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THE CORRESPONDING STATE OF MAXIMUM SURFACE TENSION OF SATURATED VAPORS

BY J. L. SHERESHEFSKY[*]

Making use of the expression developed by Laplace for the cohesion pressure of a liquid, and resorting to the well known phenomenon of capillary rise, N. Barbulescu[1] has recently derived for the surface tension of a saturated vapor the equation

$$\sigma_v = \frac{rh}{2} \rho_v \tag{1}$$

where σ_v is the surface tension of the vapor, h the height of rise of the liquid in a capillary of radius r, and ρ_v the density of the saturated vapor.

By means of this equation the values of σ_v for several saturated vapors at various temperatures were calculated and found to pass a maximum in the neighborhood of the critical temperature, the ratio of the temperature at the maximum to the critical temperature being approximately constant.

As this behavior of vapors seems to be general and the maximum apparently characteristic of all substances, it was considered of interest to relate it to the critical constants, and if possible to deduce an expression that would define this maximum.

The surface tension of a liquid at any temperature is given by

$$\sigma_l = \frac{rh}{2} (\rho_l - \rho_v) \tag{2}$$

where σ_l is the surface tension of the liquid, h the height of rise of the liquid in a capillary of radius r, and ρ_l the density of the liquid. Combining equations (1) and (2) the following relation for the surface tension of a vapor in equilibrium with its liquid is obtained:

$$\sigma_v = \sigma_l \left(\frac{\rho_v}{\rho_l - \rho_v} \right) \tag{3}$$

To express σ_v as a function of temperature equation (3) may be combined, either with the theoretical equations of van der Waals[2]

$$\sigma_l = a (1 - T/T_c)^{3/2} \tag{4}$$

and

$$-V_v - V_l = b (1 - T/T_c)^{1/2} \tag{5}$$

or with the empirical equation of D. B. Macleod[3]

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[1] Physik. Z., **31**, 48 (1930).
[2] Z. physik. Chem., **13**, 716 (1894).
[3] Trans. Faraday, **18**, 38 (1923).

$$\sigma_1 = c \, (\rho_1 - \rho_v)^4 \qquad (6)$$

and the one by D. H. Goldhammer[1]

$$\rho_1 - \rho_v = k \, (1 - T/T_c)^{1/3} \qquad (7)$$

In these equations a,b,c,k are constants characteristic of the compound, V_v and V_1 the specific volume in the vapor and liquid states respectively, and T is the absolute temperature. The van der Waals equations hold only for a very limited range of temperatures near the critical, while equations (6) and (7) are remarkably accurate for a wide range of temperatures up to .98T_c. In using the latter the lack of a theoretical foundation is compensated by the extreme accuracy of the results.

Combining equation (3) with (6) and (7) we obtain

$$\sigma_v = K(1 - T/T_c)\rho_v \qquad (8)$$

an expression relating the surface tension of a saturated vapor with temperature. Differentiating, it gives

$$\frac{d\sigma_v}{dT} = K \left[\left(1 - \frac{T}{T_c} \right) \frac{d\rho_v}{dT} - \frac{\rho_v}{T_c} \right]$$

At the maximum point

$$\left(1 - \frac{T}{T_c} \right) \frac{d\rho_v}{dT} - \frac{\rho_v}{T_c} = 0,$$

or

$$\frac{d \ln \rho_v}{dT} = \frac{1}{T_c(1 - T/T_c)}, \qquad (8a)$$

or

$$\frac{d \log \rho_v}{dT} = \frac{0.4343}{T_c(1 - T_m/T_c)} \qquad (9)$$

where T_m is the absolute temperature at which the saturated vapor has maximum surface tension.

By means of equation (9) the values of T_m for nineteen different compounds were calculated, and are given in column IV of Table I. The values in column II were obtained graphically from data taken from the Inter. Crit. Tables, Vol. 5. A glance at column V will show that the ratio of the temperatures at which the maxima occur to the critical temperatures is constant, the mean value being 0.910 and the maximum deviations being less than ±1.5 per cent. It is of interest to note that T_m/T_c for the polar compounds is somewhat higher than for the normal substances, indicating that even at these high temperatures there is a certain amount of molecular association.

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[1] Z. physik. Chem., **71**, 577 (1910).

TABLE I

The Corresponding State of Maximum Surface Tension of Saturated Vapors

I	II	III	IV	V	VI
Substance	$\dfrac{d \log \rho_v}{dT}$	T_c absolute	T_m absolute	$\dfrac{T_m}{T_c}$	Percent Deviation from the Mean
n-Pentane	.0093	470.3	423.7	.901	−0.99
n-Hexane	.0093	507.9	461.2	.908	−0.22
n-Octane	.0087	569.3	519.2	.912	+0.22
Cyclo-hexane	.0076	554.1	497.0	.897	−1.43
Carbon Tetrachl.	.0077	556.1	499.7	.899	−1.21
Benzene	.0078	561.6	505.9	.901	−0.99
Fluorobenzene	.0078	559.6	504.2	.901	−0.99
Chlorobenzene	.0076	633.1	576.0	.910	0.00
Bromobenzene	.0082	570.1	517.1	.907	−0.33
Methly Formate	.0097	487.1	442.3	.908	−0.22
Ethyl Acetate	.0098	524.1	479.8	.915	+0.55
Methyl Ether	.0106	400.0	359.2	.898	−1.32
Ethyl Ether	.0100	467.6	424.2	.907	−0.33
Acetone	.0100	508.1	464.9	.915	+0.55
Methyl Alcohol	.0109	513.1	473.3	.921	+1.21
Ethyl Alcohol	.0109	516.1	476.3	.922	+1.32
n-Propyl Alcohol	.0102	536.8	494.4	.921	+1.21
Acetic Acid	.0081	594.1	540.5	.911	+0.11
Propionic Acid	.0088	612.6	558.1	.920	+1.10
			Mean	.910	

It is also of interest to show, since T_m/T_c is a constant, that $\dfrac{d \ln \rho_v}{d \ln T}$ is a universal constant and equals 10.1.

Multiplying equation (8a) by T_m we obtain

$$\frac{T_m d \ln \rho_v}{dT} = \frac{T_m}{T_c (1 - T_m/T_c)}$$

$$\text{or} \quad \frac{d \ln \rho_v}{d \ln T} = \frac{T_m/T_c}{(1 - T_m/T_c)} = U = \frac{.91}{1 - .91} = 10.1$$

In conclusion, I wish to take the opportunity to express my appreciation of the instructive discussions with Dr. M. Muskat of the Gulf Research Laboratory.

Summary

1.   An expression relating surface tension of saturated vapors with temperature is deduced.

2.   It is shown that the ratio of the temperature at which the surface tension is a maximum to the critical temperature is constant, i.e.

$$T_m/T_c = .910 \text{ for all substances.}$$

3.   It is also shown that the slope of log ρ_v — log T curve at T_m is a universal constant, U = 10.1.   Here ρ_v is the vapor density and T absolute temperature.

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