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ORIGINAL CONTRIBUTION

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Understanding of surface tension?

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Abstract The importance of the molar dimensions for surface properties of not too large molecules is stressed. The understanding of surface properties of pure liquids is described in molar units with a simple model of normal liquids. The increasing knowledge makes it necessary to use idealized models. A hypothesis is given for the temperature constancy of the surface energy of small molecules without H-bonds, and a model is developed for the free energy σ_m and its temperature dependency. This seldom example of the direct measurement of the isothermic work or the free energy could help to illustrate the difference between energy and free energy.

Key words Surface tension · Surface energy · Surface entropy · Surface free energy

Introduction

Modern research is thinking mainly in molar dimensions. Eötvös had already suggested [1] the rare use of molar units for surface properties. However, the surface tension σ is mainly expressed as a unit: force per cm. One reason may be the uncertainty about possible differences between the density in the surface and in the bulk. This difference could be similar in homologous series and may be tolerated in the limits of errors in technology. Einstein [2] had claimed that the change of density in the surface would not be expected to be large because the surface energy U_σ of small molecules is independent of the temperature. Max Born had stressed [3, 4] that we should try to describe such properties with intuitive models.

Surface tension

Surface tension σ is mainly discussed as a force F in dyne per cm. But forces of molecules are more difficult to determine quantitatively. Spectroscopic measurements yield data mainly in energies. Therefore, σ should be better discussed in terms of the free energy to enlarge the surface or even as isothermal work [2, 4, 5]. The numbers of the quantity of σ are the same in both representations: dyne per cm or erg per cm^2. For instance, with Philipp Lenards method of moving a wire out of the liquid, the work is determined as Fdx which is necessary to enlarge the surface by 2ldx (l = length of the moved wire, and dx = dislocation):

$$\sigma = \frac{Fdx}{21dx} = \frac{F}{21} \tag{1}$$

Fig. 1 gives the σ data of Ramsay and Shields [5] and Landolt-Börnstein tables in a reduced scale T/T_K (T_K = critical temperature). H_2O has the largest surface tension σ and the organic liquids without OH open H-bonds have similar values. Generally, the surface tension σ is determined for the number of molecules per cm^2. Therefore, the values of the small molecule H_2O dominate in Fig. 1. Eötvös [1] introduced the apparent molar surface tension:

$$\sigma'_m = \sigma V_m^{2/3} \tag{2}$$

where V_m is the molar volume, and σ'_m is the work to extend the surface area by an area of $V_m^{2/3}$ (Fig. 2). The Eötvös symbol σ'_m has the strange unit (erg mol$^{-2/3}$). If we consider one mol as a cube of densely packed spherical molecules with spheric-like intermolecular

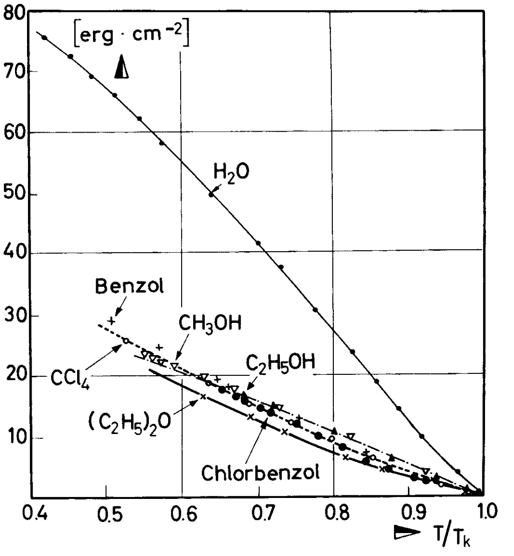

Fig. 1 The surface tension σ in (erg · cm^{-2}) as function of T/T_K

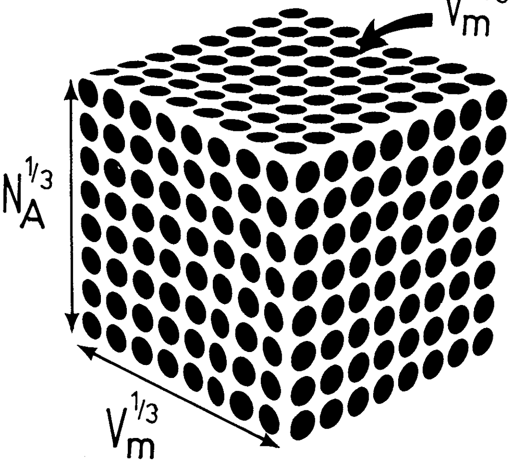

Fig. 2 Scheme for volume V_m of 1 mol spherical molecules in $N_A^{1/3}$ layers of the size $V_m^{2/3}$

potential (Fig. 2), then $N_A^{1/3}$ layers (N_A = Avogadro number) exist. Every layer of such a cube has the size $V_m^{2/3}$. Therefore, one mole at a surface occupies an area of $V_m^{2/3} \cdot N_A^{1/3}$. This view neglects differences of the density between the surface and the bulk. The work needed to bring one mol of molecules from the bulk to such an ideal surface is:

$$\sigma_m = \sigma'_m \cdot N_A^{1/3} = \sigma V_m^{2/3} \cdot N_A^{1/3} \qquad (3)$$

Fig. 3 gives the σ values of Fig. 1 recalculated as σ_m. We use for σ_m in Fig. 3 the units (kcal · mol^{-1}). Now, the dominating role of water disappears in Fig. 3. Nevertheless, the values of σ_m for water are somewhat larger than those of the alcohols. This effect may be related to the two OH groups of water compared with one OH group of the alcohols. σ_m in Fig. 3 seems to be related more directly to the intermolecular forces, contrary to σ (Figs. 1 and 3).

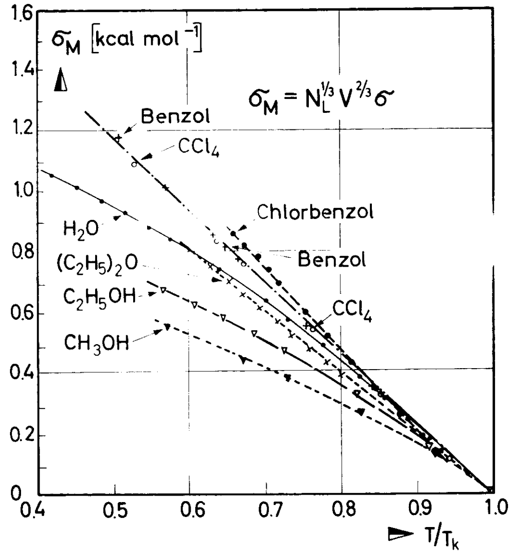

Fig. 3 Molar surface tension σ_M in (kcal · mol^{-1}) of the same molecules as in Fig. 1

Eötvös [1] observed in σ'_m-T diagrams the similar values of "simple liquids" for:

$$\frac{d\sigma'_m}{dT} = -2.1 \times 10^{-7}(\mathrm{JK}^{-1}\,\mathrm{mol}^{-2/3}) \quad \text{for } T/T_K < 0.9 \qquad (4)$$

where 2.1 is an average value. Eötvös [1] reported values between 2.04 to 2.15.

$d\sigma_m/dT$ is, in our units (R = gas constant):

$$\begin{aligned}\frac{d\sigma_m}{dT} &= -2.1 \times 10^{-7} N_A^{1/3}(\mathrm{JK}^{-1}\,\mathrm{mol}^{-1})\\ &= -17.7(\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}) = -2.13\mathrm{R}\end{aligned} \qquad (5)$$

A better linearity of σ_m as f · (T/T_K) in Fig. 3 is observed for non-H-bonded liquids at $T/T_K < 0.9$. H-bonded liquids do not belong to the class of "simple liquids" in this nomenclature [1]. The Eötvös rule (Eq. 4) is not often discussed. One reason for the scepticism about the Eötvös rule may be related to the incorrect doubts in the famous five-volume work of Jellinek [6], an important basis for the physical chemistry in the 1920s. Jellinek discussed the T-dependence of the Eötvös factor of Eq. (4) on the basis of the data of Jaeger [7] and stressed deviations for water, oleates and salt melts. At first, the data in the 214 pages collected by Jaeger [7] deviate partly from those of the more reliable paper of Ramsay and Shields [5]. In the paper by Jaeger [7] T may have been not very correct or perhaps the vapor was not under saturation conditions. For instance, Jaeger [7] and Jellinek [6] reported for CCl_4 at −18 °C < T < 55 °C three values of $d\sigma'_m/dT = -2.6$;

−1.95, and −1.5 but Ramsay and Shields [5] reported for CCl_4 in the region 80 °C < T < 250 °C in intervals of 10 degrees the following constant negative factors (in erg K^{-1} $mol^{-2/3}$) 2.09; 2.09; 2.06; 2.04; 2.09; 2.09;2.13; 2.0; 2.0; 2.0; 2.12; 2.15; 2.10; 2.15; 2.11; 2.03; 2.10. Secondly, water, oleate, and salt melts were excluded by Eötvös [1] as not being simple liquids and, therefore, are not obeying the rule of Eötvös. In addition, Jellinek [6] criticises that the temperature dependence of σ'_m varies from one liquid to the other. But he does not take into account that σ'_m contains the temperature dependence of $V_m{}^{2/3}$. Jellinek's doubts are not appropriate. In addition, Eötvös [1] derived from the T-constancy of Eq. (4) a relation also valid for σ_m:

$$\sigma_m(T_K) - \sigma_m(T) = -2.13\,R(T_K - T) \tag{6}$$

He concluded that σ_m at the critical temperature T_K is zero and, therefore, is:

$$\sigma_m(T) = 2.13\,R(T_K - T) \tag{7}$$

Eq. (7) may be called the second Eötvös rule. This proportionality of σ_m with T_K for simple molecules takes account of the experience that T_K is proportonal to the temperature coefficient C of the collision diameters in the theory of gas kinetics. This so-called Sutherland constant C is proportional to the intermolecular pair potential [8]:

$$E_{pot} = -3C \cdot R/2\,.$$

As T_K is a measure of the pair potential for simple liquid, E_{pot}, a simple and useful model for simple liquids can be derived [8].

The surface energy U_σ

We calculate the surface enthalpy H_σ or, in the liquid state, the similar energy U_σ by interpretation of σ_m as Gibbs free energy [2, 4, 5]:

$$\sigma_m = H_\sigma + T\frac{d\sigma_m}{dT} \tag{8}$$

Using the data of Fig. 3 and Eq. (8) we obtain $U_\sigma(T)$ or $H_\sigma(T)$ (Fig. 4) as temperature-independent values for $T/T_K < 0.9$. This experimental result agrees with Eq. (7) and Eq. (8) and the Eötvös value $d\sigma_m/dT = 2.13$ R:

$$H_\sigma \approx U_\sigma = 2.13\,R \cdot T_K \quad \text{for } T/T_K < 0.9 \tag{9}$$

Fig. 5 shows the proportionality of $U_\sigma(T)$ or H_σ (T) and T_K. The straight line has the slope of 2.25 R which is only slightly larger in comparison with Eq. (9). The expression (−3/2) R · T_K is a measure of the intermolecular pair potential of simple liquids interacting with van der Waals energy [8] and without H-bonds. Simple liquids consist of small molecules with spherical van der Waals potential [8]. The T-constancy of U_σ for $T/T_K < 0.9$ in Eq. (9) is seldom reported in the literature [9, 10] because the authors use the relation $\partial\sigma_\sigma/dT = V_m^{2/3}d\sigma/dT$ overlooking that V_m is also temperature dependent. This may be one reason why the cause of the T-constancy of Eqs. (4), (5), and (9) is so seldom observed.

Eqs. (7) and (9) well describe the surface properties of simple molecules for $T/T_K < 0.9$. With the knowledge or estimation of T_K or with one experimental determination of σ_m the surface properties could be estimated for simple liquids in the whole liquid temperature region with Eqs. (5) and (7) for $T/T_K < 0.9$.

The understanding surface Properties in molecular models

We try to describe the understanding of Eqs. (7) and (9) by a simplified molecular model of the liquid state [8]. Deviations from linearity between U_σ and T_K occur for He, H_2, and Ne (Fig. 5). These molecules cause deviations

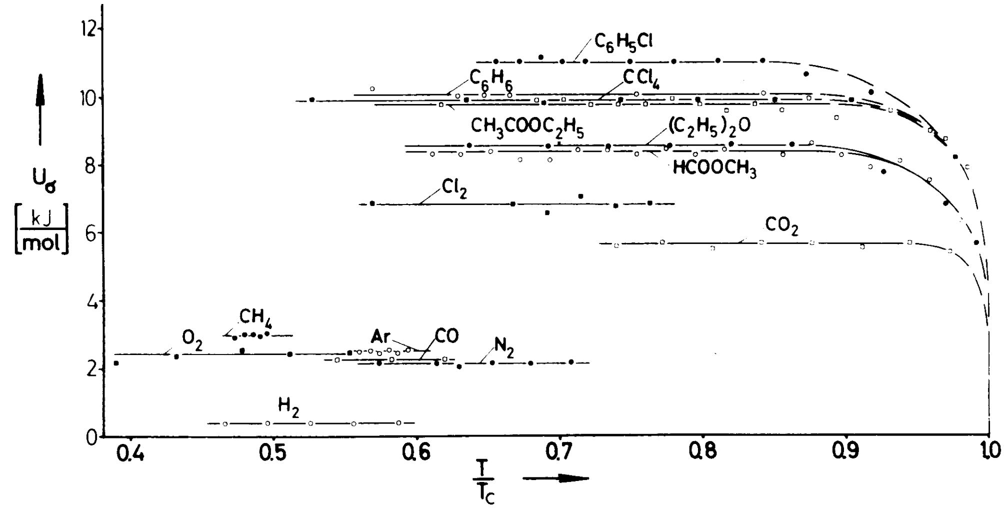

Fig. 4 Surface energy U_σ in (kcal · mol^{-1}) of simple molecules is temperature invariant at T/TK < 0.9.

from the Trouton rule [10] of the heat of vaporisation, $U_{vap}(T_B)$, divided by the boiling temperature T_B:

$$\frac{U_{vap}}{T_B}(T_B) = 21\left(\text{cal mol}^{-1}\text{T}^{-1}\right) \tag{10}$$

The deviations of $U_{vap}(T_B)$ from the straight line for He and H_2 [11] are about four time larger than the deviation of $U_\sigma = f(T_K)$ for He and H_2 in Fig. 5. These deviations are considered as being due to the influence of the relatively large zero point energies E_0 of the intermolecular potential of these molecules (12). Clusius [13] had already corrected Eq. (10) by including He and H_2:

$$\frac{U_{vap}}{T_B} + \frac{E_o}{T_B} = 21\left(\text{cal mol}^{-1}\text{T}^{-1}\right) \tag{11}$$

We expect that the energy to enlarge the surface for spheric-like molecules is proportional to the difference coordination number Z = 12 in the liquid minus coordination number at the surface, X = 9. The ratio between $U_{vap}(T_B)$ and U_σ for $T/T_K < 0.9$ in the case of cubic dense packing should be proportional to:

$$Z(Z - X) = 12/(12 - 9) = 4$$

Eqs. (7) and (9) and the ratio 12/(12–9) are reminiscent of the efficient derivation of U_{vap} for simple van der Waals interacting molecular liquids by a simplified model [8] considering the sum of potential intermolecular energies to all Z next neighbors and the kinetic thermal energy of intermolecular degrees of freedoms [8]. This model, although not well-known, is based on the observation that T_K is a measure of the intermolecular pair potential for simple liquids [8] (Fig. 6):

$$U_{vap} = (Z \cdot f \cdot R/2)[(3T_K/2) - T] \quad \text{for } T < T_B \tag{12}$$

$f = f_1 \cdot f_2$; f_1 = the fraction of the pair potentials of more distant neighbors acting on a central molecule; f_2 = factor of the approximation for the pair potential; $E_{pot} = f_2 \cdot 3\ R \cdot T_K/2$ (see [8]). Deviations from f = 1 are caused by similar effects as the so-called deviations from the corresponding states.

The relation of Eq. (12) resembles the understanding of T_K on Kepler's calculation of the planet movements with the results that two particles move on a parabola if $E_{kin} > E_{pot}$ and on an ellipse if $E_{kin} < E_{pot}$. This means, at saturation conditions:

$$\text{vapour if } \frac{3RT}{2} > \frac{3RT_K}{2} \quad \text{liquid if } 3RT/2 < 3RT_K/2 \tag{13}$$

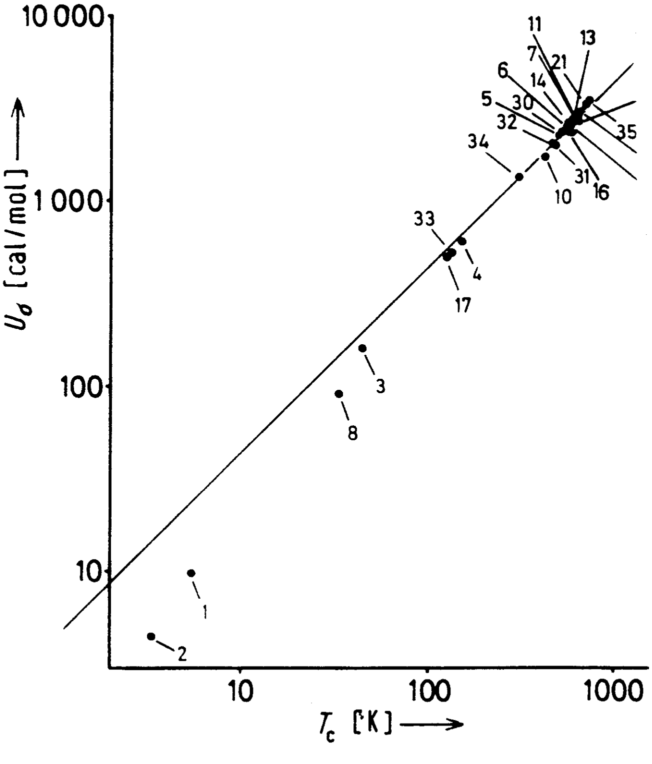

Fig. 5 The surface energy U_σ is proportional to $T_K = T_C$

1 He^4	8 H_2	1 N_2	32 Diethyl ether
2 He^3	10 Cl_2	21 Aniline	33 CO
3 Ne	14 C_6H_{12}	30 Ethyl acetate	34 CO_2
4 Ar	16 CCl_4	31 Methyl formate	35 Dimethylaniline

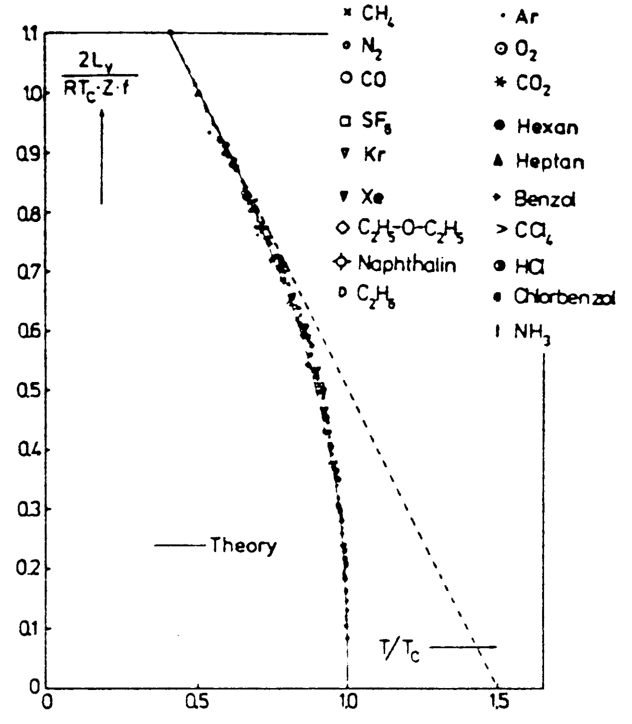

Fig. 6 Useful approximation for the heat of vaporisation U_{vap} (here = L_v) as function of $T_K = T_C$, Ordinate: 2 L_v/RT_C Z f

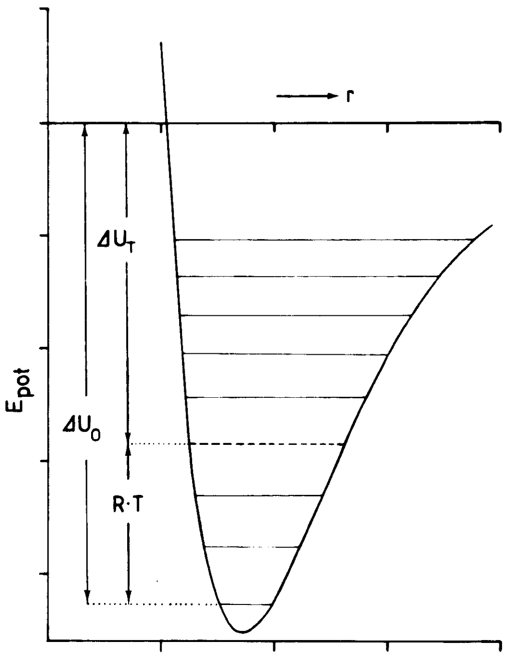

Fig. 7 Model of a vibration potenial E_{pot} of two molecules with quantised vibration levels. Averaged thermal energy RT and averaged rest potentail at T: $U_T = U_0 - RT$

$(Zf/2) \cdot 3\ RT_K/2$ gives the sum of the intermolecular potentials of 1 mol pairs of liquid spherical molecules [8]. The temperature factor was assumed as the heat content due to the vibrations in the intermolecular potential curve (Fig. 7) for every neighbour with quantized vibration levels. The RT factor is the average heat content of these intermolecular degrees of freedoms for every pair of neighbouring molecules. The assumption of such an average value of RT is realizable for the common case if RT is larger than the energy of the first vibration level. Fig. 7 gives the pair potential E_{pot} with quantized vibration levels. RT will then be the averaged level of thermal vibrations and $\Delta U_T = \Delta U_0 - RT$ is the energy that is necessary to evaporate one mol pairs of molecules.

When $T > T_B$ the right side of Eq. (12) has to be multiplied [8] by the factor $(1\text{–}2\ x_F)$. This is necessary because the non-linearity of density with T above T_B . x_F corresponds to the fraction of holes in the hole model of Eyring [14] or Cremer [15]. Or, x_F gives the deviation from the T-linear decrease of liquid density ρ_{liq} with T when $T > T_B$ (Fig. 7). This is

$$xF = \frac{\rho_{vap}}{\rho_{vap} + \rho_{liq}} \tag{14}$$

where ρ_{vap} and ρ_{liq} are the densities of the saturated vapour and the liquid. $Z(1\text{–}x_F)$ is the real first coordination number at $T > T_B$ (Fig. 6). The factor 2 for the correction factor x_F for $T > T_B$ is caused by the intermolecular forces at large vapour densities proportional to x_F [8]. {The sum $(\rho_{vap} + \rho_{liq})$ is linearly temperature-dependent for simple liquids [8].}

Figure 6 shows the usefulness of Eq. (12) together with the factor $(1\text{–}2x_F)$ for a general expression for $U_{vap} = f(T)$ for simple liquids ($U_{vap} = L_v$ and $T_K = T_C$ in Fig. 6). We estimate the factor f Z from the knowledge of U_{vap} at one T and, then, the heat of vaporization U_{vap} in the full region of T/T_K by Eq. (12) and the knowledge of the densities [Eq. (14)] [8]. We find for simple unpolar or weakly polar liquids (8) a region $12.4 < f\ Z < 14.5$. Approximate values of U_{vap} could be predicted with the assumption of $f\ Z = 12$. A further advantage of Eq. (12) is to reveal the cause of small deviations from the corresponding state. Different values of f Z depend on the type of package Z and deviations by potentials of more distant neighbours by different factors f_1 or f_2. Fig. 6 shows that factor $3\ T_K/2$ is correct in Eq. (12). The straight line in Fig. 6 crosses the abscissa at $T/T_K = 3/2$. With experimental values of f Z we obtain:

$$17 < (H_{vap}/T_B)/\text{cal mol}^{-1}\ K^{-1}) < 20.2$$

This is not so far from the Trouton value 21 [Eq. (11)].

The useful Eq. (12) is an approximation, neglecting the thermal statistics and the broadening [8] of the van der Waals pair potential at larger temperatures.

The frequency shift $d\nu(T) = \nu_{vapor} - \nu_{liquid}$ of IR vibration bands in liquids is also proportional to intermolecular interaction energies by van der Waals forces [16, 17]. Its temperature dependence is similar [16, 17] to that in Eq. (12):

$$d\nu(T) = [d\nu(T = 0) - a\ T](1 - x_F) \tag{15}$$

This expression is similar to the Badger-Bauer rule between $d\nu$ and the H-bond energies [18] but with a smaller value for pure of a for van der Waals interactions in Eq. (15). The linear expressions in Eqs. (12) and (15) were interpreted [8] as influences of intermolecular degrees of freedom on the vibration levels. This effect influences the efficient potential linearly with temperature because the quantum levels of these intermolecular potentials are in most cases small compared with RT. These vibrations in the intermolecular potential curve are the cause of the large increase of the heat capacity C_v of liquids compared with the vapour state [8].

We try to understand the surface properties of simple liquids by the same model. For instance, we expect an equation for U_σ similar to Eq. (12). Instead of Z we write the difference between the next neighbour numbers in the liquid Z and in the surface X. However, U_σ is not temperature dependent for $T/TK < 0.9$ contrary to U_{vap}. Thus, we do not have to consider the intermolecular heat capacity C_v because $\Delta C_v = O$ between the inside and the surface layer. This means that the intermolecular heat content at the surface should be equal to its value in the bulk. We can compare the temperature independent part with a relation:

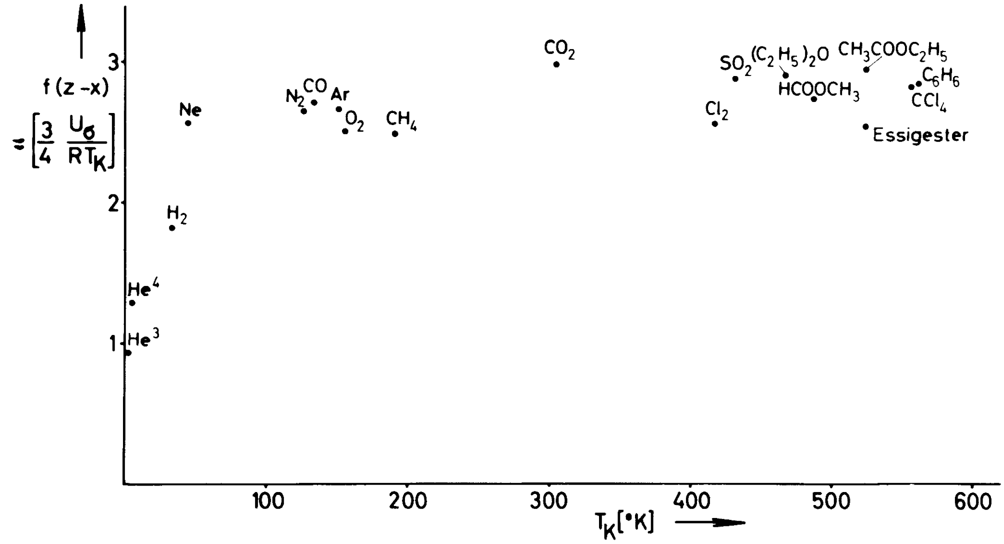

Fig. 8 The experimental factor $f(Z–X) = (3/4)U_\sigma/RT_K$ as a function of T_K

$$U_\sigma = (Z - X)f\, 3R\, T_K/4 \quad \text{for } T/T_K < 0.9 \qquad (16)$$

We arrive at the data in Fig. 8 with $4\, U_\sigma/3\, RT_K = (Z–X)\, f$. For the small temperature region 287 °C < T < 313 °C Grafe [19] gives values between $2.6 < 4\, U_\sigma/3\, RTK < 2.9$ for different molecules with 1 to 6 carbon atoms.

Figure 8 and ref. [19] give similar values for the proportionality factor (Z–X)f with the exception of the "quantum" liquids He and H_2. The average for the other compounds is $(Z–X)f = 2.85$ (Fig. 8). The average value 2.85 scatters between 2.6 and 2.9. Such scattering is specific for every liquid and is parallel to the deviations of the state of correspondence. This scattering range corresponds to the scattering between 2.04 and 2.15 observed by Eötvös (factor for R of $\delta\sigma_m/dT$ in Eq. (5).

The cubic close-packed structure of the liquid with $Z = 12$ gives $X = 9$ neighbours at the surface and, therefore $(Z - X) = 12 - 9 = 3$ in close agreement with the experimental averaged value $(Z - X)f = 2.85$ (Fig. 8) or $f = 0.95$. Our simplified model, therefore, gives some information also on surface phenomena. With the experimental mean value of 2.85 we obtain:

$$U_\sigma(Z - X)f3RT_K/4 = 2.85\, 3R\, T_K/4 = 2.14\, RT_K \qquad (17)$$

This gives a deduction and understanding of the Eötvös [1] constant 2.13 R in Eq. (7). Scattering of the values of (Z – X)f explains the small scattering of the Eötvös constant. This success gives hope that our simplified liquid model can be further applied.

Einstein concluded in 1901 [2] from the T constancy of the surface energy U_σ: "Die spezifische Wärme der Oberfläche ist s = 0. Also der Oberfläche als solcher ist kein Wärmeinhalt zuzuschreiben." [2] (The heat capacity of the surface is s = 0. Thus the surface does not have a heat content [2].) This statement can be misunderstood. The T dependence of H_σ or U_σ is proportional to the difference of the intermolecular thermal movements of the surface and the bulk. We conclude from the T independence of Eq. (9) that the heat content or the intermolecular thermal movements of the surface are the same as in the bulk. Therefore, the heat capacity difference of the intermolecular thermal movements in the surface is equal to the value inside of the liquids and not zero as claimed by Einstein [2].

On the other side, it is not so easy to understand why $\delta\sigma_m/dT \neq 0$ and U_σ is temperature independent for $T/T_K < 0.9$. $\delta\sigma_m/dT$ is equal to ΔS, applying the Gibbs-Helmholtz equation [8]. ΔS is the entropy difference between the bulk and the surface, and σ_m is the free energy, measured as isothermal work [2, 4, 5]. Why does a finite entropy difference exist if the difference of specific heats is zero? How can the free energy σ_m change with T whereas U_σ does not for $T/T_K < 0.9$? The difference between the energy U_σ or H_σ and the free energy σ_m at T = constant is due to a heat change during the enlarging of the surface at isotherm conditions. An appearing or disappearing heat must be subtracted from U_σ or H_σ to get the free energy or work σ_m under isothermic conditions. Our success with the description of the T dependence of U_{vap} was arrived at by the assumption of a heat of intermolecular vibrations for every pair of molecules. U_{vap} and U_σ are energies and σ_m is a free energy. The relatively slow measurement of σ_m gives an interesting possibility to observe directly a free energy.

We try to rationalize this effect with the following hypothetical assumptions: The intermolecular interaction is constant during the transfer from the bulk to the surface. We assume that this interaction at the surface layer exists by a weak intermolecular potential with vapour molecules near to every surface molecule. It is often discussed that the first vapour layer at a surface has a larger density as a consequence of interaction with the surface molecules. This density could decrease from the surface layer of the first vapour layer to the others. The heat content induced by an medium intermolecular potential does not depend on the size of the potential. Its first vibration level has to be smaller than RT. We then assume that the potential between the surface layer to the first neighbours in the vapour is smaller compared to the potential of liquid molecules.

Could we also assume that the first surface layer has an intermolecular heat content as a consequence of the interaction with the first vapour layer? May we assume that the molecules in this first vapour layer accept an intermolecular movement with 3RT/2? The thermal energy to excite this first vapour layer would be induced at isothermic conditions by the thermostate, and not necessarily by the free energy σ_M under isothermic conditions.

Therefore, the free energy for the surface formation for $T/T_K < 0.9$ follows from Eqs. (7), (8), (16), and (17):

$$\begin{aligned}\sigma_m &= U_\sigma - [(Z - X)\ f/2]3RT/2\\ &= [(Z - X)3R\ f/4][T_K - T] = 2.14R[T_K - T] \qquad (18)\end{aligned}$$

and

$$\begin{aligned}U_\sigma &= [(Z - X)fR3/4][T + T_K - T]\\ &= [(Z - X)fR3/4T_K] = 2.14\,RT_K \qquad (19)\end{aligned}$$

Small deviations from 2.14 are expected in the case of small variations from the averaged value of (Z−X) f = 2.85. Could this be considered by an apparent coordination number in the first vapour layer larger than 9?

The T dependence of U_{vap} becomes non-linear by the factor (1–2 x_F) for $T > T_B$. However, σ_m is not T-linear just below T_K (in the literature 6 °C) and U_σ is not temperature constant in the region just below $T > 0.9\ T_K$. Both U_{vap} and U_σ decrease to zero above $T/T_K = 0.9$. The decrease to zero starts for U_σ a little later compared with U_{vap}. The increase of the vapour density ρ_{liq} near T_K increases X to Z and (Z−X) becomes zero at T_K. A possible hypothesis to understand that σ_M and U_σ decrease at a somewhat higher temperatures in comparison to U_{vap} could be that the factor $V_m{}^{2/3}$ contains already the $(1-x_F)$ effect at temperatures near T_K.

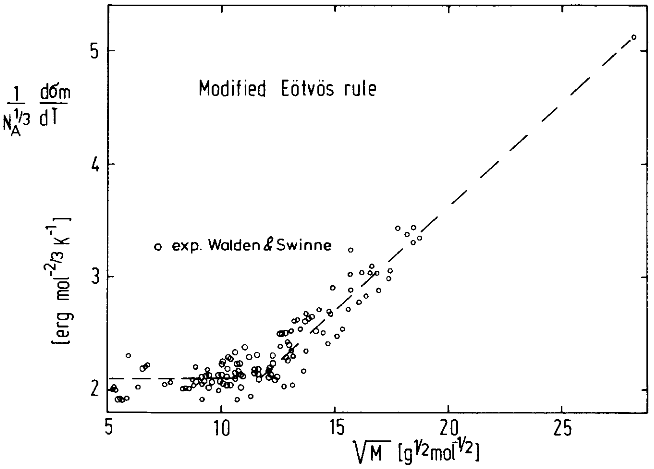

Fig. 9 The T-dependence of the surface tension $d\sigma_m/N_A{}^{1/3}dT'$ including molecules with larger molecular mass M

Surface energy in the presence of H-bonds

Liquids with H-bonds do not belong to the group of simple liquids. Their U_σ in broad temperature ranges are not independent of T [20–24]. At low temperatures, alcohols with one OH group have a region in which U_σ is T constant and very similar to the corresponding alkanes with the same number of carbon atoms. If $T/T_K > 0.65$, U_σ increases with T nearly linearly [20–24]:

$$\begin{aligned}U_\sigma(\text{alcohols}) &= U_\sigma(C_nH_{n+2})\\ &\quad + O_F U_{OH} \quad \text{for} \quad T/T_K > 0.65 \qquad (20)\end{aligned}$$

where $U_\sigma(C_nH_{n+2})$ = surface energy of the hydrophobic parts of the alcohols, U_{OH} = surface energy of OH groups if they are not H-bonded, O_F = content of open H-bonds (determined with IR overtone spectroscopy [20, 24],

O_F of simple alcohols can be neglected for $T/TK < 0.65$ [20, 24]. U_σ of all alcohols have a maximum at $T/T_K = 0.9$ and reach zero at T_K [20–24]. U_σ of water with two OH already starts to increase at $T/T_K > 0.5$. [24].

Surface tension for larger molecules

The T constancy of $d\sigma'/dT$ for larger molecules was discussed by Walden and Swinne [25].Today we know that dispersion energies are proportional to $M^{1/2}$ (M = molecular weight). Therefore, we can modify the rule of Walden and Swinne (Fig. 9):

$$d\sigma'/dT = -2.1(\text{erg}\cdot\text{mol}^{-2/3}\text{K}^{-1}) \text{ for } M < 130$$

$$\begin{aligned}d\sigma'/dT &= -(2.1 + 0.138(M^{1/2} - 11.5)) \qquad (21)\\ &\quad \times (\text{erg}\cdot\text{mol}^{-2/3}\text{K}^{-1}) \text{ for } M > 130\end{aligned}$$

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