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Surface tension and evaporation: An empirical relation for water

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Several important phenomenological relations dealing with thermophysical properties of liquids are collected. It is shown that the Laplace ratio between the surface energy and the latent heat improves substantially if we add a volume-expansion term to the surface energy.

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Extensive literature [1–4] exists on the process of vaporization, its link with the first law of thermodynamics, and the relevant role of surface tension. In particular, it has been argued [1] that the internal latent heat of a liquid is, presumably, a measure of the work done against the internal pressure, and that done by the molecules in reaching the surface. Indeed, part of the energy needed to evaporate a drop comes from the continuous decrease of the surface energy as the drop becomes smaller. Several pioneering workers have given empirical relations (see Table I) among the various physical quantities, such as the surface tension S, the latent heat L, temperature T, liquid density ρ, molecular weight M, etc., and elaborate experimental checks have been made to ascertain their domains of validity.

In the present paper, we focus attention on the quantitative link between the surface energy and the latent heat for which a formula exists in Laplace's theory [item (i) of Table I]. It is well known that the ratio of these two quantities is *not* a constant for a given liquid; rather, it increases with the temperature. We propose below to construct a better phenomenological constant by first calculating the surface energy via a simple model and then by adding the contribution from the external work done. When such a scheme is applied to water, for which extensive data [5,6] are available over a wide temperature range, we do get very encouraging results. Actually, this scheme is motivated by an earlier work [7] done in the case of liquid metals for which the data were available over a rather limited temperature range.

In order to calculate the surface energy Q_s per unit mass, we take a liquid cuboid of mass 1 g having a cross-sectional area of 1 cm^2 and height of $1/\rho$ cm. This may be imagined to have $1/d\rho$ molecular layers of unit area,

TABLE I. Important empirical relations among thermodynamic parameters of liquids. Here S is the surface tension, M the molecular weight, ρ the density of the liquid, K the Eötvös Universal constant, T the temperature, T_c the critical temperature, P the pressure, P_c the critical pressure, L the latent heat, T_B the normal boiling point, R the gas constant, ρ_v the saturated vapor density, A_1 the universal constant, β the compressibility, d the distance between molecules in the liquid, and ε_B the molecular binding energy per unit volume.

Name	Relation
(i) Laplace[a]	$\frac{\text{Molar total surface energy}}{\text{Molar internal latent heat}}=$ constant with respect to T
(ii) Eötvös[b]	$S(M/\rho)^{2/3}+kT=kT_c$
(iii) Law of corresponding states[c]	$\ln(P/P_{c)}=5.4(1-T_c/T)$ (For $0.5<T/T_c<1$)
(iv) Trouton[c]	$L/RT_B\sim 9$
(v) Macleod[a]	$S=C_1(\rho-\rho_v)^4$, $C_1=A_1T_c/M^{2/3}\rho_c^{10/3}$
(vi) Richards and Matthews[a]	$S\beta^{4/3}$ is a constant with respect to T
(vii) Parachor[a]	$MS^{1/4}/\rho$ is a constant with respect to T
(viii) Zhang[d]	$dL/dT=-5.12R$ (for water in the range 273–373 K)
(ix) Weisskopf[e]	$d=6S/\varepsilon_B$

[a] Reference [1].
[b] Reference [8].
[c] Reference [10].
[d] Reference [9].
[e] Reference [11].

where $d=(M/N\rho)^{1/3}$ is the average distance between the molecules, N being the Avogadro number. During the process of evaporation, these layers may be imagined as being removed one by one, each removal requiring an energy input of S ergs. Hence the net amount of surface energy consumed during evaporation is

$$Q_s=S/d\rho \ . \tag{1}$$

Next, when the liquid has converted itself into vapor, the magnitude of the external work done is

$$Q_w=P(V_V-V_L) \ , \tag{2}$$

where V_V and V_L are the specific volumes of the vapor and liquid, respectively, at saturation pressure P. With the help of Eqs. (1) and (2) we can construct a sum Q' and a ratio f given by

$$Q'=Q_s+Q_w, \quad f=Q/Q' \ , \tag{3}$$

where Q is the latent heat per unit mass. Now we turn to numerical application of the above results.

For the case of water, the thermodynamic parameters [5] and surface-tension [6] values over the whole temperature range from the melting point up to the critical point, viz. 0.01–374.15 °C, are given in Table II. Table III shows the results of our calculations of d, Q_s, Q_w, Q', and f over the same temperature range. The following inferences are worth mentioning. (1) The surface energy Q_s is a substantial part of the latent heat Q per unit mass in accordance with the general observation mentioned in Ref. 1. (2) The sum Q' shows a remarkable constancy in the limited interval 0.01–100 °C, in qualitative agreement with the author's [7] finding for liquid metals. Of course, if the temperature range is extended further beyond

TABLE II. Experimental values of temperature [T (°C)], vapor pressure [P (bar)], density of liquid [ρ (gm/cm^3)], density of vapor [ρ_v (g/cm ^{3})], heat of vaporization [Q (cal/g)], and surface tension of water in equilibrium with its vapor [S (ergs/cm^2)].

T	P	ρ	$10^3\rho_v$	Q	S
0.01	0.006 108	0.999 80	0.004 847	597.47	75.64
10	0.012 277	0.999 60	0.009 398	591.73	74.23
20	0.023 37	0.998 20	0.017 29	586.24	72.75
30	0.042 41	0.995 62	0.030 37	580.51	71.20
40	0.073 75	0.992 16	0.051 15	574.77	69.60
50	0.123 35	0.988 04	0.083 06	569.28	67.94
60	0.199 17	0.983 19	0.1302	563.31	66.24
70	0.3117	0.977 17	0.1982	557.33	64.47
80	0.4736	0.971 82	0.2934	551.36	62.67
90	0.7011	0.965 34	0.4235	545.15	60.82
100	1.0131	0.958 31	0.5977	539.18	58.91
110	1.4326	0.941 02	0.8264	532.73	56.96
120	1.9854	0.943 13	1.121	526.04	54.96
130	2.7011	0.934 84	1.496	519.35	52.93
140	3.614	0.926 10	1.996	512.42	50.85
150	4.760	0.916 93	2.547	505.02	48.74
160	6.810	0.907 36	3.258	497.37	46.58
170	7.920	0.897 34	4.122	489.73	44.40
180	10.027	0.886 92	5.157	481.37	42.19
190	12.553	0.876 04	6.394	472.77	39.95
200	15.551	0.864 68	7.862	463.69	37.69
210	19.080	0.852 81	9.588	453.89	35.41
220	23.201	0.840 34	11.62	443.86	33.10
230	27.979	0.827 34	13.99	433.11	30.77
240	33.480	0.813 60	16.76	421.88	28.42
250	39.776	0.799 23	19.28	409.70	26.06
260	46.94	0.784 01	23.72	396.80	23.67
270	55.05	0.767 87	28.09	383.42	21.30
280	64.19	0.750 69	33.19	368.59	18.94
290	74.45	0.732 33	39.15	352.68	16.61
300	85.92	0.712 45	46.21	335.48	14.30
310	98.70	0.691 09	54.58	316.58	12.04
320	112.90	0.667 11	64.72	295.70	9.81
330	128.65	0.640 20	77.10	272.24	7.66
340	146.08	0.610 13	92.76	245.34	5.59
350	165.37	0.574 38	113.6	213.45	3.65
360	186.74	0.527 98	144.0	171.83	1.90
370	210.53	0.450 45	203.0	104.73	0.45
374.15	221.297	0.306 75	306.75	0	0

100 °C for water, the said constancy of Q' will start to become invalid because at the critical point both Q_s and Q_w must vanish. (3) The ratio f is practically independent of the temperature, having an approximate value 6.2.

The quantity f is the desired phenomenological constant of the present paper—in fact, its constancy is much better than the parameter mentioned in item (i) of Table I. This important finding will be interpreted thermodynamically below.

With a view toward understanding thermophysically the constancy of f let us examine

$$\frac{1}{f}=\frac{Q_s}{Q}+\frac{Q_w}{Q} . \tag{4}$$

Using the celebrated Eötvös law [8] and Eq. (1), we can write (with T in degrees kelvin)

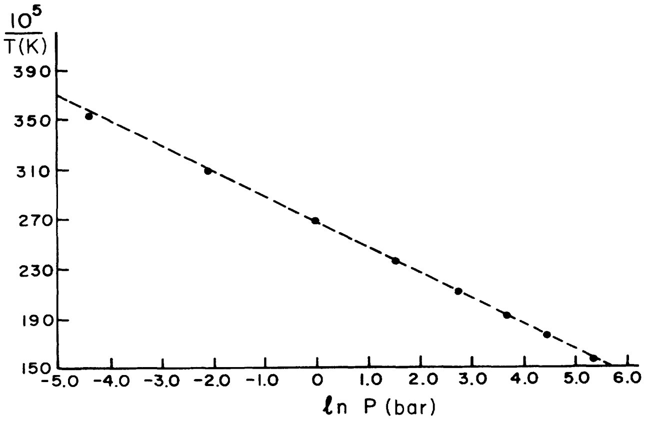

FIG. 1. Plot of $1/T$ vs. $\ln P$ for water. The data are taken from Ref. [5].

TABLE III. Calculated values of molecular size [d (cm)], heat needed to overcome surface tension [Q_s (cal/g)], external work of expansion [Q_w (cal/g)], $Q'=Q_s+Q_w$, and $f=Q/Q'$.

T (°C)	10^8d	Q_s	Q_w	Q'	f
0.01	3.1037	58.233	30.103	88.336	6.76
10	3.1039	57.155	31.211	88.366	6.70
20	3.1053	56.068	32.291	88.359	6.64
30	3.1080	54.968	33.362	88.330	6.57
40	3.1116	53.857	34.442	88.299	6.51
50	3.1159	52.719	35.476	88.195	6.46
60	3.1210	51.569	36.527	88.096	6.39
70	3.1274	50.397	37.559	87.956	6.34
80	3.1332	49.169	38.546	87.715	6.29
90	3.1402	47.931	39.526	87.457	6.23
100	3.1478	46.653	40.465	87.118	6.19
110	3.1558	45.338	41.375	86.713	6.14
120	3.1646	43.990	42.243	86.233	6.10
130	3.1739	42.615	43.054	85.669	6.06
140	3.1839	41.198	43.826	85.024	6.03
150	3.1945	39.751	44.159	84.270	5.99
160	3.2057	38.256	45.132	83.388	5.97
170	3.2175	36.737	45.690	82.427	5.94
180	3.2301	35.181	46.176	81.357	5.92
190	3.2434	33.589	46.559	80.148	5.90
200	3.2576	31.965	46.825	78.790	5.89
210	3.2726	30.310	47.006	77.316	5.87
220	3.2887	28.612	47.039	75.651	5.87
230	3.3058	26.876	46.962	73.838	5.87
240	3.3244	25.102	46.742	71.844	5.87
250	3.3442	23.293	46.379	69.672	5.88
260	3.3657	21.429	45.835	67.264	5.90
270	3.3891	19.553	45.105	64.658	5.93
280	3.4147	17.651	44.160	61.811	5.96
290	3.4430	15.737	42.995	58.732	6.01
300	3.4748	13.799	41.536	55.335	6.06
310	3.5102	11.857	39.784	51.641	6.13
320	3.5518	9.891	37.627	47.518	6.22
330	3.6009	7.938	35.061	42.999	6.33
340	3.6591	5.982	31.900	37.882	6.48
350	3.7335	4.066	27.899	31.965	6.68
360	3.8398	2.239	22.524	24.763	6.94
370	4.0485	0.589	13.630	14.219	7.37
374.15	4.6016	0	0	0	

$$\frac{Q_s}{Q}=\frac{kT_cN^{1/3}}{MQ}\left[1-\frac{T}{T_c}\right], \tag{5}$$

where T_c is the critical temperature. Taking $k=2.2$ cal/K, $T_c=647.3$ K, and the linear parametrization [9] $Q=751.7[1-0.00075T]$ cal/g, we have

$$Q_s/Q=0.21[1-0.0008T]\ . \tag{6}$$

Next, with the help of Clapeyron's relation [10], we can write

$$\frac{Q_w}{Q}=-T\frac{d(1/T)}{d(\ln P)}=0.0002T\ , \tag{7}$$

where the coefficient of T has been read off from Fig. 1 showing the plot of $1/T$ versus $\ln P$. The addition of Eqs. (6) and (7) yields, with T in degrees kelvin,

$$1/f=0.21+0.00004T\ . \tag{8}$$

The right-hand side is essentially a constant because of the small coefficient of T. In other words, the combination of Eötvös's law and Clapeyron's relation implies that f should be almost independent of the temperature. It is quite likely that the above philosophy may also be applicable to other liquids, provided enough data are available up to the critical temperature for these liquids.

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