The Effect of Pressure on Surface Tension

O. K. Rice

Additional information on J. Chem. Phys.
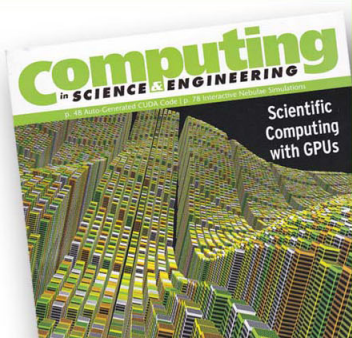
The Effect of Pressure on Surface Tension

O. K. RICE[1]

University of North Carolina, Chapel Hill, North Carolina

(Received February 25, 1947)

The thermodynamic formula for the change of surface tension with pressure is interpreted for a one-component system and for a two-component system consisting of an inert gas over a liquid. In the latter case the effect of pressure on surface tension can be attributed in part to absorption of gas at the surface of the liquid and in part to an intrinsic decrease in density of the liquid in the neighborhood of the surface. The equations are interpreted in terms of the Gibbs adsorption isotherm. The adsorption of gas at the liquid surface has been estimated in several cases from data in the literature.

THE variation of surface tension with pressure has been shown by Lewis and Randall[2] to be given by the equation

$$(\partial\gamma/\partial p)_{\sigma, T} = (\partial V/\partial\sigma)_{p, T}. \tag{1}$$

Here V is the total volume of the system and σ the total surface area, so $(\partial V/\partial\sigma)_{p, T}$ is the increase in volume produced by increasing the surface by unit area. This equation holds, as Lewis and Randall noted, for any system in which the total amount of any component remains fixed, regardless of the number of components present. γ, itself, is defined in terms of a constant pressure, as well as a constant temperature, process, namely

$$\gamma = (\partial F/\partial\sigma)_{p, T} \tag{2}$$

where F is the total Gibbs free energy of the system.

In a one-component system consisting of a liquid in equilibrium with its vapor it is not possible for the pressure to vary. Equation (1) will be applicable, nevertheless, if we can imagine the equilibrium between liquid and vapor to be frozen. In this case $(\partial V/\partial\sigma)_{p, T}$ is a measure of the difference of density of the liquid at its surface and in the bulk of the material. Since the liquid is almost certainly less dense near the surface than it is in bulk, $(\partial V/\partial\sigma)_{p, T}$ should be positive, and the surface tension should increase with pressure. This cannot, of course, be verified experimentally; conceptually, however, it is of importance and has some applications in the study of the equilib-

rium between liquid and vapor, as is shown in the preceding article.[3]

About the only available experiments on the effect of high-pressure on the surface tension of a gas-liquid interface are those done by Kundt.[4] The pressure was exerted by an inert gas over the liquid, and it was found that the surface tension was appreciably lowered. This is in contrast to the effect to be expected in a one-component system. Adam[5] has remarked upon the importance of the gas itself in this effect, and the amount of lowering of the surface tension depends upon the nature of the gas used.

Some similar effects have been observed on the surface tension of water and mercury, when these liquids are in contact with a relatively low pressure of vapor of different substances in the region above the surface. In these cases, the effect has been quite properly ascribed to the adsorption of the vapor at the surface, and the ordinary Gibbs adsorption equation has been applied.[6]

It seems almost certain that the phenomena with inert gases at high pressures have a similar origin. The surface is a favorable place for there to be some accumulation of gas. The gas is attracted to the liquid by van der Waals forces, and at the surface it is not necessary to disturb the intermolecular attractions of the liquid. If there is, thus, an excess concentration of gas molecules in the surface over that of gas molecules dissolved in the liquid, this excess (which we designate as Γ, the amount adsorbed per unit

[1] On leave 1946–47 at the Clinton Laboratories, Oak Ridge, Tennessee.

[2] G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 248.

[3] O. K. Rice, J. Chem. Phys. **15**, 314 (1947).

[4] Kundt, Ann. d. Physik **12**, 538 (1881); *Int. Crit. Tab.* **4**, 475.

[5] N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, 1941), third edition, p. 165.
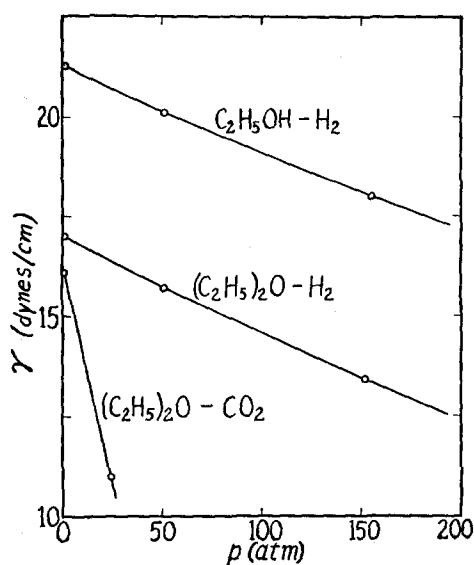
[6] See reference 5, pp. 130ff.

333

FIG. 1.

surface) must be removed from the gas phase when the surface is increased. This will result in a considerable lowering of the volume and will usually be the principal contribution to $(\partial V/\partial\sigma)_{p,T}$ in such a two-component system. If the gas may be considered to be ideal, it will be equal to $-\Gamma kT/p$, where T is the absolute temperature, k is Boltzmann's constant, and Γ is expressed in molecules per unit surface.

In addition there will be the intrinsic change of volume, due to decreased density of the surface, discussed in connection with one-component systems. If this change in volume is ΔV_σ per unit surface, we may write Eq. (1) in the form

$$(\partial\gamma/\partial p)_\sigma = (\partial V/\partial\sigma)_p = -\Gamma kT/p + \Delta V_\sigma. \quad (3)$$

If the gas is not ideal, we may set

$$(\partial\gamma/\partial p)_\sigma = -(\Gamma kT/p)(pV)_{\text{obs.}}/(pV)_{\text{i. d.}} + \Delta V_\sigma \quad (4)$$

where $(pV)_{\text{obs.}}$ is the observed value of pV, which may be obtained readily from tables, and $(pV)_{\text{i. d.}}$ is its ideal value.

The results may be interpreted in terms of the Gibbs adsorption isotherm. In fact, Eq. (1) may be readily thrown into the form of Gibbs equation. We let there be a total number of moles, $n_1, n_2, \cdots, n_i, \cdots$ of the respective components in the two-phase system. The chemical potentials are given by the usual equations

$$\mu_i = (\partial F/\partial n_i)_{p,T,\sigma,n_1,\cdots n_{i-1},n_{i+1},\cdots} \quad (5)$$

and we may define quantities $\bar{v}_1, \bar{v}_2, \cdots\bar{v}_i, \cdots$ by the equations

$$\bar{v}_i = (\partial V/\partial n_i)_{p,T,\sigma,n_1,\cdots,n_{i-1},n_{i+1},\cdots} \quad (6)$$

$\bar{v}_i$ is not the partial molal volume of either phase, since n_i is the total number of moles in both phases, but is a kind of average partial molal volume. By differentiating Eq. (5) with respect to p, noting that

$$(\partial F/\partial p)_{T,\sigma,n_1,\cdots,n_i,\cdots} = V,$$

we have

$$(\partial\mu_i/\partial p)_{T,\sigma,n_1,\cdots,n_i,\cdots} = \bar{v}_i. \quad (7)$$

The quantity $(\partial V/\partial\sigma)_{p,T}$ which appears in Eq. (1) is the volume change caused by a unit increase in surface, when $n_1, n_2, \cdots, n_i, \cdots$ are not changed. In order to restore the volume to its original value, maintaining the pressure and the composition of each phase constant, we add $\Gamma_1, \Gamma_2, \cdots, \Gamma_n, \cdots$ moles, per unit surface increase, of the various components. We may then write

$$(\partial V/\partial\sigma)_{p,T} = -\Gamma_1\bar{v}_1 - \Gamma_2\bar{v}_2 - \cdots - \Gamma_i\bar{v}_i - \cdots. \quad (8)$$

Inserting Eq. (8) in Eq. (1), and applying Eq. (7) we obtain

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \cdots - \Gamma_i d\mu_i - \cdots \quad (9)$$

which is the general form of the Gibbs equation for constant temperature. The proof is not general, because it takes into account only such changes of the μ's as may be caused by the total pressure. In this respect it supplements proofs of Gibbs equation which assume that the pressure remains constant. It is possible, however, to give a proof which is perfectly general.[7]

For a two-component ideal system of gas above liquid it is clear that $\Gamma_1\bar{v}_1$ in Eq. (8) corresponds exactly to $\Gamma kT/p$ in Eq. (3), if the gas is assigned the subscript 1, and it is equally clear that $-\Gamma_2\bar{v}_2$ can be equated to ΔV_σ. The correspondence between Eq. (3) and the Gibbs equation is thus brought out.

Equation (4) makes it possible to attempt to calculate the amount of gas adsorbed at the surface. In Fig. 1 we have plotted the data of Kuntz for hydrogen above ethyl alcohol, hydro-

---

[7] See reference 5, pp. 109ff.

gen above diethyl ether, and carbon dioxide above diethyl ether. We have used this curve to determine $(\partial\gamma/\partial p)_{\sigma,T}$. It is possible to obtain $(pV)_{obs}$ for hydrogen from either the Landolt-Börnstein Tables, or the International Critical Tables. For carbon dioxide we have used Eq. (3), which should suffice at 10 atmospheres.

The values of $(\partial\gamma/\partial p)_{\sigma,T}$ for the case with hydrogen, when converted to cc per cm², turn out to be 2 to 3×10^{-8}. This is unquestionably of the same order of magnitude as ΔV_σ. If, as in Table I, we set $\Delta V_\sigma=0$, we can obtain only the order of magnitude of Γ. Γ may be considerably larger than the value given, but it is, in any case, sufficiently small so that we may say that in no case is a complete monomolecular layer very closely approached.

That carbon dioxide should have a much greater effect than hydrogen is entirely to be expected, on account of the large van der Waals attraction between it and the surface of the ethyl ether. Adam noted this but had a slightly different, though related, explanation.

The calculations suggest that it would be of

TABLE I. Surface tensions at various pressures and 21°C.

	p atm.	$\partial\gamma/\partial p$ dynes/cm atm.	$(pV)_{obs}./(pV)_{i.\,d.}$	$\Gamma\times10^{-14}(\Delta V_\sigma=0)$ molecules/cm²
C₂H₅OH with H₂	10	0.0256	1.006	0.00063
	50	.0220	1.031	.0026
	100	.0205	1.061	.0048
	150	.0192	1.092	.0065
(C₂H₅)₂O with H₂	10	0.0272	1.006	0.00067
	50	.0242	1.031	.0029
	100	.0230	1.061	.0054
	150	.0218	1.092	.0074
(C₂H₅)₂O with CO₂	10	0.222		0.0055

interest to perform experiments with helium as the inert gas. Helium would probably be less adsorbed than hydrogen, and in this case ΔV_σ might be the predominant term so that $\partial\gamma/\partial p$ would become positive. Unfortunately, it does not seem possible to separate the two effects, though the approach to saturation (possibly hinted at in the results discussed) might throw some light on the matter. For this purpose measurements at higher pressures would be needed.