SURFACE TENSION AT THE BOUNDARY BETWEEN TWO GAS PHASES AT HIGH PRESSURES

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Abstract

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SURFACE TENSION AT THE BOUNDARY BETWEEN TWO GAS PHASES AT HIGH PRESSURES

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At the present time there is no doubt as to the existence of gas–gas equilibrium (^{1,2}). The present work was undertaken for the purpose of further study of this interesting phenomenon, namely, the measurement of the surface tension at the boundary between two gas phases.

The helium–ethylene system was chosen as the object of investigation (^{3}). The surface tension was measured by the capillary-rise method (^{4,5}). The principle of the method consists in measuring the difference in heights Δh of the columns of the phase in capillaries of radii R_1 and R_2. If the contact angle Θ of the wall of the capillary with the heavy phase is zero, and R_1 and R_2 are small, then

$$\sigma_{21} = \frac{\Delta h}{1/R_1 - 1/R_2}\,\frac{1}{2}\,g(\rho' - \rho''), \tag{1}$$

where ρ' and ρ'' are the densities of the phases and g is the acceleration due to gravity.

We measured the densities of the phases in the helium–ethylene system by the method proposed earlier (^{6}). Helium and ethylene were introduced into a high-pressure apparatus; conditions were created under which the mixture separated into layers; the phases were stirred with an electromagnetic stirrer and the upper phase was withdrawn for analysis at constant pressure. Having determined the composition of the phase from its molecular weight, a part of this phase was released into calibrated vessels, while at the same time, by means of a calibrated press, such an amount of mercury was introduced into the apparatus that the pressure remained constant. Knowing the amount of mercury supplied and the phase withdrawn, the density of the latter was determined. Then the entire upper phase was released from the apparatus and an analogous operation was carried out with the lower phase.

Table 1

Densities and compositions of phases in the helium–ethylene system (ρ'' and ρ' are the densities of the light and heavy phases; N_2'' and N_2' are the mole percentages of ethylene in the light and heavy phases)

Temperature	p, kg/cm^2	N_2''	ρ'', g/cm^3	N_2'	ρ', g/cm^2
At 13°	220	57.8		80.5	
At 13°	280	37.5	0.142	79.3	0.327
At 13°	360	35.4	0.153	76.6	0.350
At 13°	400	33.6		71.8	
At 13°	420	30.4	0.158		
At 13°	550	23.5	0.164	69.7	0.410
At 13°	660	20.0	0.173	71.8	0.406
At 16°	300	50.4	0.211	76.0	0.323
At 16°	420	29.5	0.166	73.0	0.349
At 16°	500	27.5	0.168	73.0	0.391
At 16°	600	18.0		70.0	
At 16°	680	20.0	0.186	69.0	0.394
At 18°	400	40.4	0.212	65.5	0.299
At 18°	490	28.8	0.180	68.0	0.363
At 18°	620	23.1	0.174	66.0	0.385
At 18°	720	20.8	0.184	65.9	0.388

The data obtained on the composition and densities of the phases in the system studied are given in Table 1. The phase compositions at 16° differ somewhat from those reported in work ([3]); however, preference should be given to the later data, obtained with intensive stirring of the phases.

* A. N. Kofman took part in the experimental portion of the work.

Capillary rise was determined in an apparatus (Fig. 1) consisting of a high-pressure column 1, located in a thermostat. In the column, opposite windows 2, capillaries 3 were placed, fastened to frame 4; behind the capillaries there was a ground glass 7. When the frame, connected to the armature of electromagnetic stirrer 5, moved, the phases were mixed both inside the vessel and inside the capillaries themselves.

Helium and ethylene were fed into the apparatus in such proportions as to obtain a mixture of prescribed composition, and mercury was forced by a press into vessel 6, compressing the mixture to the required pressure. The amount of mixture was chosen so that the phase boundary lay opposite the observation windows and, at the same time, the ends of the capillaries were immersed in the heavy phase.

The height of rise of the heavy phase in capillaries of different diameter (from 0.2 to 0.6 mm) was measured with a KM-6 cathetometer with an accuracy up to 0.005 mm. By placing three capillaries of different diameters in the frame, we were able to determine, in one experiment, three differences of levels.

For the investigation, helium of 99.6% purity and ethylene purified by the method of forming a complex with cuprous chloride (7) were used. The results of the measurements (the capillary constant $a^2 = \dfrac{\Delta h}{1/R_1 - 1/R_2}$) are presented in Table 2.

Table 2

Capillary constant a^2 in the helium–ethylene system

p, kg/cm^2	$a^2 \cdot 10^5$, cm^2	p, kg/cm^2	$a^2 \cdot 10^5$, cm^2
At 13°		**At 16°**	
227	48.0	415	54.0
300	49.0	450	104.0
310	105	480	104
355	129	520	207
380	150	550	256
400	196	590	315
415	205	650	410
480	284	680	446
520	344	**At 18°**	
535	354	490	51.6
600	470	505	66.0
635	550	575	140
665	592	610	207
		655	267
		720	362

Table 3

Surface tension in the helium–ethylene system (interpolated data)

p, kg/cm^2	σ, erg/cm^2	p, kg/cm^2	σ, erg/cm^2
At 13°		**At 16°**	
280	0.055	420	0.050
300	0.070	450	0.105
350	0.125	480	0.255
400	0.190	500	0.195
450	0.275	550	0.280
500	0.360	600	0.355
550	0.460	650	0.420
600	0.561	680	0.440
650	0.654	**At 18°**	
		490	0.045

p, kg/cm^2	σ, erg/cm^2	p, kg/cm^2	σ, erg/cm^2
		500	0.055
		550	0.110
		600	0.190
		650	0.270
		720	0.355

To determine the contact angle, we photographed, at different pressures and temperatures, capillaries immersed in the heavy phase, and, on examining enlarged images of the capillaries, established that it is equal to zero. The data on surface tension, calculated from expression (1), are given in Table 3 and in Fig. 2.

An estimate of the errors in measuring the quantities entering into (1) showed that the total maximum relative error in measuring the surface tension, allowing for the accuracy of pressure and temperature measurements, is $\sim 5\%$.

It may be assumed that the curves in the $\sigma - p$ coordinates approach the abscissa axis with a horizontal tangent, and the surface tension becomes equal to zero at the critical point (Fig. 2).

According to Gibbs (8), adsorption at the interface of coexisting phases can be expressed by the equation

$$\Gamma_{2(1)} = -(\partial \sigma / \partial \mu_2)_{\text{coex.},\, T}; \tag{2}$$

here μ_2 is the chemical potential of component 2; $\Gamma_{2(1)}$ is the excess of moles of the 2nd component, referred to unit area of the surface layer, in comparison with the number of moles that would have been at the surface if the concentration of the component in the volume of the phase remained unchanged up to the geometrical dividing surface. The position of this surface was chosen so that the excess of the other component (in the present case, the 1st) was equal to zero ($\Gamma_{1(2)} = 0$). Since

Fig. 1. Apparatus for measuring capillary rise

$$(d\mu_2)_{\text{vessel},T} = \left(\frac{\partial \mu_2}{\partial N_2}\right)^{\text{r}}_{T,p} dN_2 + \left(\frac{\partial \mu_2}{\partial p}\right)_{T,N_2} dp, \tag{3}$$

$$\left(\frac{\partial \mu_2}{\partial p}\right)_{T,N_2} = \bar{v}_2, \tag{4}$$

where $\bar{v}_2$ is the partial molar volume of the component, then

Fig. 2. Surface tension in the helium—ethylene system

Figure 1: Fig. 2. Surface tension in the helium—ethylene system

Fig. 3. Dependence of σ on $(p - p_{\text{cr}})^2$

Figure 2: Fig. 3. Dependence of σ on $(p - p_{\text{cr}})^2$

$$\frac{d\sigma/dp}{\left(\frac{\partial\mu_2}{\partial N_2}\right)_{p,T}\left(\frac{\partial N_2}{\partial p}\right)_{\text{vessel},T} + \bar{v}_2} = -\Gamma_{2(1)}. \tag{5}$$

For the critical phase of a binary solution $(d\mu_2/dN_2)_{p,T} = 0$. Therefore, at the critical point

$$-\Gamma_{2(1)} = \frac{1}{\bar{v}_2}\frac{d\sigma}{dp}. \tag{6}$$

But at the critical point all properties of both phases are identical; therefore $\Gamma_{2(1)} = 0$, and consequently $d\sigma/dp = 0$. Therefore the analytical curve expressing the dependence of σ on p may be a parabola of the second degree.

On this basis one may write that

$$\sigma = \alpha\,(p - p_{\text{cr}})^2, \tag{7}$$

where α is a constant. Plotting the values of σ obtained by us in the coordinates σ, $(p - p_{\text{cr}})^2$, we obtained a straight line (Fig. 3), on which the points for all three temperatures lay over a large pressure interval.

Fig. 2. Surface tension in the helium—ethylene system

Fig. 3. Dependence of σ on $(p - p_{\text{cr}})^2$

For coexisting phases,

$$(\partial\mu_2)_{\text{coex.},T} = \frac{v' N_1'' - v'' N_1'}{N_1'' - N_1'}\,dp, \tag{8}$$

where v' and v'' are the molar volumes of the heavy and light phases; N_1' and N_1'' are the mole fractions of the first component (in our case helium) in the heavy and light phases. Combining equations (4) and (8), it can be shown that at the critical point

$$-\Gamma_{2(1)} = \frac{N_1'' - N_1'}{v' N_1'' - v'' N_1'}\left(\frac{\partial\sigma}{\partial p}\right)_{\text{coex.},T}. \tag{9}$$

Fig. 4. Change of adsorption with pressure in the helium—ethylene system

Figure 3: Fig. 4. Change of adsorption with pressure in the helium—ethylene system

Further, since from (7) it follows that

$$\left(\frac{\partial \sigma}{\partial p}\right)_{\text{coex.}, T} = 2\alpha(p - p_{\text{cr}}),$$

then finally

$$-\Gamma_{2(1)} = \frac{2\alpha(p - p_{\text{cr}})(N_1'' - N_1')}{v' N_1'' - v'' N_1'}. \tag{10}$$

Fig. 4. Change of adsorption with pressure in the helium—ethylene system

Having determined the coefficient α from the slope of the straight line in Fig. 3, we calculated $-\Gamma_{2(1)}$ for three temperatures and plotted these data in the coordinates $-\Gamma_{2(1)}$, pressure. As is seen from Fig. 4, the points over a wide pressure interval lay well on straight lines.

The results of the work show that the surface tension at the interface between two gas phases increases considerably with pressure. The cause of the growth of σ may be the change in the composition of the phases and of the surface layer (adsorption), as well as the large change in the density of the phases with pressure.

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Note: Figure translations are in progress. See original paper for figures.