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## Surface tension, evaporation and Eotvos law for liquid metals

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**Abstract.** In the process of vaporisation, the heat contribution from overcoming the surface tension added to the relevant volume expansion term shows a remarkable constancy with respect to temperature in the case of alkali liquid metals. This sum also exhibits a definite power dependence on the molecular weight. These features lead to direct physical interpretation of the Eotvos law.

### 1. Introduction

The process of evaporation of a liquid is of paramount interest in condensed matter physics because it vividly illustrates the concepts of phase transformation and the first law of thermodynamics. The standard decomposition (Sonntag and Wyler 1982) of the heat  $Q$  of vaporisation per unit mass is  $Q_u + Q_w$  where  $Q_u$  denotes the internal energy added to the system and  $Q_w = p(V_V - V_L)$  represents the external work of expansion. Here  $V_V$  and  $V_L$  are the specific volumes of the vapour and liquid, respectively, at saturation pressure  $p$ . The internal energy term  $Q_u$  is expected to consist of contributions from the *bulk* and from the *surface* of the liquid. The aim of the present paper is to examine the relative importance of a contribution  $Q_\gamma$  (say) arising from overcoming the forces due to surface tension by focusing attention on the sum

$$Q' = Q_\gamma + Q_w. \quad (1)$$

As will become apparent in the following, the magnitude of  $Q_\gamma$  is quite comparable with that of  $Q_w$  for typical liquid metals such as lithium, sodium, potassium, rubidium, caesium and francium. Also, the sum  $Q'$  exhibits a remarkable constancy over the relevant temperature ranges together with a definite functional dependence on the molecular weight. The general theory incorporating these ideas, together with its application to the above-mentioned metals for which exhaustive data (Vargaftik 1975) are available, will be discussed in § 2.

In § 3, we elucidate the findings of § 2 in relation to the celebrated Eotvos law (Allen 1972) which represents the empirical link between the surface tension, density, molecular weight and temperature for liquids. There we point out the hitherto unknown physical interpretation of each term in the law and suggest algebraic expressions for the various parameters involved. The main conclusions of the paper are summarised in § 4.

## 2. Theory and applications

In order to calculate  $Q_\gamma$ , we take a liquid cuboid of mass 1 g having a cross sectional area of  $1 \text{ cm}^2$  and a height of  $\rho_L^{-1} \text{ cm}$ ,  $\rho_L$  being the density. This may be imagined to have  $1/d\rho_L$  molecular layers of unit area, where  $d$  is the average distance between molecules. During the process of evaporation these layers are removed one by one, each such removal requiring an energy input of  $\gamma_{LV}$  erg,  $\gamma_{LV}$  being the surface tension of the liquid in contact with its saturated vapour at temperature  $T$ . Hence the net amount of heat needed to evaporate against surface tension is

$$Q_\gamma = \gamma_{LV}/d\rho_L. \quad (2)$$

For molten alkali metals (except francium) the thermodynamic parameters at saturation over a wide temperature range were taken from the compilation of Vargaftik (1975) in order to calculate  $Q_w$ . To compute  $Q_\gamma$ , surface tension and density values were obtained from the same reference and  $d$  was evaluated by the three different methods described below.

### 2.1. Choice of $d$

As far as the value of the average molecular inter-layer distance  $d$  is concerned there are three possible candidates: the length of an elementary cube attached to the molecule, the first peak position of the radial distribution function (RDF) and the inter-planar distance of the most densely packed surfaces of the underlying BCC structure. Numerical work on these choices are reported below.

*2.1.1. Choice I.* If  $M$  is the molecular weight and  $N$  the Avogadro number, we can imagine an effective cubical volume  $M/N\rho_L$  attached to every molecule. Thus the simplest model for  $d$  is

$$d = d_A \equiv (M/N\rho_L)^{1/3}. \quad (3)$$

Table 1(a)–(e) shows the results of our calculations of  $d$ ,  $Q_\gamma$ ,  $Q_w$ ,  $Q'$  and  $f = Q/Q'$  over the temperature range for which data are available. The ratio  $f$  just indicates how many times the total heat of vaporisation  $Q$  is equal to the sum  $Q'$ . It is evident here that, while  $Q_\gamma$  steadily decreases with increasing temperature, the term  $Q_w$  monotonically increases in such a way that the sum  $Q'$  remains essentially constant with respect to the temperature.

Next, let the symbols  $\bar{Q}'$  and  $\bar{M}$ , respectively, denote the averages of  $Q'$  and molecular weight values for a typical metal over the whole temperature range. It is worth pointing out that, because of the possible presence of varying concentrations of main and trace isotopes, the experimental molecular weight values reported by Vargaftik (1975) do change with the temperature. A plot of  $\log_{10}(\bar{Q}')$  against  $\log_{10}(\bar{M})$  in figure 1 displays a striking linear nature which implies a power-dependence fit of the form

$$\bar{Q}' = 9304(\bar{M})^{-1.208} \text{ cal g}^{-1} \quad (4)$$

for molten alkali metals.

While carrying out the above analysis for francium, also an alkali metal, we found that experimental data on  $\gamma_{LV}$ ,  $\rho_L$ ,  $\rho_V$ ,  $p$  and  $Q$  as functions of temperature were not available. However, empirical dependences of  $\gamma_{LV}$  and  $\rho_L$  on  $T$  were mentioned

**Table 1.** Calculated values of molecular size  $10^8d$  with choice I, heat  $Q_\gamma$  needed to overcome surface tension, external work  $Q_w$  of expansion,  $Q' = Q_\gamma + Q_w$  and  $f = Q/Q'$  for liquid metals.

$T$ (K)	$10^8d$ (cm)	$Q_\gamma$ (cal g <sup>-1</sup> )	$Q_w$ (cal g <sup>-1</sup> )	$Q'$ (cal g <sup>-1</sup> )	$f$
(a) Lithium					
800	2.8863	598.43	227.30	825.73	6.36
900	2.9139	581.03	253.81	834.84	6.22
1000	2.9446	562.85	279.18	842.03	6.09
1100	2.9808	544.73	303.23	847.96	5.96
1200	3.0175	525.20	326.19	851.39	5.84
1300	3.0560	505.25	364.12	869.37	5.62
1400	3.0959	484.96	368.82	853.78	5.63
1500	3.1392	465.15	389.25	854.40	5.52
1600	3.1808	444.29	409.18	853.47	5.43
1700	3.2227	423.19	428.65	851.84	5.35
1800	3.2646	401.84	448.15	849.99	5.24
1900	3.3067	380.15	467.48	847.63	5.20
2000	3.3489	358.09	486.74	844.83	5.13
(b) Sodium					
400	3.4608	146.22	34.58	180.80	5.98
500	3.4959	141.01	43.06	184.07	5.80
600	3.5353	135.38	51.26	186.64	5.64
700	3.5839	129.47	59.03	188.50	5.48
800	3.6392	123.26	66.33	189.59	5.33
900	3.6995	116.83	73.16	189.99	5.20
1000	3.7613	110.15	79.62	189.77	5.08
1100	3.8263	103.45	85.84	189.29	4.97
1200	3.8920	96.65	91.87	188.52	4.88
1300	3.9570	89.75	97.94	187.69	4.79
1400	4.0241	82.66	103.86	186.52	4.70
1500	4.0903	75.42	109.76	185.18	4.63
(c) Potassium					
400	4.3046	71.46	20.33	91.79	5.72
500	4.3531	68.23	25.32	93.55	5.53
600	4.4071	64.75	30.16	94.91	5.36
700	4.4725	61.12	34.75	95.87	5.20
800	4.5442	57.26	39.08	96.34	5.06
900	4.6241	53.31	43.16	96.47	4.94
1000	4.7075	49.25	47.07	96.32	4.82
1100	4.7954	45.14	50.88	96.02	4.70
1200	4.8815	40.86	54.63	95.49	4.60
1300	4.9705	36.50	58.45	94.95	4.49
1400	5.0568	31.95	61.50	93.45	4.42
(d) Rubidium					
400	4.6299	29.70	9.29	38.99	5.55
500	4.6887	28.17	11.55	39.72	5.35
600	4.7592	26.53	13.71	40.24	5.17
700	4.8410	24.80	15.73	40.53	5.01
800	4.9315	22.99	17.64	40.63	4.86
900	5.0273	21.12	19.45	40.57	4.74
1000	5.1260	19.20	21.19	40.39	4.63
1100	5.2259	17.23	22.90	40.13	4.52
1200	5.3260	15.19	24.62	39.81	4.42

Table 1—continued

(e) Caesium					
400	4.9875	17.91	5.98	23.89	5.53
500	5.0492	16.96	7.44	24.40	5.33
600	5.1224	15.96	8.84	24.79	5.14
700	5.2088	14.88	10.15	25.03	4.98
800	5.3036	13.76	11.40	25.16	4.84
900	5.4049	12.59	12.59	25.18	4.71
1000	5.5097	11.40	13.55	24.95	4.63
1100	5.6205	10.18	14.64	24.82	4.52
1200	5.7427	8.95	15.73	24.68	4.41
1300	5.8673	7.66	16.85	24.51	4.30

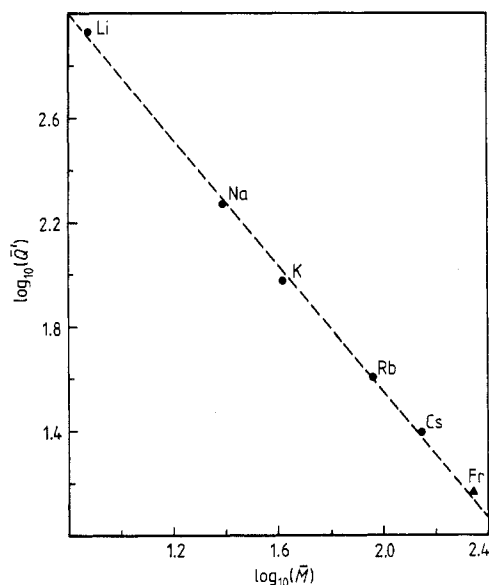


Figure 1. Plot of  $\log_{10}(\bar{Q}')$  against  $\log_{10}(\bar{M})$  for molten alkali metals (● for notation see the text): a least-squares fit yields the expression  $\log_{10}(\bar{Q}') = 3.969 - 1.208 \log_{10}(\bar{M})$ ; ▲, point corresponding to francium.

(Smithells 1976). This information gives us  $Q_\gamma$  but, to calculate  $Q_w$ , we made the perfect-gas approximation (which is reasonably accurate):

$$Q_w = p(V_V - V_L) \approx RT/M \quad (5)$$

$R$  being the gas constant. The corresponding calculated values for this metal are reported in table 2 from 50 to 1000 °C. We observe that  $Q'$  is again a constant and falls on the curve of equation (4) (figure 1).

2.1.2. *Choice II.* Since the probability distribution between pairs of molecules in the liquid is determined by the RDF  $g(r)$ , a realistic choice for  $d$  would be

$$d = d_B \equiv \text{the first peak position of } g(r). \quad (6)$$

The experimental RDF values for the alkali liquid metals are available (Waseda 1980) only at a few temperatures. Using those  $g(r)$  values, we find that  $d_B$  is generally 10% larger than  $d_A$  and the output results analogous to choice I are reported in table 3. It is observed that the constancy of  $Q'$  now for the metals sodium and potassium is not as

**Table 2.** As table 1 except that the entries refer to liquid francium.

$T$ (°C)	$10^8 d$ (cm)	$Q_v$ (cal g <sup>-1</sup> )	$Q_w$ (cal g <sup>-1</sup> )	$Q'$ (cal g <sup>-1</sup> )
50	5.4209	11.49	2.88	14.37
100	5.4520	11.20	3.32	14.52
200	5.5165	10.60	4.21	14.81
300	5.5841	9.98	5.10	15.08
400	5.6552	9.32	6.00	15.32
500	5.7301	8.64	6.89	15.53
600	5.8091	7.92	7.78	15.70
700	5.8926	7.17	8.67	15.84
800	5.9811	6.37	9.56	15.93
900	6.0753	5.52	10.45	15.97
1000	6.1756	4.62	11.34	15.96

**Table 3.** As table 1 except that the  $d$ -values correspond to choice II.

$T$ (°C)	$10^8 d$ (cm)	$Q_v$ (cal g <sup>-1</sup> )	$Q_w$ (cal g <sup>-1</sup> )	$Q'$ (cal g <sup>-1</sup> )	$f$
(a) Lithium					
190	2.9594	625.02	130.98	756.00	7.12
250	2.9580	618.90	148.76	767.66	6.99
(b) Sodium					
105	3.6665	139.12	32.62	171.74	6.31
200	3.6473	135.92	40.83	176.75	6.07
300	3.6777	132.14	49.10	181.24	5.83
450	3.6730	124.86	60.72	185.58	5.54
550	3.6546	121.07	67.95	189.04	5.32
(c) Potassium					
70	4.5612	68.45	17.45	85.90	6.18
105	4.5620	68.03	19.23	87.26	6.05
200	4.5632	65.52	23.99	89.51	5.80
350	4.5601	61.62	31.25	92.87	5.45
450	4.5645	59.06	35.77	94.83	5.23
(d) Rubidium					
40	4.8410	29.22	7.29	36.51	6.00
100	4.8965	28.30	8.67	36.97	5.87
200	4.9176	27.19	10.95	38.14	5.60
(e) Caesium					
30	5.0730	18.23	4.64	22.97	5.86
100	5.1483	17.53	5.60	23.13	5.74
200	5.1618	16.79	7.05	23.84	5.48

good as it was for choice I. This may be just because the  $d_B$ -values obtained for these metals either do not change with increasing temperature or occasionally decrease with increasing temperature (which is physically unrealistic) whereas the reported number density (Waseda 1980) consistently decreases. In contrast, for rubidium and caesium

**Table 4.** As table 1 except that the  $d$ -values correspond to choice III.

$T$ (°C)	$10^8 d$ (cm)	$Q_v$ (cal g <sup>-1</sup> )	$Q_w$ (cal g <sup>-1</sup> )	$Q'$ (cal g <sup>-1</sup> )	$f$
(a) Lithium					
190	2.5157	735.26	130.98	866.24	6.21
250	2.5273	724.39	148.76	873.15	6.14
(b) Sodium					
105	3.0803	165.60	32.62	198.22	5.47
200	3.1017	159.83	40.83	200.66	5.34
300	3.1380	154.87	49.10	203.97	5.18
450	3.1697	144.69	60.72	205.41	5.00
550	3.1989	138.32	67.95	206.27	4.88
(c) Potassium					
70	3.8091	81.96	17.45	99.41	5.36
105	3.8292	81.05	19.23	100.28	5.26
200	3.8593	77.47	23.99	101.46	5.12
350	3.9139	71.79	31.25	103.04	4.92
450	3.9592	68.08	35.77	103.85	4.78
(d) Rubidium					
40	4.0822	34.65	7.29	41.94	5.23
100	4.1083	33.73	8.67	42.40	5.12
200	4.1577	32.16	10.95	43.11	4.95
(e) Caesium					
30	4.3590	21.04	4.64	25.68	5.24
100	4.4289	20.38	5.60	25.98	5.11
200	4.4777	19.36	7.05	26.41	4.94

the  $d_B$ -values consistently increase with increasing temperature, thereby maintaining the constancy of  $Q'$ . The dependence of averaged  $Q'$  on the molecular weight in the present case is

$$Q' = 7481M^{-1.189} \text{ cal g}^{-1}. \quad (7)$$

2.1.3. *Choice III.* Since the liquid state is obtained by melting the underlying solid phase, which is BCC in the case of alkali metals, the final choice for  $d$  could be the interplanar distance of the most densely packed surfaces of the BCC structure, i.e.

$$d = d_C \equiv d_{110} \equiv (2)^{-1/6}(M/N\rho_L)^{1/3}. \quad (8)$$

These  $d_C$ -values were calculated using the number densities (Waseda 1980) at the same temperature points as for choice II, and the results are given in table 4. We find that  $d_C$  is generally 10% smaller than  $d_A$  and the constancy of  $Q'$  now has improved somewhat in comparison with choice II for all alkali metals. This is physically understandable because we have pictured the evaporation process as the removal of molecular layers one by one which tallies well with the concept of crystalline planes. Moreover, the number densities reported in Waseda's book decrease monotonically with increasing

**Table 5.** Experimentally estimated critical temperatures  $T_c$  along with the theoretically predicted values for alkali liquid metals.

Metal	Experimental $T_c$ (K)	Theoretical $T_c$ (K)
Lithium	3800	3131
Sodium	2500	2440
Potassium	2250	2185
Rubidium	2100	1857
Caesium	2050	1694
Francium	—	1521

temperature so that the corresponding  $d_c$ -values steadily increase, which is physically realistic. The least-squares fit between the averaged  $Q'$  and  $M$  is

$$Q' = 8558M^{-1.193} \text{ cal g}^{-1}. \quad (9)$$

Before ending this section, it should be emphasised that a very detailed comparison of the above three choices of  $d$  is not desirable because ours is an empirical work whose objective is to show that  $Q'$  has little temperature dependence and is linked to the Eotvos law in a manner to be described below.

### 3. Comparison with the Eotvos law

Inserting our value of  $d = d_A$  (equation (3)) into the general formula for  $Q_\gamma$  (equation (2)), we obtain

$$Q_\gamma = \gamma_{LV}[N/M\rho_L^2]^{1/3}. \quad (10)$$

Combining this  $Q_\gamma$  with  $Q_w$  as given by equation (5) and comparing with the fit (equation (4)), we get

$$\gamma_{LV}(M/\rho_L)^{2/3} + RT/N^{1/3} \approx 9304/M^{0.208} N^{1/3}. \quad (11)$$

This relation bears a strong resemblance to the well known phenomenological Eotvos law (Allen 1972)

$$\gamma_{LV}(M/\rho_L)^{2/3} + KT = KT_c \quad (12)$$

where  $T_c$  is the critical temperature and  $K$  is a parameter which tends to the value  $1.53 \times 10^{-8} \text{ cal K}^{-1}$  for metals as proposed in earlier literature. Comparison of equations (11) and (12) yields the estimates of the parameters:

$$K = R/N^{1/3} = 2.39 \times 10^{-8} \text{ cal K}^{-1} \quad (13)$$

$$T_c = 9304/RM^{0.208} \text{ K}.$$

The magnitude of the parameter  $K$  in our approach is larger than that reported by Eotvos—this may be because our analysis is based on a larger number of data points measured with relatively high precision while Eotvos had to rely on analysing meagre data measured with less precision. The above expression for  $T_c$  can be profitably used to predict the critical temperature of the alkali metals including francium and the results are summarised in table 5 which also includes experimentally estimated values compiled



by Vargaftik (1975). It is seen that, except for lithium, our predictions match the experimental results.

#### 4. Conclusions

Our inferences may be summarised as follows.

(i) The heat  $Q_\gamma$  needed to overcome surface tension is quite substantial and should not be neglected in comparison with  $Q_w$  in all cases.

(ii) The sum  $Q' = Q_\gamma + Q_w$  shows a remarkable constancy in the temperature ranges for which data are available. This conclusion is insensitive to a precise definition of the average molecular inter-layer distance. The constancy of  $Q'$  is physically understandable because, as the value of the product  $pV_V$  increases with increasing temperature, the surface tension contribution decreases.

(iii) The dependence of  $Q'$  on the molecular weight is well fitted by a power law (equation (4)).

(iv) Our approximate analysis of the meagre data on francium confirms all the above three conclusions.

(v) The physical origin of the Eotvos law (equation (12)) can be explained satisfactorily, and a comparison of the expression of  $Q'$  with the Eotvos law gives a formula for the critical temperature  $T_c$  (equation (13)) for the surface tension of alkali liquid metals. The predicted  $T_c$  values are in agreement with the experimental ones.

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