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Surface Tension of Saturated Vapors and the Equation of Eotuos

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SURFACE TENSION OF SATURATED VAPORS AND THE EQUATION OF EÖTVÖS

BY J. L. SHERESHEFSKY

In discussing phenomena of solid-liquid or liquid-liquid surfaces it is usually emphasized that the properties under consideration belong to neither of the phases making up the interface, but to the interface proper. Thus it is made clear that the tension in a benzene-water interface is characteristic, neither of the benzene, nor of the water, but of the new phase of the interface which is made up of the latter two. But there is generally a lack of definiteness when dealing with liquid surfaces in contact with their own vapors. The properties of such surfaces are usually ascribed to the liquids concerned, without giving due consideration to the effect that the respective vapor phases undoubtedly have on these properties.

Van der Waals was the first to point out that the surface represents a third phase whose properties differ from those of the liquid or vapor. There is thus a complete parallelism between liquid-liquid and liquid-vapor interfaces. The surface tension, say, of benzene is therefore understood to refer neither to the liquid benzene, nor to the benzene vapor, but to the benzene (liquid)-benzene (vapor) interface, and is also conceived as the resultant of two effects produced by the surfaces presented by the liquid and the vapor.

The Surface Tension of Saturated Vapors

The tension in a liquid-liquid interface as determined by the method of capillary rise is given by the expression

$$\sigma = \tfrac{1}{2} r \, h \, g \, (\rho_1 - \rho_2) \tag{1}$$

where h is the height of rise, r the radius of the capillary, and ρ_1 and ρ_2 the densities of the immiscible liquids in equilibrium with each other. This expression also holds for the interface between a liquid and its vapor, ρ_1 and ρ_2 being the respective densities.

It is therefore evident that the tension of a surface formed by the contact of two fluid phases, whether they be two immiscible liquids, or a liquid and its vapor, is given by the difference of two terms, and thus is analogous to Antonoff's[1] rule, which states that the interfacial tension between two liquids is equal to the difference of the surface tensions of the liquids in equilibrium with each other. Thus, if σ is the relative, or interfacial tension, σ_1 the surface tension of liquid (1) in equilibrium with the vapor of liquid (2), and σ_2 is the surface tension of liquid (2) in equilibrium with the vapor of (1), Antonoff's rule may be expressed by the equation

$$\sigma = \sigma_1 - \sigma_2 \tag{2}$$

[1] Phil. Mag., (6) **36**, 377 (1918).

Applying this rule to an interface between a liquid and its vapor σ represents the relative surface tension, σ_1 the tension of the liquid surface proper, that is, of a hypothetical liquid surface whose vapor was momentarily removed or frozen, and σ_2 is the tension of the surface presented by the vapor. From this follows by analogy that

$$\sigma_1 = \tfrac{1}{2} \text{ rhg}\rho_1 \tag{3}$$

and

$$\sigma_2 = \tfrac{1}{2} \text{ rhg}\rho_2 \tag{4}$$

A more rigorous derivation of these equations may be obtained from considerations of equation (1) as applied to liquid surfaces in contact with vapors. At temperatures far removed from the critical the vapor density term, ρ_2, is usually omitted, since it is negligible with respect to the density of the liquid. As a result equation (1) becomes only approximate and assumes the more simplified form of

$$\sigma = \tfrac{1}{2} \text{ rhg}\rho_1 \tag{5}$$

This expression increases in accuracy at lower temperatures, and becomes exact as the vapor pressure of the liquid approaches zero. At this state of the liquid the relative surface tension, σ, becomes equal to the absolute tension, σ_1, of the liquid surface proper. Since this state also corresponds to the hypothetical liquid surface postulated above equation (5) becomes identical with equation (3), which defines the absolute surface tension of a liquid.

The surface tension of a vapor as defined in equation (4) may now be obtained by combining equation (3) with the expression for the relative surface tension of a liquid as given by equation (1), and with equation (2) expressing Antonoff's rule.

Entirely different consideration led N. Barbulescu[1] to the same conclusions.

The Surface Tension of Saturated Vapors and Temperature

To relate the surface tension of saturated vapors to temperature the following two equations are utilized.

$$\sigma = K_1 T_c V^{-\frac{2}{3}} (1 - T/T_c)^{1.2} \tag{6}$$

and

$$\rho_1 - \rho_2 = K_2 \rho_c (1 - T/T_c)^{0.3} \tag{7}$$

Equation (6) was deduced by van der Waals from his theory of corresponding states, and later modified by S. Sugden.[2] Equation (7) was suggested by D. H. Goldhammer[3] and corrected by S. Sugden[4]. Here T_c and ρ_c are the

[1] Physik. Z., **31**, 48 (1930).
[2] J. Chem. Soc., **125**, 32 (1924).
[3] Z. physik. Chem., **71**, 577 (1910).
[4] J. Chem. Soc., **130 II**, 1780 (1927).

critical temperature and critical density respectively, V the molar volume of the liquid, and K_1 and K_2 constants which are approximately universal for all non-polar liquids.

Combining these with equations (1) and (4), we obtain the expression

$$\sigma_2 = \frac{\triangle T_c}{\rho_c^{1/3} M^{2/3}} \left(1 - T/T_c\right)^{0.9} \rho_2 \qquad (8)$$

which relates the surface tension of saturated vapors to the density of the vapor, its critical constants and temperature. The constant $\triangle$ equals K_1/K_2 and is nearly the same for all non-associated substances, M is the molecular weight, and the other terms have the designated significance.

To test the validity of this equation the surface tension of the saturated vapors of six liquids at various temperatures were calculated and compared with observed values. The agreement as shown in Tables I to VI inclusive is very good up to the critical temperature for all substances except carbon

TABLE I

Surface Tension of Saturated Vapors

Benzene
$\qquad \triangle = 1.39 \qquad$ Mol. Wt. $= 78.05$; $T_c = 561.5 \qquad \rho_c = .3045$

I	II	III	IV	V	VI
					Percent
t°C	$1 - T/T_c$	ρ_2	σ_2(obs.)	σ_2(calc.)	Deviation
90	.353	.0036	.0904	.0935	3.43
120	.302	.0076	.1640	.1640	0.00
150	.247	.0144	.262	.260	0.76
180	.193	.0249	.357	.360	0.84
210	.140	.0421	.453	.456	0.66
240	.086	.0715	.483	.498	3.11
280	.016	.2209	.344	.340	1.16

TABLE II

Surface Tension of Saturated Vapors

Chlorobenzene
$\qquad \triangle = 1.39 \qquad$ Mol. Wt. $= 112.5$; $T_c = 632.2 \qquad \rho_c = .3654$

I	II	III	IV	V	VI
					Percent
t°C	$1 - T/T_c$	ρ_2	σ_2(obs.)	σ_2(calc.)	Deviation
150	.332	.0054	.105	.1057	0.67
180	.283	.0102	.172	.173	0.58
210	.236	.0180	.253	.258	1.98
240	.188	.0301	.348	.353	1.44
270	.141	.0494	.433	.446	3.00
300	.093	.0778	.490	.485	1.02
320	.062	.1075	.456	.465	1.98
333	.042	.1360	.450	.415	7.78

TABLE III

Surface Tension of Saturated Vapors

Ethyl Ether

$\triangle = 1.39$ Mol. Wt. $= 74.1$; $T_c = 466.8$ $\rho_c = 0.2625$

I	II	III	IV	V	VI
					Percent
t°C	$1 - T/T_c$	ρ_2	σ_2(obs.)	σ_2(calc.)	Deviation
20	.373	.00187	.0447	.0442	1.12
50	.308	.00508	.1037	.1013	2.32
80	.245	.01155	.1880	.1875	0.27
110	.179	.02349	.2880	.2870	0.35
140	.114	.04448	.3610	.3610	0.00
170	.049	.08731	.3280	.331	0.91
185	.017	.1320	.1960	.194	1.02

TABLE IV

Surface Tension of Saturated Vapors

Carbon Tetrachloride

$\triangle = 1.39$ Mol. Wt. $= 153.84$; $T_c = 556.2$ $\rho_c = 0.5576$

I	II	III	IV	V	VI
					Percent
t°C	$1 - T/T_c$	ρ_2	σ_2(obs.)	σ_2(calc.)	Deviation
90	.3475	.0079	.1010	.0995	1.49
120	.293	.0163	.1770	.1765	0.28
150	.239	.0302	.2683	.2720	1.38
180	.185	.0525	.3730	.3780	1.34
210	.132	.0879	.4660	.465	0.22
240	.077	.1464	.4300	.477	10.95
270	.0225	.2710	.222	.298	34.20

TABLE V

Surface Tension of Saturated Vapors

Methyl Formate

$\triangle = 1.31$ Mol. Wt. $= 60.04$; $T_c = 487$ $\rho_c = 0.3489$

I	II	III	IV	V	IV
					Percent
t°C	$1 - T/T_c$	ρ_2	σ_2(obs.)	σ_2(calc.)	Deviation
50	.337	.0043	.095	.0955	0.53
80	.275	.0105	.193	.1943	0.67
110	.2125	.0216	.316	.317	0.28
140	.152	.0412	.438	.447	2.06
170	.090	.0763	.497	.516	3.83
200	.028	.1524	.340	.361	6.18

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TABLE VI

Surface Tension of Saturated Vapors

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Ethyl Acetate

$\triangle = 1.43$ Mol. Wt. $= 88.06$; $T_c = 523.1$ $\rho_c = 0.3077$

I	II	III	IV	V	VI
$t°C$	$1 - T/T_c$	ρ_2	σ_2(obs.)	σ_2(calc.)	Percent Deviation
90	.307	.0047	.0918	.0907	1.20
120	.248	.0103	.1645	.1643	0.12
150	.192	.0206	.260	.260	0.00
180	.134	.0388	.353	.346	2.76
210	.077	.0712	.400	.396	1.00
240	.019	.1500	.229	.237	3.49

tetrachloride. In the latter case the divergence is most probably due to the doubtful data in the neighborhood of the critical temperature. The observed values in the fourth column of each table were taken from the data of Ramsay and Shields as recalculated and corrected by S. Sugden.[1]

It is to be observed that the surface tension of saturated vapors attains a maximum value near the critical temperature, the ratio of the temperature at which the maximum occurs to the critical temperature being the same for all substances, as was shown by the author in a preceding paper.[2]

The Law of Eötvös

To express the relationship between surface tension of a liquid-vapor surface and temperature Eötvös suggested, in analogy to the gas law PV = RT, the similar equation

$$\sigma(M/\rho_1)^{2/3} = K(T_c - T) \tag{9}$$

As this equation was only exact for low temperatures and was far from reproducing the experimental results for the whole range of temperatures up to the critical, Ramsay and Shields have introduced after an extensive investigation an arbitrary constant "d", thus modifying the equation to the form

$$\sigma(M/\rho_1)^{2/3} = K(T_c - T - d) \tag{10}$$

This equation, while it has improved upon the Eötvös equation in accuracy, has lost its symmetry and is not consistent with the theory of corresponding states. It furthermore shares, with the original Eötvös equation, the fault that it takes no consideration of the density of the vapor, which has as it was shown above an important effect upon the surface tension of the interface.

A relationship which shall be consistent with the theory of corresponding states, and which shall also take account of the vapor density, may be developed on the basis of the conclusions arrived at in the preceeding section in this paper.

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[1] J. Chem. Soc., **125**, 32 (1924).

[2] J. Phys. Chem., **34**, 1947 (1930).

Combining equations (1) and (4), we obtain

$$\sigma_2 = \sigma \left(\frac{\rho_2}{\rho_1 - \rho_2} \right) \tag{11}$$

which relates the relative surface tension, σ, with the surface tension of the vapor, σ_2. Substituting for the latter its equivalent in equation (8), we obtain

$$\sigma \left(\frac{M^{2/3}}{\rho_1 - \rho_2} \right) = \triangle \frac{T_c}{\rho_c^{1/3}} (1 - T/T_c)^{0.9} \tag{12}$$

which in multiplying by $(\rho_1 - \rho_2)^{1/3}$ assumes a form that is very similar to the original expression of Eötvös' Law, namely

$$\sigma \left(\frac{M}{\rho_1 - \rho_2} \right)^{2/3} = \triangle T_c \left(\frac{\rho_1 - \rho_2}{\rho_c} \right)^{1/3} (1 - T/T_c)^{0.9} \tag{13}$$

A similar relationship was suggested by N. Katayama[1] as shown by equation (14)

$$\sigma \left(\frac{M}{\rho_1 - \rho_2} \right)^{2/3} = K(T_c - T) \tag{14}$$

This equation accounts for the vapor density as well as equation (13), but is not as complete in its relationship to the theory of corresponding states, since the latter includes the critical volume as well as the critical temperature. It is also not in as good agreement with experiment, as equation (13), as is evidenced in Tables VII to XII inclusive. The values of σ calculated by

TABLE VII

The Equation of State for Liquid-Vapor Interfaces

Benzene (liquid)-Benzene (vapor)

$\triangle = 1.39$ Mol. Wt. $= 78.05$ $T_c = 561.5$ $\rho_c = .3045$

I t°C	II $1 - T/T_c$	III $\rho_1 - \rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
13.5	.490	.8857	29.72	29.70	
20.5	.477	.8782	28.91	28.86	
32.5	.456	.8653	27.30	27.20	
39	.445	.8581	26.36	26.40	
41.5	.439	.8553	26.08	26.00	
54.8	.417	.8400	24.28	24.38	
61	.406	.8330	23.61	23.60	
72	.386	.8207	22.15	22.70	
90	.353	.8006	20.13	20.00	19.08
120	.302	.7616	16.42	16.52	15.67
150	.247	.7166	13.01	12.98	12.37
180	.193	.6657	9.56	9.65	9.22
210	.140	.6011	6.45	6.53	6.23
240	.086	.5137	3.47	3.60	3.47
270	.033	.3696	1.05	1.09	1.06
280	.016	.2305	0.36	0.36	0.36

[1] Tohoku Imp. Univer. Science Reports, (1) 4, 373 (1916).

TABLE VIII

The Equation of State for Liquid-Vapor Interfaces

Chlorobenzene (liquid)-Chlorobenzene (vapor)

$\triangle = 1.39$ Mol. Wt. $= 112.5$; $T_c = 632.2$ $\rho_c = .3654$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
12	.549	1.118	34.36	34.40	
18.7	.538	1.108	33.35	33.50	
24.1	.523	1.102	32.85	32.40	
41	.503	1.083	30.78	30.85	
50	.488	1.073	29.83	29.70	
62.1	.470	1.059	28.20	28.40	
81	.440	1.039	26.10	26.25	
93	.422	1.025	24.99	24.90	
123	.373	.9910	21.63	21.53	
150	.332	.9545	18.55	18.65	17.57
180	.283	.9122	15.40	15.50	14.61
210	.236	.8622	12.16	12.38	11.71
240	.188	.8054	9.30	9.45	8.94
270	.141	.7341	6.43	6.63	6.29
300	.093	.6442	4.05	4.01	3.83
320	.062	.5628	2.39	2.43	2.32
333	.042	.4914	1.63	1.50	1.41

TABLE IX

The Equation of State for Liquid-Vapor Interfaces

Ethyl Ether (liquid)-Ethyl Ether (vapor)

$\triangle = 1.39$ Mol. Wt. $= 74.1$; $T_c = 466.8$ $\rho_c = 0.2625$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
20	.373	.7109	17.01	16.80	16.12
50	.308	.6713	13.69	13.35	12.81
80	.245	.6286	10.25	10.20	9.71
110	.179	.5707	7.00	6.97	6.81
140	.114	.4936	4.00	4.01	3.97
170	.049	.3785	1.42	1.44	1.47
185	.017	.2698	0.40	0.40	0.46

TABLE X

The Equation of State for Liquid-Vapor Interfaces

Carbon Tetrachloride (liquid)-Carbon Tetrachloride (vapor)

$\triangle = 1.39$ Mol. Wt. $= 153.84$; $T_c = 556.2$ $\rho_c = 0.5576$

I t°C	II $1 - T/T_c$	III $\rho_1 - \rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
20	.473	1.593	26.95	26.60	25.55
33	.450	1.567	25.22	25.00	
45.9	.426	1.540	23.63	23.40	
90	.3475	1.4475	18.51	18.25	17.59
120	.293	1.3740	14.95	14.90	14.35
150	.239	1.2914	11.46	11.62	11.24
180	.185	1.1945	8.50	8.60	8.27
210	.132	1.0687	5.67	5.66	5.44
240	.077	0.8980	2.64	2.92	2.86
270	.0225	0.5955	0.49	0.66	0.56

TABLE XI

The Equation of State for Liquid-Vapor Interfaces

Methyl Formate (liquid)-Methyl Formate (vapor)

$\triangle = 1.31$ Mol. Wt. $= 60.04$; $T_c = 487$ $\rho_c = 0.3489$

I t°C	II $1 - T/T_c$	III $\rho_1 - \rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
50	.337	.9251	20.48	20.52	19.96
80	.275	.8698	15.95	16.10	15.68
110	.2125	.8048	11.77	11.80	11.55
140	.152	.7156	7.63	7.77	7.65
170	.090	.6081	3.96	4.12	4.06
200	.028	.4131	0.92	0.98	1.00

TABLE XII

The Equation of State for Liquid-Vapor Interfaces

Ethyl Acetate (liquid)-Ethyl Acetate (vapor)

$\triangle = 1.43$ Mol. Wt. $= 88.06$; $T_c = 523.1$ $\rho_c = 0.3077$

I t°C	II $1 - T/T_c$	III $\rho_1 - \rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
90	.307	.8065	15.74	15.58	15.04
120	.248	.7580	12.08	12.10	11.73
150	.192	.7005	8.85	8.84	8.56
180	.134	.6265	5.70	5.58	5.57
210	.077	.5232	2.94	2.92	2.82
240	.019	.3278	0.50	0.52	0.52

means of equation (13) are regularly lower than those calculated by means of equation (14) and those observed, particularly for the lower temperatures where the accuracy of the observations is quite certain.

The data of the third and fourth columns were taken from S. Sugden.[1] In the fifth column are given the values calculated by means of equation (13), and in the sixth—the values calculated by means of equation (14) as taken from N. Katayama.[2] Table XIII gives the constants Δ, which are ap-

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TABLE XIII

The Equation of State for Liquid-Vapor Interfaces
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Constants

	Δ	K
Benzene	1.39	2.04
Chlorobenzene	1.39	2.02
Ethyl Ether	1.39	2.04
Carbon Tetrachloride	1.39	2.05
Methyl Formate	1.31	2.15
Ethyl Acetate	1.43	1.97

proximately the same for all unassociated substances for both liquid and vapor states. In the second column of this table is also given the constant K of equation (14).

Summary

1. On the basis of Antonoff's rule and the capillary rise equation of surface tension, an expression is deduced which determines the surface tension of saturated vapors.

2. This expression is further developed into a form which relates surface tension of saturated vapors with temperature. The equation is tested for six unassociated vapors and found to reproduce observed results with fair accuracy.

3. The various modifications of Eötvös' law are discussed, and a new one is developed which takes account of the vapor density and is based on the theory of corresponding states. This new equation is tested against the same six compounds in the liquid state and is found to be in good agreement with observed data.

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[1] Loc. cit.
[2] Loc. cit.