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EFFECT OF WETTING HYSTERESIS ON STATE OF GAS TRAPPED BY LIQUID IN A CAPILLARY

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Abstract—State equations were obtained for gas trapped by liquid in a capillary and kinetic equations set up for change of this gas volume incorporating the effect of wetting hysteresis. These equations were verified for air trapped by water in a glass capillary and the results of the experiment appear to agree fairly well with predicted values.

NOMENCLATURE

σ,	surface tension;
r,	capillary radius;
θ_1, θ_2,	contact angles of forward moving and retracting meniscus;
n_g,	number of moles of trapped gas;
n'_g,	number of moles of gas dissolved in liquid;
P_a,	air pressure;
V_g,	volume of trapped gas;
T,	temperature;
p_p,	partial vapour pressure in capillary over meniscus;
μ,	kilomoles of liquid;
V_l,	liquid volume;
ρ,	liquid density;
k,	the Henry's law constant;
D_g,	gas diffusivity in liquid;
D_v	vapour diffusivity in gas;
C,	concentration of dissolved gas;
τ,	time;
l,	liquid column length;
m,	mass of trapped gas;
R,	universal gas constant.

STUDY of the state of gas trapped by liquid in a capillary is of great interest for it greatly affects kinetics of processes involved in capillary impregnation [1, 2] and drying at variable temperatures and pressures. In the present work an attempt was made to obtain equations of state and kinetics of variation of a gas volume under these conditions when temperature and pressure change. The equations obtained were checked experimentally.

Capillary phenomena are known to have no effect on the surface tension [3] and the Henry's law coefficient [4] at capillary radii up to hundredths of a micron, deviations from the Kelvin law being negligible [5]. Change of the contact angle during liquid motion in a capillary can have influence only on kinetics, the effect being pronounced only at large velocities [6].

Wetting hysteresis makes the main contribution to the results of this experiment [7] because liquid begins to move only when the value of the excess pressure becomes

$$\frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1). \qquad (1)$$

Wetting hysteresis takes place if the contact angle differs from 0 and π, therefore it is not taken into account at complete wetting. However at the capillary walls an adsorbed film is formed whose properties differ from those of the bulk liquid [8] and this results in the contact angle between the liquid and the adsorbed film being different from zero [9]. Thus, wetting hysteresis may occur. It was found in particular in experiments [10] where water viscosity was measured inside a capillary.

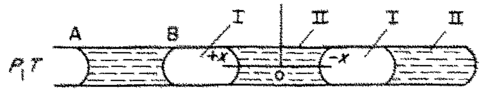

FIG. 1. Schematic drawing of filling a capillary for checking the state equation of trapped gas.

Figure 1 illustrates the behaviour of gas 1 trapped by liquid II in a capillary, the system being isolated from the surroundings by an inert liquid piston AB impermeable to gas and very sensitive to external pressure. For such a model system estimations are made in order to find the dependence of the volume of the gas trapped on the pressure and temperature, calculations being then checked experimentally.

As the quantity of gas remains unchanged when the surroundings change, then

$$n_{0g} + n'_g = n_{0g} + n'_g \,. \tag{2}$$

Considering the gas to be governed by the Clapeyron–Mendeleev law, we find

$$n_{0g} = \frac{(P_{0g} - P_{0v})V_{0g}}{RT} \tag{3}$$

$$n_g = \frac{\left[P - P_v \pm \frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1)\right] V_g}{RT} \,. \tag{4}$$

In equation (4) the sign before the last term in brackets is negative for decreasing volume and positive as the volume increases.

Taking into account that the gas is sparingly soluble, we find from Henry's law that

$$n'_{0g} = \frac{(P_{0a} - P_{0v})\, V_{0l}\rho_0}{k_0\mu} \tag{5}$$

When temperature changes, the volume of the gas varies as

$$V_l = \frac{\rho_0}{\rho} V_{0l} \tag{6}$$

so the number of moles dissolved will be

$$n'_g = \frac{\left[P_a - P_v \pm \frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1)\right] V_{0l}\rho_0}{k\mu} \,. \tag{7}$$

Substituting (3)–(6) into equation (2), making transformations and neglecting small quantities, we obtain the state equation of the gas

$$\frac{V_g}{V_{0g}} = \frac{(P_{0a} - P_{0v})\left(1 + \frac{\rho_0 R T_0 V_{0l}}{k_0 \mu V_{0g}}\right) - \frac{1}{k}\left[P_a - P_v \pm \frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1)\right]\frac{\rho_0 R T_0 V_{0l}}{\mu V_{0g}}}{P_a - P_v \pm \frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1)} \cdot \frac{T}{T_0} \tag{8}$$

When checking experimentally the equation obtained, it is necessary to determine the time required for the steady state corresponding to the new conditions to develop. With this aim we shall solve the diffusion equation for the case of one-dimensional problem, the convection being neglected as the meniscus velocity in the experiment was negligible

$$D_g \cdot \frac{\partial^2 C(x;\tau)}{\partial x^2} = \frac{\partial C(x;\tau)}{\partial \tau} \,. \tag{9}$$

Let the origin of the coordinates be in the middle of the liquid column (Fig. 1). With the notations $L = l/2$ and knowing that sorption and desorption take place through both menisci, we obtain the following initial and boundary conditions

$$C(x;0) = C_{0g}; \qquad C(-L;\tau) = C_g;$$
$$C(L;\tau) = C_g; \qquad \left.\frac{\partial C(x;\tau)}{\partial x}\right|_{x=0} = 0 \tag{10}$$

Using the operational method, we can obtain the following solution [11]:

$$C(x;\tau) = C_g + (C_{0g} - C_g) \sum_{n=1}^{\infty} \frac{4}{(2n-1)\pi} (-1)^{n+1} \frac{\pi}{2} \frac{x}{L} \exp - \frac{(2n-1)^2 \pi^2 D_g \tau}{4L^2}. \tag{11}$$

The series converges rapidly so the gas concentration in liquid corresponds to the new state with an accuracy of $\Delta C \simeq 10^{-4}$ $(C_{0g} - C_g)$, if the first term of the series is less than 10^{-4} That is the case when

$$\Delta\tau_0 > 0.38 \frac{L^2}{D_g} \tag{12}$$

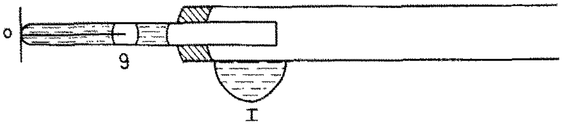

FIG. 2 Schematic drawing of filling a capillary for checking the kinetic equation of change of gas volume trapped by liquid.

A similar solution will be obtained for different boundary conditions (Fig. 2) of a water column being bound by the sealed end of the capillary. Such a model allows a simpler experimental check of kinetics of increasing volume of the trapped gas. In this case the initial and boundary conditions will be

$$C(x;0) = C_{0g}; \qquad C(0;\tau) = C_g;$$
$$\left.\frac{\partial C(x;\tau)}{\partial x}\right|_{x=l} = 0. \tag{13}$$

Using operational method [11], we obtain the following solution

$$C(x;\tau) = C_{0g} + (C_g - C_{0g}) \sum_{n=1}^{\infty} (-1)^{n+1} \times \left[\operatorname{erfc} \frac{(2n-1)l + x}{2\sqrt{(D_g\tau)}} + \operatorname{erfc} \frac{2nl - x}{2\sqrt{(D_g\tau)}}\right]. \tag{14}$$

The series obtained converges rapidly, thus if we assume the second term of the first expression to be less than 10^{-4}, that is the case when

$$1 > 5\,4\sqrt{(D_g\tau)} \tag{15}$$

we obtain, with the above accuracy,

$$C(x;\tau) = C_{0g} + (C_g - C_{0g}) \operatorname{erfc} \frac{x}{\sqrt{(D_g\tau)}}. \tag{16}$$

This equation coincides with a similar one obtained by Deryagin and Altshuler [2] for an infinite column.

Equation (15) thus allows us to determine the condition (the column length) when semi-infinite approximation can be used for estimates, i.e. formula (16) may be used.

The mass of the gas trapped at a certain moment can be determined as

$$m = m_0 \pm \int_0^{\tau} D_g \left|\frac{\partial C(x;r)}{\partial r}\right| \pi r^2 \, d\tau. \tag{17}$$

Using the Clapeyron–Mendeleev law and Henry's law and considering the pressure in the trapped gas at the beginning to be equal to the ambient pressure and knowing that during the change of ambient conditions hysteresis takes place, we obtain after integration

$$V_g = V_{0g} \frac{(P_{0a} - P_{0v})\,T}{\left[P_a - P_v \pm \frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1)\right] T_0} \pm 2 \sqrt{\left(\frac{D_g}{\pi}\right)} \frac{RT}{\mu} \times \left\{ \frac{(P_{0a} - P_{ov})\,\rho_0}{k_0 \left[P_a - P_v \pm \frac{2\sigma}{r}(\cos\theta_2 - \cos\theta_1)\right]} - \frac{\rho}{k} \right\} \sqrt{(t)}\,\pi r^2. \tag{18}$$

This equation will determine the kinetics of change in the volume of the gas trapped by the liquid caused by the dissolution of gas. Equilibrium vapour pressure corresponding to a new temperature T develops more quickly and equation (18) is not taken into consideration. Now we determine the time during which a new partial vapour pressure develops in the entrapped volume. Substituting the diffusivity of water vapours in air D_v for D_g in equation (13), we find for air and water that in 0·02 s vapour pressure in the volume trapped attains the value corresponding to a new temperature, even though the air column length is 0·2 cm.

EXPERIMENTAL PROCEDURE

In the experiments capillaries made from glass tubes were employed. They were washed by chrome mixture and then by twice distilled water. Cylindrical form of the capillary was checked before filling by means of a microscope and during filling by visualization of water column motion. The capillary radius was measured by a microscope and compared with that obtained by Fedyakin's method [12].

Filling of the capillary by twice distilled water in the case of checking the state equation of trapped gas was carried out in such a way that between the water columns, the length of which satisfied conditions (13), columns of air were formed as shown in Fig. 1. A capillary prepared in such a way was fixed in a glass tube with a larger diameter by means of epoxy resin (Fig. 2). Hole I in this tube was filled with salt solution of such concentration that vapour pressure above the solution was equal to the vapour pressure above the meniscus in the capillary. This reduced losses of water from the capillary because of its evaporation to the atmosphere (increased distance from the front meniscus to the mouth of the capillary reduced water losses). The tube with the capillary was mounted in a chamber thermostated with the accuracy of ±0·5°.

The free end of the tube was connected by means of a series of valves with the vacuum pump or the compressor or atmosphere depending on the aims of the experiment.

For checking of equation (18), the capillary was filled as shown in Fig. 2, the length of the longest column of water being matched so that it satisfied condition (15).

The lengths of air and water columns were measured by a comparator (accuracy 1 μ) and the capillary was illuminated from the side. Low pressures were measured by a mercury manometer and at increased pressures a high precision manometer was used.

EXPERIMENTAL RESULTS

For comparison of experimental data with those predicted by the equations, the value of the hysteresis angle of wetting was primarily determined. One end of the vertical capillary was immersed into twice distilled water Just

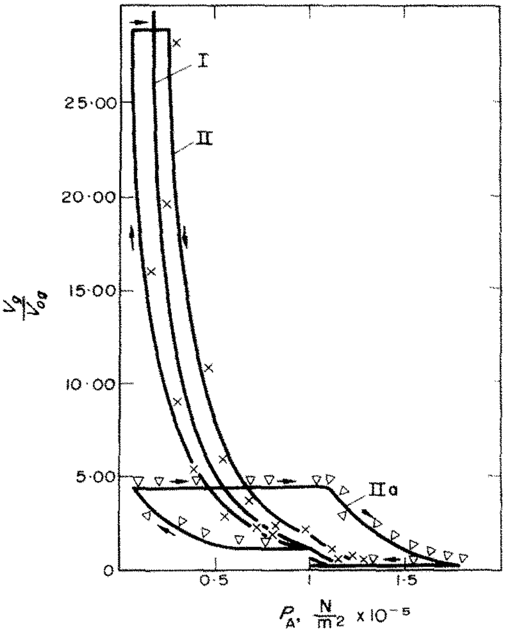

FIG. 3. Comparison of state equation of gas trapped in a capillary with experimental data at T = const. I. theoretical curve, wetting hysteresis not accounted for; II. Theoretical curve with wetting hysteresis accounted for in a capillary with r = 5·2 μ when V_{01}/V_{0g} = 181; X. experimental points; IIa. Theoretical curve incorporating wetting hysteresis in capillary with r = 1·0 μ when V_{0l}/V_{0g} = 175; ∇, experimental points.

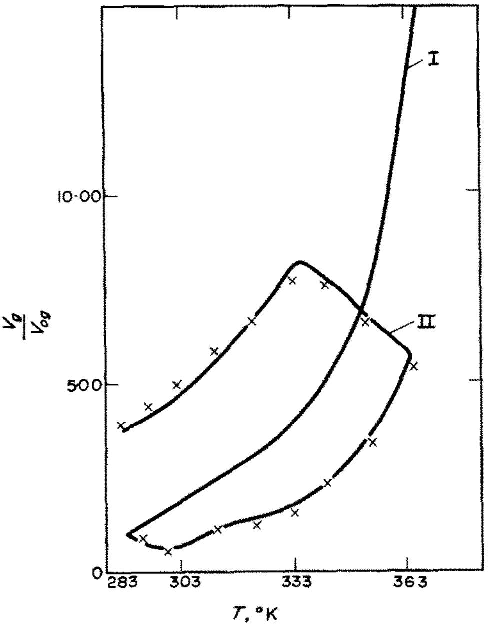

FIG. 4. Comparison of state equation for gas trapped by liquid in a capillary with experimental data (P = const). I. Theoretical curve without taking into account wetting hysteresis; II. Theoretical curve incorporating wetting hysteresis in capillary with $r = 1{\cdot}3\,\mu$ when $V_{0l}/V_{0g} = 141$; ×, experimental points.

after the capillary was filled, a slight deviation of the capillary from a vertical was sufficient to make the water move, but some time after filling, commencement of water motion occurred only at a slope of the capillary of 30–40°, the value of this slope being independent of the capillary radius.

The value of the angle measured in this way can be taken as the value of the hysteresis angle of wetting for the meniscus moving forward θ_1. For glass, the angle of wetting of retracting meniscus can be assumed to be equal to zero.

Figure 3 furnishes the results of checking equation (8) under isothermal conditions. It is characteristic that the change of the trapped volume takes place only after external pressure has attained some limit value which increases as the capillary radius decreases.

Figure 4 shows the results of comparison of the same equation with experimental data for an isobaric process. It should be noted that in this case increasing temperature at the initial moment results in decreasing the air volume as expanding water presses the air until the pressure becomes sufficient for the meniscus to move. This was taken into account during estimation of curve II. Figure 5 shows the results of comparison of equation (18) with experimental data during the isothermal process.

As it may be seen from the Figs. 3–5, experimental data agree fairly well with the predicted values only when wetting hysteresis is taken into account (curves II). Comparison of experimental data with the predicted results without taking into account wetting hysteresis (curves I) shows that this effect controls the behaviour trapped in thin capillaries. The influence of wetting hysteresis will be still more pronounced if the boundary angle of wetting differs considerably from zero,

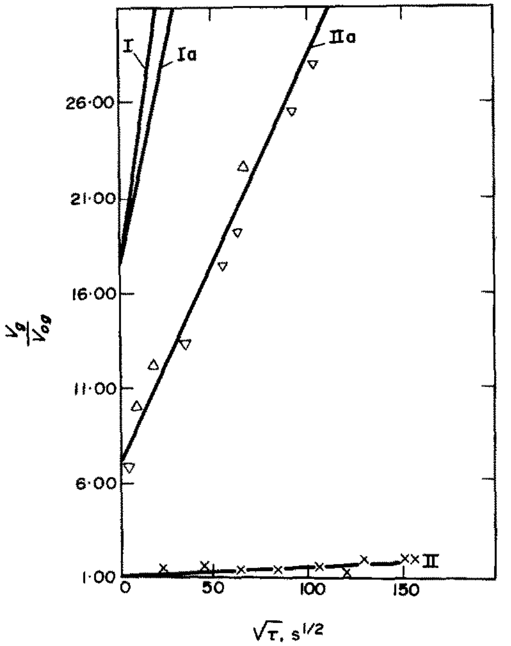

FIG. 5. Comparison of kinetic equation with experiment. I. Theoretical curve for a capillary with $r = 0{\cdot}6\,\mu$ at pressure changing from $P_{0a} = 10^5 \mathrm{N/m^2}$ to $P_a = 0{\cdot}85 . 10^4 \mathrm{N/m^2}$; II. The same with wetting hysteresis included; x, experimental points; Ia. Theoretical curve for capillary with $r = 5{\cdot}6\,\mu$ at pressure changing from $P_{0a} = 10^5 \mathrm{N/m^2}$ to $P_a = 0{\cdot}21 . 10^4 \mathrm{N/m^2}$; IIa. The same, wetting hysteresis taken into account; ×, experimental points.

as in such a case the hysteresis angle is known to be even obtuse [7].

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EFFET DU MOUILLAGE AVEC HYSTÉRÈSE SUR L'ÉTAT D'UN GAZ PIÉGÉ PAR UN LIQUIDE DANS UN CAPILLAIRE

Résumé—On obtient les équations d'état pour un gaz piégé par un liquide dans un capillaire et les équations cinétiques du changement de volume de ce gaz en prenant en compte un mouillage avec hystérèse. Ces équations sont vérifiées pour l'air piégé par l'eau dans un capillaire en verre et les résultats de l'expérience sont en bon accord avec les calculs.

EINFLUSS DER BENETZUNGS-HYSTERESIS AUF DEN ZUSTAND VON GAS, DAS DURCH FLÜSSIGKEIT IN EINER KAPILLARE EINGESCHLOSSEN IST

Zusammenfassung—In dem Artikel sind Zustandsgleichungen für Gas angegeben, das durch eine Flüssigkeit in einer Kapillare eingeschlossen ist, und Bewegungsgleichungen für die Änderung dieses Gasvolumens, wobei die Benetzungs-Hysteresis berücksichtigt wurde. Diese Gleichungen wurden für Luft, die in einer Glaskapillare durch Wasser eingeschlossen war, bewiesen.

Die Ergebnisse des Experiments zeigen gute Übereinstimmung mit den vorausgesagten Werten.

ВЛИЯНИЕ ГИСТЕРЕЗИСА СМАЧИВАНИЯ НА СОСТОЯНИЕ ГАЗА, ЗАЩЕМЛЕННОГО ЖИДКОСТЬЮ В КАПИЛЛЯРЕ

Аннотация—В работе получены уравнения состояния защемленного жидкостью газа в капилляре и кинетики изменения объема этого газа при изменении температуры и давления с учетом гистерезиса смачивания. Эти уравнения проверялись для воздуха, защемленного водой в стеклянном капилляре, причем эксперимент дал хорошее совпадение с расчетом.