# On the Thermodynamic Theory for the Effect of Pressure on Surface Tension

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Dedicated to Professor *Ole Lamm* on his 60th birthday

Using the thermodynamic methods for treating planar surface
systems which have previously been discussed by the author, equa-
tions are derived stating the effect of pressure upon the surface tension
of binary liquid-gas systems. By applying these equations to experi-
mental data it is shown that the pressure dependence of the surface
tension can be predicted with satisfactory accuracy for pressures up
to several hundred atm. The calculated molecular surface areas
for the gaseous components are in reasonable agreement with the
corresponding surface areas which are commonly employed in the
BET surface area method.

It has long been recognized that the surface tension derivative with respect to pressure fulfills the relationship

$$\left(\frac{\partial \gamma}{\partial p}\right)_{T,A} = \left(\frac{\partial V}{\partial A}\right)_{T,p} \tag{1}$$

where $V$ is the total volume and $A$ the surface area of the system. Lewis and Randall [1] pointed out that this equation should be valid for *all* closed equilibrium systems, regardless of the number of constituents present and of possible dissolution and adsorption equilibria. This statement is apparently correct, since for a closed equilibrium surface system the Gibbs free energy differential is

$$dG = -SdT + Vdp + \gamma dA \tag{2}$$

$G$ being defined as $G = U - TS + pV$. It thus appears that the condition for the validity of eqn. (1) is that $G$ is a state function, *i.e.* that $dG$ is a total differ-
ential. Rice [2] deduced that the volume change, caused by an increase in the surface area of a liquid-gas system at constant $T$ and $p$, is mainly made up of two counteracting contributions *viz.* (a) an intrinsic volume increase due to the decreased density of the surface phase, (b) a decrease of the gas phase volume

caused by adsorption at the liquid-gas interface. He also concluded that the first-mentioned effect might be predominating only when using an inert gas like helium which is weakly adsorbed. In such a case it could therefore be expected, according to eqn. (1), that the surface tension increases when applying a higher pressure. This prediction was later confirmed experimentally by Slowinski, Jr. *et al.*[3] for water-helium and by Gielessen and Schmatz [4] for hexane-helium and nonane-helium. For all other liquid-gas systems so far investigated the converse behaviour has been found [3-5]. Although Gibbs' adsorption formula has been applied to cases of surface tension lowering [6], evidently no detailed theory based on Gibbs' thermodynamics for surface systems has yet been developed which may account quantitatively for all the experimental finding, including the behaviour of the liquid-helium systems and the course of $\gamma$-$p$ curves at higher pressures. The present author therefore judged that it might be worth while to apply the theoretical methods described in an other paper [7] to these questions.

## THEORY

It has been shown (*cf.* Ref.[7]) that for a planar equilibrium system the chemical potential $\mu_i^s$ of a substance in a surface phase is related to $\mu_i^b$, the chemical potential in a bulk phase, by

$$\mu_i^s = \mu_i^b + A_i \gamma \tag{3}$$

where $\gamma$ is the surface tension and $A_i$ the partial molar surface area defined as $A_i = v_i^s/\tau$ where $v_i^s$ denotes the partial molar volume in the surface phase and $\tau$ the thickness of the surface phase, *i.e.* the depth of the region near the surface with properties differing from the bulk phase properties. $\mu_i^s$ as well as $v_i^s$ should be regarded as mean values of the local properties within this surface layer. It is evident that $A_i$ corresponds to the projected area of a molecular volume only in the case of a monolayer. In this connection we may conveniently regard $A_i$ as independent of pressure (but not of composition), thus postponing the most general treatment.

If it were possible to subject a two-component liquid-gas system to pressure at constant temperature without the appearance of adsorption and dissolution reactions of the gaseous component, we would expect that the surface tension would increase. This is because on differentiating eqn. (3), applied to the liquid component $B_1$, with respect to pressure and taking into account that for 1 mole of a pure substance (* denoting the pure state)

$$\left(\frac{\partial \mu_i^{s*}}{\partial p}\right)_T = v_i^{s*} \qquad \left(\frac{\partial \mu_i^{b*}}{\partial p}\right)_T = v_i^{b*} \tag{4 a, b}$$

the eqn.

$$\left(\frac{\partial \gamma_1^*}{\partial p}\right)_T = (v_1^{s*} - v_1^{b*})/A_1^* \tag{5}$$

is obtained, where $v_1^{s*} - v_1^{b*} > 0$ for most liquids [8]. Actually, these circumstances are never encountered; it is instead necessary to regard both the liquid bulk phase (b') and the surface phase (s) as mixtures consisting of two components.
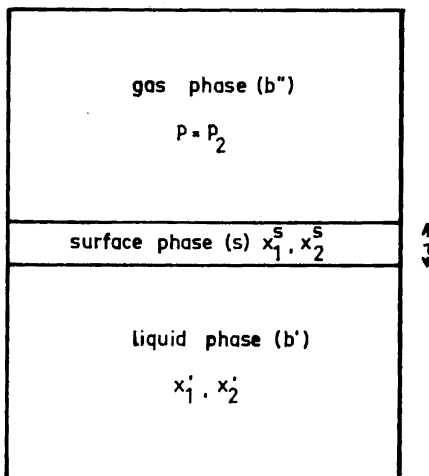
gas phase (b")

$P = P_2$

surface phase (s) $x_1^s, x_2^s$

$T$

liquid phase (b')

$x_1', x_2'$

*Fig. 1.* Sketch of the system studied.

However, since the vapour pressure of the liquid component is often comparatively small, the gas phase (b") may be considered as containing only the gaseous component $B_2$, implying that the total pressure $p$ can be equalled to the pressure $p_2$. Only binary systems of the above category will be dealt with here (*cf.* Fig. 1). Thus we have to investigate the consequences of the following equilibrium conditions

$$\mu_1^s = \mu_1' + A_1\gamma \tag{6}$$

$$\mu_2^s = \mu_2' + A_2\gamma \tag{7}$$

$$\mu_2' = \mu_2'' \tag{8}$$

where *indices* ' and " refer to the two bulk phases b' and b" and all $\mu$:s should be regarded as functions of composition and pressure. By introducing Lewis' activity definition and taking the pure substances at the temperature $T$ and the varying pressure $p$ as the *reference states* [9], eqns. (6) and (7) can be written

$$x_1^s/x_1' = F_1 \exp[(A_1\gamma - A_1^*\gamma_1^*)/RT] \tag{9}$$

$$x_2^s/x_2' = F_2 \exp[(A_2\gamma - A_2^*\gamma_2^*)/RT] \tag{10}$$

$F_i$ denoting a ratio of activity factors *viz.*, $f_i'/f_i^s$. It is, however, easily derived on integrating eqn. (5) and the corresponding eqn. for pure $B_2$ and inserting $A_i^* = A_i^o$ that at constant $T$

$$A_i^*\gamma_i^* = A_i^o\gamma_i^o + \int_1^p (v_i^{s*} - v_i'^*) \, dp \tag{11}$$

where *index*° refers to a *standard state* defined as the pure substance at the temperature $T$ and a pressure of 1 atm. Since the pressure dependence of $F_i$ is given by

$$\left( \frac{\partial \ln F_i}{\partial p} \right)_{T,x} = \frac{(v_i' - v_i'^*) - (v_i^s - v_i^{s*})}{RT} \tag{12}$$

it may thus be derived from eqns. (9) and (10) that

$$x_1^s/x_1' = F_1^o \; \Gamma_1 \; \exp \; [(A_1\gamma - A_1^o\gamma_1^o)/RT] \tag{13}$$

$$x_2^s/x_2' = F_2^o \; \Gamma_2 \; \exp \; [(A_2\gamma - A_2^o\gamma_2^o)/RT] \tag{14}$$

where $F_i^o$ is the activity factor ratio referred to 1 atm pressure and $\Gamma_i$ is defined by

$$\Gamma_i = \exp \left[ - \int\limits_1^p \frac{v_i^s - v_i'}{RT} \, \mathrm{d}p \right] \tag{15}$$

As the compressibility of a liquid is usually very small and as the volume change due to mixing is often of neglible magnitude it might be postulated that at the temperature $T$ the relationships

$$v_i^s = v_i^{s*} = v_i^{so} \; , \; v_i' = v_i'^* = v_i'^o, \quad A_i = A_i^* = A_i^o \tag{16, a, b, c}$$

are approximately fulfilled for many solutions. Eqn. (16 c) also presupposes that no molecules show a concentration dependent orientation at the interface. In the case of liquid-gas solutions, the application of (16) implies that the dissolved gas is supposed to behave as a *liquid* component. A satisfactory approximation for eqn. (15) may thus be

$$\Gamma_i = \exp \; [-(v_i^{so} - v_i'^o)(p-1)/RT] \tag{17}$$

The standard state of $B_2$ used here, *i.e.* the liquid state of pure $B_2$ at the (room) temperature $T$ and pressure 1 atm, comprises a *hypothetical* standard state which is characterized by the surface tension $\gamma_2^o$, the molar surface area $A_2^o$ and the molar volumes $v_2^{so}$ and $v_2'^o$. Such a liquid state of $B_2$ could only be forced to exist if it were possible to increase the *internal* pressure by supplying stronger intermolecular attraction forces opposing the effect of thermal motion. We may therefore conclude that $\gamma_2^o$ often attains a *negative* value for this unrealizable state, at least for gases with low critical temperatures. One may also discuss this standard state from a formal point of view, regarding its properties as calculation constants which *in principle* can be obtained through extrapolation of the corresponding properties of the existing solutions. However, it also seems plausible to introduce an assumption of equality between the molar valumes of the dissolved and the condensed gas. Such a hypothesis would make it possible to calculate the properties of the standard state of $B_2$ from the properties of the condensed gas. This procedure will subsequently be shown to be rather successful. Concerning the activity factors $f_1^s$ and $f_2^s$ appearing in eqns. (9) and (10), it has previously been emphasized that they may contain a structure-dependent factor which equals unity only for a homogeneous surface phase or for a monolayer (*cf.* Ref.[7]).

Proceeding in a similar way from eqn. (8), eqn. (18) may be derived, if the standard states are chosen as the ideal gas at 1 atm and the hypothetical liquid state of pure $B_2$,

$$x_2'/p = F_H^o \Gamma_H K_H = H \tag{18}$$

Here $K_H$ denotes the gas solubility at 1 atm, *i.e.* approximately the inverse Henry law constant, and $F_H^o$ is an activity factor expression referred to 1 atm *viz.*,

$$F_H^o = (f_2')_{K_H}^o / (f_2')_{x_2'}^o \tag{19}$$

whereas $\Gamma_H$ is defined by

$$\Gamma_H = \exp\left[\int_1^p (\alpha/p - v_2'/RT) \, dp\right] \tag{20}$$

supposing that the compressibility factor of the gas may be written

$$pV/RT = 1 + \alpha \tag{21}$$

$\alpha = \alpha(p)$ standing for the virial expansion expressed in powers of the pressure. It appears that $K_H$ in the ideal case, when $F_H^o = 1$, $\alpha = 0$ and $v_2' = v_2'^o$, is

$$K_H^{id} = (1/\bar{p}_2) \exp\left[(\bar{p}_2 - 1) \, v_2'^o/RT\right] \tag{22}$$

$\bar{p}_2$ symbolizing the hypothetical vapour pressure of pure liquid $B_2$. Thus the ideal solubility of the gas is established as

$$(x_2')^{id} = (p/\bar{p}_2) \exp[(\bar{p}_2 - p) \, v_2'^o/RT] \tag{23}$$

Obviously, this equation is a generalized form of Raoult's law. However, in this connection non-ideal behaviour should be assumed for the solutions under study. From eqns. (18), (19) and (20) we then get

$$(f_2')_{K_H}^o = \frac{1}{\bar{p}_2 \, K_H} \exp\left[\int_1^{\bar{p}_2}\left(\frac{v_2'}{RT} - \frac{\alpha}{p}\right) dp\right] \tag{24}$$

On combining eqns. (13) and (14) it can be shown that

$$x_1' F_1^o \Gamma_1 \, e^{\Delta g_1} + x_2' F_2^o \Gamma_2 e^{\Delta g_2} = 1 \tag{25}$$

where for convenience the abbreviated notation

$$\Delta g_i = (A_i \gamma - A_i^o \gamma_i^o)/RT \tag{26}$$

has been introduced. Since $x_2'$ is determined by eqn. (18) it follows that

$$(1 - Hp) \, F_1^o \Gamma_1 e^{\Delta g_1} + Hp \, F_2^o \Gamma_2 e^{\Delta g_2} = 1 \tag{27}$$

This equation states in an implicit form the dependence between the variables $\gamma$ and $p$ for the systems studied, and it constitutes therefore the main equation of the present paper. The pressure derivative of $\gamma$ can be calculated from eqn. (27) and for subsequent use it is written here in two different forms, *viz.*

$$A_1\left(\frac{\partial \gamma}{\partial p}\right)_T = \frac{v_1^s - v_1' - HRT(K_L - 1)(1 + \alpha) - Hp(v_2' + v_1^s - v_1' - K_L v_2^s)}{1 + Hp(rK_L - 1)} \tag{28}$$

$$\left(\frac{\partial \gamma}{\partial p}\right)_T = \frac{x_1^s(v_1^s - v_1') + x_2^s[v_2^s - K_L^{-1}v_2' - (1 - K_L^{-1})v_2'']}{x_1^s A_1 + x_2^s A_2} \tag{29}$$

where $K_L$ denotes the expression

$$K_L = \frac{F_2^o \Gamma_2}{F_1^o \Gamma_1} \exp\ (\Delta g_2 - \Delta g_1) = (x_2^s/x_2')(x_1'/x_1^s) \tag{30}$$

and $r$ is the ratio $A_2/A_1$. It may readily be demonstrated that the assumptions $K_L = $ constant and $x_2'$, $K_H \ll 1$ lead to the Langmuir adsorption law because then eqn. (30) can be approximated to

$$x_2^s = \frac{K_L K_H p}{1 + K_L K_H p} \tag{31}$$

When $A_1 = A_2$ this expression represents a good approximation because in that case $K_L$ remains almost a constant, but for the general case this condition is not fulfilled. When $x_2'$ and $p$ approach zero $K_L$ attains the value

$$K_L = F_2^o\ \exp[A_2^o(\gamma_1^o - \gamma_2^o)/RT] = F_2^o K_e^o \tag{32}$$

if the very small influence of the $\Gamma$-factors is neglected and if it is supposed that $\gamma_1^*$ (0 atm) $\approx \gamma_1^o$ and $A_i = A_i^o$. The index $e$ in $K_e^o$ symbolizes that $K_e^o$ is the equilibrium constant referred to 1 atm for the *exchange* (adsorption) reaction (*cf.* Ref.[7])

$$rB_1^s + B_2' \rightarrow rB_1' + B_2^s \tag{33}$$

occurring at the actual temperature $T$ and pressure $p$. For small pressures eqn. (28) thus reduces to

$$A_1\left(\frac{\partial \gamma}{\partial p}\right)_T = v_1^s - v_1' - K_H RT\ (K_e^o F_2^o - 1) \tag{34}$$

There are other ways of deducing an expression for $(\partial\gamma/\partial p)_T$ $(=(\partial\gamma/\partial p)_{T,A}$ since $\gamma$ is independent of $A$ for the systems studied) which will also be described. According to eqn. (1) the desired relationship could be obtained by analyzing the derivative $(\partial V/\partial A)_{T,p}$. The physical meaning of this derivative is obviously the volume change per unit area at a reversible increase of the system's surface area carried out at constant $p$ and $T$ and constant *total* amounts of the components. Since a reversible increase of the surface area must be considered to imply a reversible transport of molecules from the bulk phases to the surface phase, we may conveniently introduce a *transport reaction*

$$v_1' B_1' + v_2' B_2' + v_2'' B_2'' \rightarrow v_1^s B_1^s + v_2^s B_2^s \tag{35}$$
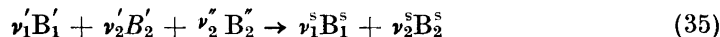
Here $v_1'$ symbolizes the stoichiometric coefficient associated with the transport of $B_1$ from the b'-phase, *etc.* Evidently, because the system is closed, the following relationships must be satisfied

$$v_1' = v_1^s \tag{36}$$

$$v_2' + v_2'' = v_2^s \tag{37}$$

In order to calculate $\Delta V$ for the transport reaction we thus have to know the ratio of $v_2'$ and $v_2''$. Since it is necessary for the reaction (35) to proceed at constant $p$ and $T$ it is realized that $x_2'$ must be maintained constant (cf. eqn. (18)). We may therefore write

$$v_1'/v_2' = v_1^s/v_2' = x_1'/x_2' \tag{38}$$

and since $v_1^s$ and $v_2^s$ state the equilibrium composition of the surface phase we have

$$v_1^s/v_2^s = x_1^s/x_2^s \tag{39}$$

On combining these eqns. it is found that

$$v_2' = K_L^{-1}v_2^s \tag{40}$$

$$v_2'' = (1-K_L^{-1})v_2^s \tag{41}$$

The volume change per Donder of the transport reaction is consequently

$$\Delta V = v_1^s(v_1^s-v_1') + v_2^s[v_2^s-K_L^{-1}v_2'-(1-K_L^{-1})v_2''] \tag{42}$$

As the corresponding increase of the surface area is given by

$$\Delta A = v_1^s A_1 + v_2^s A_2 \tag{43}$$

and since all of $V$ and $A$ are extensive properties it may be concluded that

$$\left(\frac{\partial \gamma}{\partial p}\right)_T = \left(\frac{\partial V}{\partial A}\right)_{T,p} = \frac{x_1^s(v_1^s-v_1') + x_2^s[v_2^s-K_L^{-1}v_2'-(1-K_L^{-1})v_2'']}{x_1^s A_1 + x_2^s A_2} \tag{44}$$

i.e. the same expression as was derived above (eqn. (29)) using other methods. On the other hand it is not possible to obtain eqn. (28) along these lines without making use of eqns. (13) and (14). It appears clearly that the concept of a physical surface phase which is characterized by a certain composition, volume $V^s = \Sigma n_i^s v_i^s$ and surface area $A = \Sigma n_i^s A_i$ and which contains only the region influenced by surface forces is essential for the present deduction. Actually, this concept also constitutes the basis of eqn. (3) which was the starting point of the first deduction. In Gibbs' theory of capillarity [10] a surface phase with the volume $V^G$ is considered instead which must be chosen in such a way as to contain also parts of the bulk phases. At constant $T$, Gibbs adsorption formula viz.,

$$-A \, d\gamma = n_1^E \, d\mu_1^b + n_2^E \, d\mu_2^b \ldots \tag{45}$$

always holds for a planar equilibrium surface system, $n_i^E$ denoting the surface excess $n_i^G - n_i' - n_i''$ where $n_i'$ and $n_i''$ are the mole numbers we would have within $V^G$ if the bulk phases extended to the Gibbs dividing surface. For the bulk phases, however, the Gibbs-Duhem equation should be applicable, implying for the system under consideration that

$$n_1' \, d\mu_1^b + n_2' \, d\mu_2^b = V' \, dp \tag{46}$$

$$n_2'' \, d\mu_2^b = V'' \, dp \tag{47}$$

and since $V' + V'' = V^G$, it is found that

$$-A \; \mathrm{d}\gamma = n_1^G \; \mathrm{d}\mu_1^b + n_2^G \; \mathrm{d}\mu_2^b - V^G \; \mathrm{d}p \tag{48}$$

If now the Gibbs surface phase is divided into three sub-phases

$$V^G = V^s + V^{G'} + V^{G''} \tag{49}$$

$V^s$ representing as before the physical surface phase and $V^{G'}$ and $V^{G''}$ the parts with bulk phase properties, it becomes evident that eqn. (48) may be reduced to

$$-A \; \mathrm{d}\gamma = n_1^s \; \mathrm{d}\mu_1^b + n_2^s \; \mathrm{d}\mu_2^b - V^s \; \mathrm{d}p \tag{50}$$

since again the Gibbs-Duhem equation should hold for the bulk phase regions. This equation can also be transformed into eqn. (29) by taking into account eqns. (46) and (47) and provided that the assumptions $V^s = \Sigma n_i^s v_i^s$ and $A = \Sigma n_i^s A_i$ are introduced. In Gibbs' theory no such assumptions are included, thus securing perfect universality, since the actual surface phase properties are not *a priori* well-defined due to the presumed non-homogeneity. However, precise definitions can be established (*cf.* Ref.[7]). Obviously, if the physical surface phase concept is consistently introduced much more detailed predictions about surface systems can be made. The applicability of the equations derivable from eqn. (3) to experimental data comprises the crucial test of this approach.
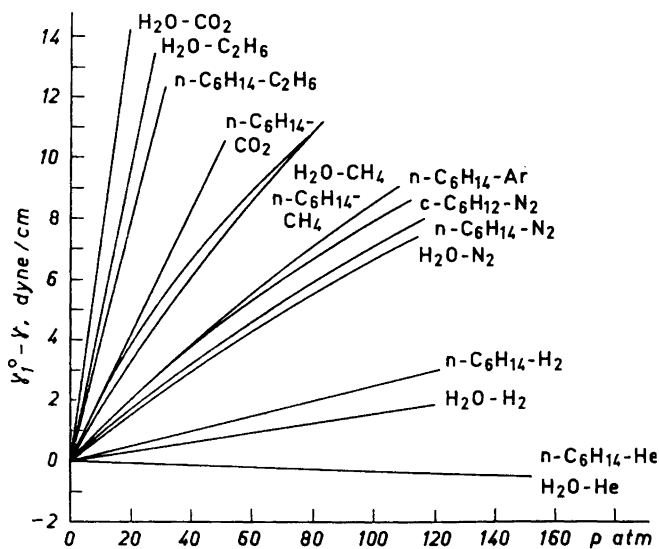


*Fig. 2.* Experimental $\gamma$-$p$ curves at room temperature according to Refs.[3,4]

## CALCULATIONS

By means of eqns. (27) and (34) we have carried out tentative calculations on the experimental $\gamma\text{-}p$ curves given by Slowinski et al.[3] and Gielessen and Schmatz [4] (cf. Fig. 2) assuming the restrictions (16) to be fulfilled for the solutions studied. The gas solubilities at 1 atm, $K_H$, were taken or, in some cases, estimated from the critical review of solubility experiments given by Jolley and Hildebrand [11] and from the compilation in *Handbook of Chemistry and Physics* [12]. The molecular surface areas $A_1^o$ for the solvents water, hexane and cyclohexane were chosen as 17 [7], 51 [13], and 51 Å[2], respectively. The activity factor expressions could be estimated in the following way. For a regular mixture as defined by Hildebrand [14] the relationships

$$\ln (f_1')^o = (W/RT)(x_2')^2$$
$$\ln (f_2')^o = (W/RT)(x_1')^2 \qquad (51 \text{ a, b})$$

hold true, $W$ denoting a characteristic constant which can be evaluated from heat of mixing data. For a monolayer, it is reasonable, according to the discussion given by Hoar and Melford [15], to put

$$\ln (f_1^s)^o = l'(W/RT)(x_2^s)^?$$
$$\ln (f_2^s)^o = l'(W/RT)(x_1^s)^2 \qquad (52, \text{ a, b})$$

where $l'$ is a fractional factor, the numerical value of which lies within the range 0.5—0.75. Choosing $l' = 2/3$ we obtain

$$\ln F_1^o = (W/RT) \ [(x_2')^2 - 2/3(x_2^s)^2]$$
$$\ln F_2^o = (W/RT) \ [(x_1')^2 - 2/3(x_1^s)^2] \qquad (53 \text{ a, b, c})$$
$$\ln F_H^o = (W/RT) \ [(1-K_H)^2 - (x_1')^2]$$

For small $p$, $F_1^o$ and $F_H^o$ may consequently be put equal to unity because generally $K_H \ll 1$ whereas

$$\ln F_2^o = (1/3)(W/RT) \approx \tfrac{1}{3} \ln (f_2')^o_{K_H} \qquad (54)$$

However, using eqn. (24), $(f_2')^o_{K_H}$ can be evaluated if $\bar{p}_2$, $v_2'^o$ and $a$ are known thus enabling the determination of $W/RT$. It should be mentioned here that the activity factor expressions (51) and (52) are based upon the assumption of equal molecular volumes of the two components. Hence eqns. (53) are to be regarded only as rather rough estimations of the activity factor ratios. We have supposed that the properties of the dissolved gas are related to the properties of the condensed gas. Thus the $\bar{p}_2$-values were estimated from the vapour pressure equations for the gaseous components [16] (cf. Saylor and Battino [17]) and the molar volume of the dissolved gas was calculated from the density of the condensate at the boiling point. The surface tension $\gamma_2^o$, ascribed to the standard state of $B_2$, could be evaluated through extrapolation of the surface tension of the real liquid at low temperatures [18]. This extrapolation of $\gamma_2^*$ vs. temperature should be performed linearly since from eqn. (3) on assuming $A_2^*$ to be temperature independent

*Table 1.* Calculations on experimental data using eqn. (34).

| System liquid-gas | $t\,^{\circ}C$ | $\left(\dfrac{d\gamma}{dp}\right)_{p=0} \times 10^2$ erg cm$^{-2}$ atm$^{-2}$ | $A_1^{\circ}\left(\dfrac{d\gamma}{dp}\right)_{p=0}$ ml mole$^{-1}$ | $K_H \times 10^5$ atm$^{-1}$ | $\gamma_2^{\circ}$ dyn cm$^{-1}$ | $\bar{p}_2$ atm | $(f_2')^{\circ} K_H$ | $v_2^{\circ}$ ml mole$^{-1}$ | $K_e^{\circ}$ | $A_2^{\circ}$(calcd) Å$^2$ molecule$^{-1}$ | $A_2^{\circ}$(BET) Å$^2$ molecule$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O-He$ | 25 | 0.3 | 3.0 | 0.691 | $-33.7$ | 66.3 | 2245 | 32 | 12.1 | 9.8 | 15.4 |
| $n\text{-}C_6H_{14}-He$ | 22 | 0.3 | 9.1 | 26.0 | $-33.4$ | 66.2 | 59.7 | 32 | 3.11 | 8.9 | 15.4 |
| $H_2O-H_2$ | 25 | $-1.6$ | $-16.2$ | 1.42 | $-45.3$ | 758 | 141 | 29 | 25.7 | 11.4 | 14.2 |
| $n\text{-}C_6H_{14}-H_2$ | 25 | $-2.5$ | $-75.8$ | 63.0 | $-45.3$ | 758 | 3.16 | 29 | 7.60 | 15.8 | 14.2 |
| $H_2O-N_2$ | 25 | $-7.7$ | $-77.8$ | 1.22 | $-39.2$ | 2791 | 82.1 | 35 | 74.6 | 16.0 | 16.2 |
| $n\text{-}C_6H_{14}-N_2$ | 22 | $-8.8$ | $-267$ | 140 | $-38.5$ | 2671 | 0.74 | 35 | 12.4 | 17.9 | 16.2 |
| $c\text{-}C_6H_{12}-N_2$ | 22 | $-10.0$ | $-303$ | 75.5 | $-38.5$ | 2671 | 1.225 | 35 | 20.4 | 19.4 | 16.2 |
| $H_2O-CH_4$ | 25 | $-21.6$ | $-218$ | 2.42 | $-20.9$ | 383 | 296 | 39 | 63.0 | 18.4 | 18.1 |
| $n\text{-}C_6H_{14}-CH_4$ | 25 | $-16.2$ | $-491$ | 468 | $-20.9$ | 383 | 1.53 | 39 | 5.19 | 17.4 | 18.1 |
| $H_2O-C_2H_6$ | 25 | $-49.9$ | $-504$ | 3.30 | 0.1 | 41.6 | 1159 | 46 | 58.2 | 23.2 | 22.2 |
| $n\text{-}C_6H_{14}-C_2H_6$ | 25 | $-38.0$ | $-1152$ | 3770 | 0.1 | 41.6 | 1.01 | 46 | 2.33 | 19.1 | 22.2 |
| $H_2O-CO_2$ | 25 | $-79.3$ | $-801$ | 60.8 | $-0.7$ | 63.5 | 89.4 | 62 | 12.8 | 14.4 | 17.0 |
| $n\text{-}C_6H_{14}-CO_2$ | 25 | $-21.1$ | $-640$ | 1240 | $-0.7$ | 63.5 | 4.38 | 62 | 2.06 | 15.8 | 17.0 |
| $n\text{-}C_6H_{14}-Ar$ | 22 | $-10.1$ | $-306$ | 253 | $-42.7$ | 1026 | 0.95 | 24 | 7.37 | 13.3 | 14.4 |

$$\left(\frac{\partial \gamma_2^*}{\partial T}\right)_p = -(s_2^{s*} - s_2^{b*})/A_2^* \tag{55}$$

and according to Eötvös' rule [19], $s_2^{s*} - s_2^{b*}$ has a constant value approximately equal to 4.2 cal mole$^{-1}$ deg$^{-1}$ for many liquids. The temperature variation of $A_2^*$ within the range of the surface tension measurements is certainly small, and since the desired $\gamma_2^\circ$-value should correspond to a density typical for the liquid state, $\gamma_2^*$ had to be extrapolated linearly. Actually, the $\gamma_2^*$-$T$ relationships for the considered condensates were linear to a good degree of accuracy. It may also be deduced from eqn. (5) that $(\partial \gamma_2^*/\partial p)_T$ has the order of magnitude $10^{-2}$ erg cm$^{-2}$ atm$^{-1}$ for the liquids involved. Hence no large errors were introduced in the calculations when surface tension values, measured for the liquid under its own vapour pressure ranging from 0—5 atm, were ascribed to the pressure of 1 atm, *i.e.* to the pressure of the standard state. The described procedure for evaluating $\gamma_2^\circ$ implies that the surface enthalpy, $h_2^{s*} - h_2^{b*}$, is considered as temperature independent, a consequence which is consistent with the assumption of constant molar volumes for the pure condensed state. The value of $\alpha$ at different pressures was obtained from $pVT$-data [20,21] for the corresponding gas. Rice [22] estimated the volume difference $v_i^{so} - v_i'^{o}$ to be of the same order of magnitude as $v_i'^{o}$ itself. The most consistent results were obtained with the present calculations if $v_1^{so} - v_1'^{o}$ for water, hexane and cyclohexane were given the values 30, 80, resp. 80 ml mole$^{-1}$. In Table 1 the results of the calculations based upon eqn. (34) are summarized. In view of the approximations involved the calculated molecular surface areas for the gaseous components seem rather conclusive. The corresponding BET molecular surface areas were calculated from the formula [23]

$$A_2^\circ \text{ (BET)} = 1.091 \ (v_2'^{o}/N)^{2/3} \ \text{Å}^2 \tag{56}$$

This expression is exact for a monolayer surface consisting of closepacked equal-sized, spherical molecules. Since the BET surface areas substantially agree with the calculated surface areas except for helium for which eqn. (56)
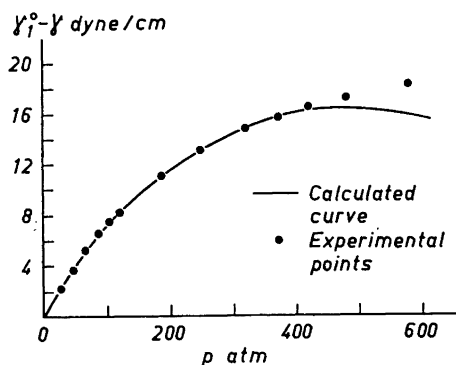


*Fig. 3.* The interfacial tension of $n$-$C_6H_{14}$—$N_2$ *versus* pressure at 22°C.

is known from specific surface area measurements to yield too large a value, we may conclude that the monolayer description is adequate and that the presumed relationships between the properties of the dissolved and the condensed states are reasonable for the systems treated.

The validity of eqn. (27) was investigated for hexane-nitrogen. For this system $\gamma$ has been measured over a wide pressure range (cf. Ref.[4]). The previously calculated $A_2^o$-value was inserted and $v_2^{so} - v_2^{'o}$ was put equal to 30 ml mole$^{-1}$. As is seen from Fig. 3 the agreement with experiment is satisfactory up to 400 atm corresponding to $x_2' = 0.30$ and $x_2^s = 0.96$. It is of course unlikely that eqns. (16) would be fulfilled at high concentrations of $B_2$. Moreover, since the $\Gamma$-factors become very important at high pressures, errors in the values for $v_1^{so} - v_1^{'o}$, $v_2^{so} - v_2^{'o}$, $v_2^{'o}$ may also seriously affect the result.

## DISCUSSION

A characteristic feature of the experimental $\gamma$-$p$ curves is (cf. Fig. 2) that the derivatives $(\partial\gamma/\partial p)_\Gamma$ for $p \approx 0$ for systems with different liquid components but with the same gaseous component have the same order of magnitude. An explanation of this fact may be attempted along the following lines. For small $p$, $K_H RT K_e^o F_2^o$ is the predominant term of eqn. (34) for most of the systems. According to an empirical relationship pointed out by Uhlig[24], a low solubility of a certain gas is connected with a high surface tension $\gamma_1^o$ of the solvent and vice versa, i.e. the magnitudes of $K_H$ and $K_e^o$ are changed in opposite directions when passing between liquid components with different $\gamma_1^o$-values (cf. eqn. (32) and Table 1). Thus the variation of $(\partial\gamma/\partial p)_T$ for $p \approx 0$ should be limited for this category of systems if the $A_1^o$-values are not widely different. This conclusion is not affected by the approximate relationship $F_2^o = (\bar{p}_2\ \bar{\Gamma}_H K_H)^{-1/3}$ which can be derived from eqns. (24) and (54). The converse behaviour could be expected for systems with the same liquid component but different gaseous components that have approximately equal $\gamma_2^o$-values, because a large molar surface area $A_2^o$ (i.e. a large $K_e^o$) should be associated with a large polarizability and thus also a high solubility of the gaseous component.

It is interesting to note that the performed calculations indicate that $\tau$, the thickness of the surface monolayer, for the water and hexane solutions would be 4—5 Å and 6—7 Å, respectively. The fact that the $A_2^o$-values are not much affected by changing the substrate and that the BET-formula (eqn. (56)), based upon the molar volume $v_2^{'o}$, is applicable suggests that molecules in a surface phase are characterized by an increased amplitude of thermal motion mainly in the direction perpendicular to the surface. This observation is in good agreement with the molecular theory of surface tension based on the cell theory for liquids. Accordingly, a molecule at a surface has a larger *free volume* than a molecule in a bulk phase since the former is surrounded by fewer molecules than the latter[25]. However, this difference of the free volumes cannot account for all the entropy difference so it is also necessary to assume that more holes are present in the surface phase[26].

The present investigation lends strong support to the validity and applicability of the thermodynamic method for treating surface systems founded on the physical surface phase concept which has been discussed elsewhere by the author. Actually, the monolayer model is adequate for the systems dealt with in this paper. However, it would also be of value to test the derived formulae on systems with a more complicated surface phase structure. Likewise, the interfacial tensions of liquid-liquid systems could be studied using analogous methods.

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