater than only a few molecular diameters will be largely hydrodynamic in character. Thus even in the case of exceedingly small capillary spaces we

<sup>1</sup> Viscosity itself is, of course, related to molecular diffusive properties, directly in the case of gases and more or less inversely in the case of liquids.

must know something concerning the density of the fluid before we can tell whether the flow mechanism is likely to be largely hydrodynamic or largely diffusive in character. When the capillary passages are of molecular dimensions or smaller, relatively large attractive and repulsive forces are involved, and large forces are required to force molecules through the repulsive regions, i. e., the flow is controlled by the "activation energies" corresponding to the potential energy barriers through which the molecules must flow. The flow mechanism in this case will be largely diffusive in character. (3)

Before discussing the influence of surface forces on the flow of fluids through capillary systems, the nature of the solid surface forces which are associated with adsorption and capillarity will be discussed briefly.

Just as flow mechanisms were divided into two broad categories, surface forces at room temperature can be divided into two distinct classes, namely: (4, 5) (a) Surface forces associated with definite isolated high energy sites, the whole volume of the energy field associated with the site being comparable with, or less than the volume of a single adsorbate molecule. The surface forces of such sites are large and lead to quantized energy states or to bond formation and chemisorption. In this case the adsorbate molecules become practically a part of the solid surface and, compared with molecules in a liquid or gas, such chemisorbed molecules are largely immobilized. (b) Surface forces associated with relatively large areas of the solid surface or with many "sites" the fields of which overlap so as to form a surface region or layer of considerable volume under the influence of an attractive force field. Energy states of molecules due to these fields only are not quantized but are continuous and behave classically. Thus molecules of adsorbate in such regions will have properties closely resembling the properties of the adsorbate in bulk at corresponding densities and temperatures. The thickness of the layer will depend on the size and nature of the adsorbate molecules and may be of the order of 10 Å. For approximate calculations we may use overlapping Leonard-Jones six-twelve potentials taking the size of adsorbate molecules into consideration.

If molecules of a condensable gas are allowed to fall into such regions the equilibrium density of the gas molecules in the surface region may be much higher than that remote from the surface and hence at some critical density may condense to the corresponding liquid under the influence of their own attractive forces. Once the liquid is formed, the liquid vapour interface will have a surface potential peculiar to the particular adsorbate. In general, this potential will be of opposite sign to the potential of the solid surface. Thus the formation of liquid-vapour surfaces of tension will tend to reduce the net surface potential. Adsorption phenomena in such regions will be essentially Polanyi adsorption.

While in general any surface will have surface forces of both these extreme types as well as those of intermediate character, the behaviour of active adsorbents such as active carbon indicates that the bulk of the net adsorption phenomena is of the latter type, since the adsorption is readily reversible and strongly influenced by the condensability of the adsorbate. (6)

In the case of transient or non-steady state flow, if the total surface area is at all large, all of the different types of surface forces will influence the rate of adsorption and permeation of the capillary system. In the case of steady-state flow, however, surface forces of the first type will have a negligible influence in most cases since molecules once adsorbed will be largely immobilized. The number of such very high energy sites being comparatively small any effect on the dimensions of the capillary passages will be small in cases where the mean pore sizes are reasonably large (i. e., 10 Å or more).

In what follows we will confine our discussion to cases where the surface forces are entirely of type (b), i. e., to cases where any effect of surface forces leads to a Polanyi type adsorption mechanism.

#### INFLUENCE OF SURFACE FORCES ON PRESSURE AND DENSITY OF FLUIDS IN CAPILLARY SPACES

In order that an equilibrium exist between the fluid within the capillary system and the fluid remote from surface forces their thermodynamic potentials must be the same,

i. e.,  $\mu_a = \mu$  where the subscript  $a$  refers as before to the fluid in the capillary system. As the pressure of the fluid remote from the surface is varied, the temperature being constant, the thermodynamic potentials must remain equal to preserve the equilibrium. Since  $d\mu = -Sdt + vdp$ , we have the following isothermal equilibrium condition equation:

$$\delta v_{ai} \cdot dp_{ai} = \delta v_i \cdot dp$$

where  $\delta v_{ai}$  is any element of volume of the fluid in the capillary region and  $dp_{ai}$  the pressure change in this element while  $\delta v_i$  is an element of volume of the reference fluid remote from the surface forces which contains the same matter as  $\delta v_{ai}$  and  $dp$  is the change in the uniform pressure of this reference fluid. Hence for the whole of the adsorbate:

$$\sum_{v_a} \delta v_{ai} \cdot dp_{ai} = \sum_v \delta v_i \cdot dp$$

or

$$v_a \cdot d\bar{p}_a = v dp$$

where  $\bar{p}_a$  is the volumetric mean pressure of the adsorbate. Hence,

$$d\bar{p}_a = \rho_a / \rho \cdot dp$$

where  $\rho_a$  is the mean adsorbate density, and  $\rho$  the density of the reference fluid. On integrating:

$$\bar{p}_a = \int_{P=0}^{P=P} \frac{\rho_a}{\rho} \cdot dp = aP$$

where  $a$  as defined by the equation is the mean value of  $\rho_a/\rho$  over the pressure interval 0-P. Thus the volumetric mean pressure of the adsorbate  $\bar{p}_a$  is given by the integral of  $\rho_a/\rho$  from 0 to P, P being the pressure of the reference fluid or gas remote from the surface;  $\rho_a$  the mean adsorbate density will be given by the total weight of adsorbate divided by the void volume of the capillary system. Thus if X is the weight adsorbed per gram of capillary then (N.B.: the weight

$$\frac{X + \rho v_a}{v_a} = \rho_a$$

adsorbed is usually taken to be the weight in excess of that which the void volume would contain in the absence of surface forces, i. e., in excess of  $\rho v_a$ .) Since  $\rho = \frac{pM}{RT}$

for an ideal gas,  $\bar{p}_a = \int_0^P \left( \frac{XRT}{pMv_a} + 1 \right) dp$

Thus when  $X = 0$ ,  $\bar{p}_a = P$  and when X is much greater than  $pM/RT$ ,  $\bar{p}_a$  is much greater than P.  $\bar{p}_a$  can be obtained graphically from the adsorption isotherm.<sup>2</sup>

<sup>2</sup> It is of course much better to obtain this integral graphically from a known observed reversible isotherm than from an assumed adsorption isotherm equation. Equation 1 is exactly equivalent to Guggenheim's "spreading pressure" and like the spreading pressure is thermodynamically necessary regardless of any assumption concerning the mechanism of the adsorption. However, in the case of chemisorption the "spreading pressures" are not even approximately hydrostatic pressures of the adsorbate or of the adsorbate-adsorbent interface, but rather are analogous to osmotic pressures. In the general case the spreading pressure is measured by that external force which must be exerted (parallel with the surface) on a movable mechanical wall or barrier dividing the adsorbed layer from the clean surface, the height of barrier extending to the limit of the range of the surface forces. If such an equilibrium can exist then the external force divided by the area of the barrier is the spreading pressure. However, under the assumed conditions these mean adsorbate pressures are mean hydrostatic pressures and are closely analogous to the mean horizontal pressure exerted on the vertical walls of a tall water tank due to gravity or any other scalar force field.

If hysteresis occurs so that a second thermodynamically reversible path intersects the path along which  $p$  increases from  $O$  to  $P$ , and the pressure is reduced from  $P$  to say  $P'$ , the mean adsorbate pressure is obtained from the equation,

$$\bar{p}_a = \int_0^P \rho_a/\rho \cdot dp - \int_{P'}^P \rho_a'/\rho \cdot dp \quad (1)$$

where  $\rho_a'$  is the mean density along this second path. If  $\rho_a'$  greatly exceeds  $\rho_a$ ,  $\bar{p}_a$  may become negative. But along any reversible path of increasing equilibrium pressure  $\bar{p}_a$  cannot become negative.

Evidently when a long porous body which adsorbs vapour appreciably is exposed at its extremities to two different pressures, the pressure gradient along its length within the porous body may be much greater than that corresponding to the pressure gradient that would subsist in the absence of surface forces, i. e., in the absence of adsorption or any other conditions which can maintain an appreciable density difference between the fluid within and that outside of the capillary system.

In pipes of diameters consistent with hydrodynamic or laminar viscous flow we might expect the flow rate in mass units to be proportional to the adsorbate density and to the adsorbate pressure gradient. Thus we might expect that we could write

$$Q_m = -A \rho_a \cdot \frac{dp_a}{dz}$$

where  $Q_m$  is the flow rate in mass units,  $A$  a constant characteristic of the pipe,  $\rho_a$  the mean density of the fluid within the pipe, and  $dp_a/dz$  the pressure gradient within the pipe. However, it is immediately evident that if the "viscosity" is variable, near the wall approaching say liquid viscosity while remote from the wall approaching gas viscosity,  $A$  will not be by any means a constant but will be a complex function of  $\rho_a$ . The complete equation in this case is very complex and involves a number of unknown parameters. However, there are two special cases where the complete equation can be greatly simplified and leads to a useful equation. The simplest case is that where the fluid is well below the critical temperature and where the surface forces condense the vapours to liquids or to thin liquid films on the surface of the capillary region and where  $\rho_a \gg \rho$ . Assuming now that the condensed liquid has the normal liquid viscosity it can be shown that for small pipes of circular cross-section the flow rate is given by

$$Q_m = -\frac{\pi r^4}{8\eta_l} \cdot \rho_a \frac{dp_a}{dz}$$

and since  $dp_a = \rho_a/\rho \cdot dp$ ,

$$Q_m = -\frac{\pi r^4}{8\eta_l} \cdot \frac{\rho_a^2}{\rho} \cdot \frac{dp}{dz} = \frac{\pi r^4}{8\eta_l} L \cdot \int_{P_1}^{P_2} \frac{\rho_a^2}{\rho} \cdot dp$$

where  $L$  is the length of the pipe and  $P_1$ ,  $P_2$  the input and output pressures respectively.

This equation is applicable only when the relative contribution from the simultaneous gaseous flow is negligible. It is to be emphasized that the equation is a simplification of a much more complex equation. (7) Even the shape of the pipe will modify the form of the integrand. However, with suitable numerical coefficients the equation should be approximately valid for pipes of more or less square or circular cross-section where the range of the surface forces or the thickness of the dense surface layer is comparable with the dimensions of the pipe.

Where the equation is applicable to a single capillary a similar equation will of course be applicable to bundles of parallel capillaries of the same dimensions and having the same film thicknesses. The equation will be approximately valid for bundles of parallel capillaries whose radii vary a little provided that corresponding variations in film thickness are roughly inversely proportional to  $r$ , i. e., that the fields are somewhat higher in the smaller capillaries ( $r^4$  is of course replaced by  $\overline{Nr^4}$  in such cases).

In the case of large pores, where the density of the fluid in the capillary system under static equilibrium conditions is practically the same as that of the fluid outside of the capillary system, the flow rates for pipes of lengths comparable with their diameters will be given by the following classical equations:

For liquids:

$$Q_m = \frac{\pi r^4}{8\eta_1} \rho_1 \frac{P_1 - P_2}{L}$$

where  $\rho_1$  is the density of the liquid and  $\eta_1$  its viscosity.

For ideal gases:

$$Q_m = \frac{\pi r^4}{8\eta} \frac{M}{RT} \frac{P_1^2 - P_2^2}{L} + \frac{\pi r^3}{2} \left( \frac{\pi M}{2RT} \right)^{1/2} \left( \frac{2-f}{f} \right) \frac{P_1 - P_2}{L}$$

where  $\eta$  is the gas viscosity (more or less independent of density) and  $f \approx 0.9$ .

Gaseous flow rates are commonly expressed in K units, i. e., in pv units divided by  $\Delta P$ . In these units,

$$\begin{aligned} K &= \frac{Q_{pv}}{P_1 - P_2} = \frac{Q_m}{P_1 - P_2} \frac{RT}{M} \\ &= \frac{\pi r^4}{8\eta L} \frac{P_1 + P_2}{2} + \frac{\pi r^3}{2L} \left( \frac{\pi RT}{2M} \right)^{1/2} \left( \frac{2-f}{f} \right) \end{aligned}$$

in which  $f$  is the fraction of the tangential momentum convected to the surface of the pipe per second by thermal motion which is actually transferred to the surface (i. e.,  $f = 0$  for specular reflection and  $f = 1$  if every molecule striking the surface sticks to it).

Since  $(P_1 + P_2)/2$  is the mean of the input and output pressures, when  $K$  is plotted against  $\bar{P}$  we get a straight line, the slope of which is given by the first term of the right hand member of the equation and the intercept by the second.

This is Maxwell's equation with slip. At very low densities the flow mechanism becomes molecular effusion which is a different phenomenon. The flow rate is given by an expression which resembles the term in  $r^3$  but is numerically different. In the case of long narrow capillaries the effusive or Knudsen flow in K units is given by

$$K = \frac{4\pi r^3}{3L} \left( \frac{2RT}{\pi M} \right)^{1/2} \frac{2-f}{f}$$

This term is larger than Maxwell's slip term, hence when  $K$  is plotted as a function of  $\bar{P}$  the graph should show a minimum.

However, as shown by Clausing (8) in the case of short tubes the effusion flow becomes practically identical with the "slip flow". In more or less granular isotropic or porous bodies the "bottle necks" controlling the flow rates should have lengths comparable with their diameters. Accordingly, no minimum is to be expected in the case of gaseous flow through porous or granular beds when surface forces can be neglected.

In cases of complex capillary systems where there are both micropores and macropores, the micropore and macropore systems should be treated separately if at all possible. In the case of many active adsorbents the two pore systems are quite distinct, the micropore systems having nearly uniform pore diameters of the order of 10 to 20 A while the macropore systems have pore diameters showing a considerable variation from the mean, the mean being of the order of  $10^3$  or  $10^4$  A. If the volumes of these two pore systems are at all comparable it is evident that the permeability of the micropore system will be quite negligible compared with that of the macropore system in the absence of surface forces or some agency which profoundly modifies the flow mechanism. Since surface forces may easily increase fluid densities by factors of  $10^4$  and more, and accordingly increase pressure gradients by similar factors, flow rates may be increased a million fold even when the viscosity of the adsorbed material is increased a hundredfold. We have found experimentally that the flow rates of a number of vapours through both the macropores and micropores of some activated carbon rods may be described quite well by means of the following equation

$$Q_m = - \frac{A}{\eta_1} \frac{\rho a^2}{p} \frac{dp}{dz} - \frac{\beta}{\eta} p \frac{dp}{dz} - c \frac{dp}{dz}$$

In the case of water vapor in adsorptive states of flow<sup>3</sup> the equation describes the results probably within the experimental error (see Fig. 1). The equation also describes the flow of rates of vapors of methanol, ethyl chloride, diethyl ether and benzene quite well. However, the experiments (9) indicate that the temperature coefficient of the viscosity of adsorbed water is somewhat higher than that of liquid water especially at temperatures below 0 C and hence that the viscosity itself is probably appreciably greater at room temperature than that of ordinary water. This might be expected if the surface forces fall off rapidly with distance so that the deformation accompanying the laminar flow state involves work against the surface forces.

Where  $p_a$  is relatively low and the adsorbed material largely gaseous in character the flow equation becomes more involved. However at very low equilibrium gas pressures where even the adsorbed material behaves largely as an ideal gas, if  $p_a \gg p$ , the last two terms may vanish and the flow become virtually a molecular effusion or a "surface diffusion" through the micropore system alone. The terms B and C refer of course to the macropore system while A refers to the micropore system. If the distributions of pore sizes are known, as well as their shapes, etc., the equation can be used for estimating pore sizes of both micropores and macropores. For a macropore system of parallel capillary passages B contains  $Nr^4$  while C contains  $Nr^3$ . When the frequency distribution of pore radii of the macropore system is of the form  $N(r) = Nhe^{-hr}$ , then  $\bar{r}^4 = 4\bar{r}^3 = 24\bar{r}^2$ .

### STRESSES AND STRAINS

The basic thermodynamic equations enable one to estimate the solid stresses resulting from the adsorption reaction. The volumetric mean stress intensity of the solid is given by (10, 11, 12)

$$\bar{p}_c^v = \left[ 1 + \frac{v_a}{v_c} (1-a) \right] P$$

where  $v_a$  is the void volume and  $v_c$  the solid volume so that the total volume of the porous body is  $v_a + v_c$  and as before,  $\bar{p}_a = aP$ . The linear mean stress intensity may be written

$$\frac{\bar{L}}{\bar{p}_c} = \left[ 1 + K_p \cdot K_s \frac{v_a}{v_c} (1-a) \right] P$$

solid cross-section of typical linear filaments of the solid.  $K_p$  is a statistical correlation factor which may be greater or less than unity (usually less) but which approaches unity at high adsorbate densities. Since the elongation accompanying an adsorption reaction is given by  $\partial l/l = -\beta \partial \bar{p}_c^L$  where  $\beta$  is roughly  $1/3$  of the bulk compressibility of the solid, the dimensional changes may be used as a rough measure of

<sup>3</sup> Where hysteresis occurs there will be a difference in flow rates between adsorption and desorption states. Adsorption states are obtained by exposing the sample to gradually increasing gas pressures equilibrating at the desired output pressure, then increasing and maintaining constant the pressure on the input side until a steady state of flow is reached. The desorption state by decreasing the gas pressure from saturation to the input pressure equilibrating at the input pressure and then lowering the output pressure, etc.

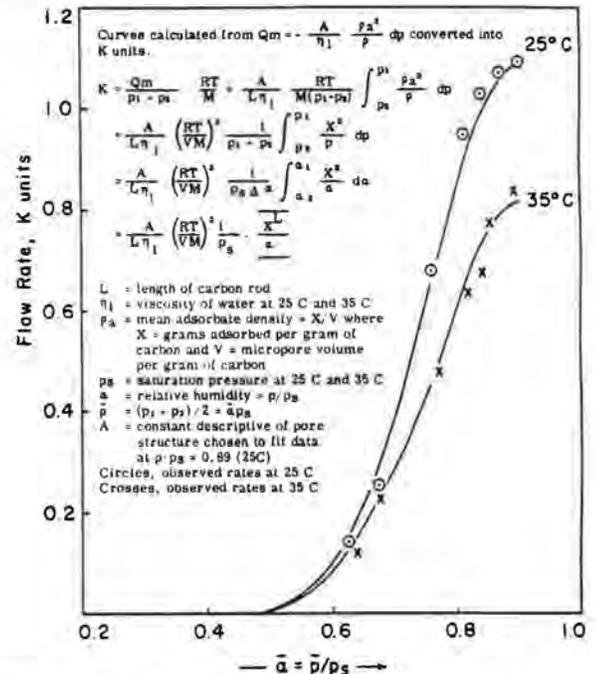


Figure 1. Flow rates of water vapour through the micropore system of an activated carbon rod; adsorption state. (By permission of the Canadian Journal of Chemistry).

where  $K_s$  is a numerical constant which is in general greater than unity (usually about 3) which measures the variation in

$\bar{p}_a$  and hence of the adsorption potential.<sup>4</sup> This might prove of value in cases where for practical reasons adsorption isotherms cannot be measured directly e.g., oils of very low vapour pressure.

It may be remarked that one must be careful in the use of spreading pressures such as  $\bar{p}_a$  in estimating say the tendency of a paint film to be "lifted" from a porous body by moisture since the "spreading pressure" of the paint film may actually exceed that of the water. Where adsorbed layers of two different materials are completely immiscible everywhere in the surface region the tendency of one to displace the other will be measured by the difference of their spreading pressures.

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<sup>4</sup> Where the solid and fluid are practically incompressible the entropy of the system adsorbent-adsorbate (the adsorbent being completely filled with fluid) and the sum of the entropies of the two separately should be practically the same in many cases. In such cases the adsorption or surface potential will appear wholly as an energy and the heat of immersion will provide a measure of the adsorption potential. In general, the heat of immersion will vary for different fluids, i. e., the surface potential is not due wholly to the surface free energy of the solid alone by any means.