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True molar surface energy and alignment of surface molecules

R. Thomas Myers

Department of Chemistry, Kent State University, Kent, OH 44242, USA

Abstract

By use of data for surface tension, for the first time a method is presented for calculating true molar surface properties of liquids: free energy, entropy, and enthalpy. These new data allow full comparison with other molar quantities, such as enthalpy and entropy of vaporization. All data are at the normal boiling point. There are differences in behavior between various classes of nonpolar compounds. Rare gases and tetrahydrides of Group 14 form a separate category. The results agree with the experimental findings that water and alcohol molecules are aligned with the –OH groups attached to the surface. The data indicate that hydrogen peroxide and 1,2-ethanediol also have one –OH group directed toward the surface and one directed out toward the vapor phase. Small straight-chain amines have some structure at the surface, but the larger ones behave like the corresponding alkanes. Very polar compounds, such as nitriles, nitro compounds, and aldehydes, have little or no increased degree of order of molecules at the surface. Except for hydrogen-bonded compounds, molecules at the surface have surroundings similar to those in the bulk liquid.
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1. Introduction

In 1886 Baron Roland von Eötvös [1] proposed the concept of molar surface energy, defined as follows, where E_m is the molar surface free energy, γ is the surface tension, and V_m is the molar volume:

$$E_m = \gamma (V_m)^{2/3}.$$

However, this equation is incorrect, for two reasons. The first is that the molar surface energy is not the surface energy of one mole of bulk liquid, but rather the energy involved in moving one mole of substance to the surface. The second error is that the dimensions of E_m are incorrect. This was pointed out by Adamson [2], who said: "...it would appear that its dimensions are energy per mole$^{2/3}$." Of course the correct dimensions must be energy per mole.

Even though erroneous, the Eötvös equation has been of use. It is not productive to survey the entire literature. A good summary was given by Harkins [3]. For example, he deduced that alcohol molecules are standing on end, with the polar end toward the liquid phase. He gave no data, or conclusions, for water. Good [4] gave a statistical treatment of nonpolar and polar compounds, based on his view of molar surface entropy. He too concluded that alcohols (except tertiary alcohols) and water are oriented. But he also concluded that surface molecules of aldehydes, nitro compounds, and nitriles are oriented, in the latter case with the CN group away from the surface.

Shen and co-workers [5,6] and also Richmond and co-workers [7,8] have shown experimentally that water molecules are bonded at one hydrogen atom to the surface, with an OH group extending out toward the vapor phase. Shen and co-workers have also shown experimentally that linear alcohols are also oriented [9] at the vapor–liquid interface, with the –OH group toward the surface, and the alkyl group oriented toward the vapor phase.

2. Derivation of equations

Let us assume for the time being that the area of a molecule on the surface is the same as that in the liquid. To calculate the latter, consider a cube within the liquid which contains one mole of substance. Let n be the number of molecules along one edge of the cube, measured in cm. Then $n^3 = N_A$, where N_A is the Avogadro constant. The number of molecules in one face is equal to $N_A^{2/3}$. The area per mole-

E-mail address: rtmyers@aol.com.

cule is as follows:

$$\frac{A}{n_A} = \frac{V_m^{2/3}}{N_A^{2/3}} \ cm^2/molecule.$$

The area per mole follows from this result:

$$A_m = \frac{V_m^{2/3}}{N_A^{2/3}} N_A = V_m^{2/3} N_A^{1/3} \ cm^2/mol.$$

Multiplication by the surface tension gives energy per mole. Using appropriate constants, the molar free surface energy is given by the following equation, in which the units of γ are ergs/cm^2 or mJ/m^2:

$$\Delta G_s = 0.00845 V_m^{2/3} \gamma \ kJ/mol.$$

Thus the molar surface free energy is proportional to $V_m^{2/3}$, but the proportionality constant is not as simple as Eötvös proposed. The molar surface entropy is obtained from the slope of the graph of surface tension vs temperature.

$$\Delta S = -8.45 V_m^{2/3} \left(\frac{-d\gamma}{dT} \right)_P \ J/K/mol.$$

In their treatment of surface tension Prigogine and Saraga [10] assumed that there was a small space between the surface molecules. If true, my calculation for surface area will be a little low, perhaps 10%. This will make no difference in the conclusions which are drawn. In addition, there are classes of molecules, such as alcohols, for which the surface area is probably less than the area in the bulk liquid. This will become clear in the discussion of the results for such compounds.

3. Results and discussion

The source of most of the surface tension data is the comprehensive summary by Jasper [11]. The sources of other surface tension data are indicated in the tables of data. All calculations are at the normal boiling points of the liquids,

which provides a comparison at corresponding states, at least in the classical sense.

In addition to boiling point T_b (K), each table lists the following useful quantities: molar surface free energy, ΔG_s^b; molar surface entropy, ΔS_s^b; molar surface enthalpy, ΔH_s^b; the difference between the Trouton constant (molar entropy of vaporization), ΔS_v^b, and the surface entropy, $\Delta S_{vs}^b = \Delta S_v^b - S\Delta_s^b$; and the ratio of molar surface internal energy to molar internal energy of vaporization, ΔE_r^b. Since there is a very small volume change on moving molecules to the surface, the internal energy change, ΔE_s^b, is essentially equal to the enthalpy change. The ratio gives the energy to move molecules to the surface, as compared to the energy needed to separate the molecules entirely into the vapor.

3.1. Rare gases

The logical beginning, Table 1, gives data for the simplest of substances, the rare gases. (Helium is included in order to demonstrate its unusual behavior.) There is a steady increase in ΔG_s^b and ΔH_s^b as atomic weight increases. On the other hand, the molar surface entropy, ΔS_s^b, is virtually constant, 20 J/K/mol. The internal energy ratio, ΔE_r^b, is also constant, close to 0.50. The constancy of these values indicates that the environment of the surface molecules is similar to the bulk liquid, except that they have fewer neighbors. In addition, it takes about half as much energy to move a molecule to the surface as it does to separate it entirely from its neighbors. This makes sense, because surface molecules have lost approximately half of their near neighbors.

The molecules which actually evaporate are surface molecules. However, these are replaced immediately with molecules from the bulk liquid. This process of replacement requires energy and also involves an entropy change. Therefore ΔH_v^b and ΔE_v^b are energies needed to move molecules from the bulk liquid to the gaseous state. This is also true of the entropy change, ΔS_v^b. Therefore the difference between the Trouton constant and the molar surface entropy change represents the entropy change in moving molecules

Table 1
Surface thermodynamic data: rare gases and group 14 tetrahydrides

Substance	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
He[a]	4.22	0.0174	6.94	0.0467	0.083	13	0.97
Ne[b]	27.07	0.263	18.2	0.754	0.171	46.1	0.500
Ar	87.4	0.986	19.6	2.70	6.43	54.0	0.473
Kr	121.33	1.37$_7$	18.7	3.61$_7$	9.08	56.1	0.450
Xe	166.2	1.88$_7$	19.7	5.15$_5$	12.62	56.3	0.459
CH$_4$[c]	111.6	1.149	19.66	3.343	8.19	53.7	0.460
SiH$_4$[d]	161.3	1.78	21	5.2	12.52	57	0.470
GeH$_4$[d]	184.6	2.21	15	5.0	14.06	61	0.40
GeH$_4$[d]	184.6	2.21	(20)	5.9	14.06	(56)	(0.47)
SnH$_4$[d]	221	2.80	31	9.60	18.6	53	0.57
SnH$_4$[d]	221	2.80	(20)	(7.20)	18.6	(64)	(0.43)

[a] Ref. [16].
[b] Ref. [17].
[c] Ref. [18].
[d] Ref. [19].

from the surface into the gaseous state. If this difference is high, then the molecules on the surface have a higher degree of order than the molecules in the bulk liquid. For most "normal" liquids this is on the order of 55–65 J/K/mol. A distinctly higher difference indicates increased ordering of surface molecules.

The group 14 tetrahydrides, Table 1, behave very similarly, although much of the data are not of good quality. In two cases I have made another calculation, setting ΔS_s^b equal to 20. This produces very consistent results for the internal energy ratio, ΔE_r^b. (The surface tensions of the group 14 tetrahydrides need to be remeasured.)

3.2. Group 14 tetrahalides (Table 2)

Data are available for only one fluoride, CF_4, with a higher value of ΔS_s^b, 25 J/K/mol, and consequently a high internal energy ratio. The chlorides are consistently slightly lower. However, the entropy change for all compounds is higher than that for the previous two groups, and the internal energy ratio is consistently lower. A difference is expected, as shown by Myers [12] in his calculations of the normal boiling points of these substances. In that study the rare gases and Group 14 tetrahydrides fall on one line, and the tetrahalides on another.

3.3. Diatomic molecules (Table 3)

The surface tension data for H_2 are not of good quality, so the high value for the internal energy ratio, ΔE_r^b, is probably in error. The other elements give fairly consistent results. The value of ΔS_s^b (and consequently ΔH_s^b) is no doubt too low for both F_2 and I_2, and the surface tension for these two elements needs to be redetermined. The small diatomic substances behave much like the Group 14 tetrahydrides. This is expected, because an analysis of data according to the Myers procedure puts them on a line very close to these substances.

The molar surface entropy and enthalpy for HF are extremely low, and the entropy of vaporization of surface molecules is very high. This indicates a very high degree of order for the surface molecules. Perhaps they exist as six-membered rings. The Trouton constant is high, which of course indicates association in the liquid. The data indicate no association (hydrogen bonding) of the other group 17 hydrides. This agrees with the experimental results of Andreani et al. [13].

3.4. Straight-chain alkanes (Table 4)

The results for these "linear" molecules are very similar to those for the Group 14 tetrahalides, with ΔE_r^b near 0.43,

Table 2
Surface thermodynamic properties: group 14 tetrahalides and SF_6

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (KJ/mol)
CF_4[a]	145.5	1.416	25.1	5.07	12.33	59.6	0.456
CF_4[a]	145.5		(22)	(4.62)	12.33	(63)	(0.415)
CCl_4[b]	350	3.75$_7$	22.8	11.74	29.82	62.4	0.436
$SiCl_4$[b]	331	3.19$_5$	22.5	10.66	29.35	66.2	0.401
$GeCl_4$[b]	357	3.56	24.2	12.19	31.78	64.8	0.423
$SnCl_4$[b]	387	3.76	23.6	12.92	34.18	64.7	0.417

[a] Ref. [19].
[b] Ref. [20].

Table 3
Surface thermodynamic properties: diatomic molecules

Substance	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
H_2	20.36	0.150	13.25	0.420	0.908	31.4	0.563
N_2	77.35	0.800	20.4	2.38	5.59	51.9	0.481
O_2	90.19	1.029	20.1	2.84	6.82	55.5	0.468
F_2	85.01	1.08	12.0	2.10	6.62	65.8	0.355
Cl_2	238.5	2.83$_7$	20.4	7.69	20.41	65.2	0.317
Br_2	331.9	4.18$_6$	21.8	11.43	29.95	68.4	0.420
I_2[a]	457.5	6.43	17	14.1	44.57	74	0.346
I_2[a]	457.5	6.43	(20)	(15.5)	44.57	(71)	(0.38)
HF	292.7	0.568	5.03	2.042	28.7[b]	93.1	0.0764
HCl[c,d]	188.1	1.917	15.5	4.84	16.15	70.4	0.332
HBr	206.1	2.44	18.8	6.31$_5$	17.61	66.6	0.397
HI[e]	237.4	2.89	20.6	7.79	19.76	62.6	0.438

[a] Ref. [21].
[b] Vaporizing to monomer.
[c] Ref. [22]
[d] Ref. [23].
[e] Ref. [24].

Table 4
Surface thermodynamic properties: straight-chain alkanes

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
C_2H_6	184.5	1.944	20.2	5.68	14.69	59.6	0.432
C_3H_8[a]	231.08	2.330	22.0	7.42	19.04	60.4	0.433
n-C_4H_{10}	272.65	2.663	21.5	8.51_5	22.44	60.8	0.422
n-C_5H_{12}	309.21	2.91	22.7	9.92	25.79	60.7	0.427
n-C_6H_{14}	341.88	3.07	23.3	11.05	28.85	61.4	0.425
n-C_7H_{16}	371.6	3.145	24.8	12.35	31.77	60.3	0.433

[a] Ref. [25].

Table 5
Surface thermodynamic properties: rodlike molecules

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
C_2H_2[a]	188.4	2.00	19.6	5.70	17.88	75.3	0.349
$CH_3C{\equiv}CH$[b]	249.8	2.67_5	19.9	7.64_5	23.3	73.4	0.360
$MeC{\equiv}CMe$[b]	300.2	2.56_5	17.6	7.86	26.9	72.0	0.322
$MeC{\equiv}CMe$[b]	300.2	2.56_5	(20)	(8.57)	26.9	(70)	(0.35)

[a] Ref. [26].
[b] Ref. [27].

and ΔS_s^b near 20, although they increase slightly as chain length increases. Even so, these liquids behave very similarly to all the other nonpolar substances studied so far. This indicates that the environment of molecules in the surface is similar to that of the molecules in the bulk liquid. A molecular dynamics simulation by Kayamata and Yamamoto [14] shows that the molecules on the surface are disordered and entangled, at temperatures well above the freezing point.

3.5. Rod-like molecules (Table 5)

Data are available for only three substances, and no doubt the slope of the surface tension graph for 2-butyne is too low. Inserting a value of 20 J/K/mol for ΔS_s^b gives a very consistent set of data for all three. The reason for the low values of ΔE_r^b is not clear. Perhaps the molecules tend to lie parallel to each other in the liquid, and also lie nearly flat on the surface. Such a change will require less energy than for the other substances and will explain the normal value for ΔS_s^b and the slightly elevated value for the entropy of vaporization of the surface molecules, above 70 J/K/mol. It would be very instructive to have good surface tension data for similar molecules, such as 1,3-pentadiyne and 2,4-hexadiyne.

3.6. Alcohols (Table 6)

Here we see a considerable deviation from the behavior of nonpolar molecules. ΔS_s^b and ΔE_r^b are much lower than for all the preceding substances, and the values for ΔE_r^b are not constant, but increase greatly as chain length increases, more than doubling from methanol to 1-hexanol. The very low values for ΔS_s^b indicate a great deal of structure for the surface molecules, as compared with the molecules in the bulk liquid, which would be true if they were upright, with the –OH groups attached to the surface. This agrees with the experimental results of Chen. The very low internal energy ratio shows that very few hydrogen bonds are broken as molecules move to the surface. This agrees with the previous calculations.

If the molecules are on end, then the value used so far for the area of alcohol molecules in the surface is in error. To correct for this I assume that the area of all the alcohols (except 2-methyl-2-propanol) is nearly the same as for CH_3OH and make a new set of calculations in the lower part of the table. The values for ΔS_s^b and ΔE_r^b are now almost constant, as with all the preceding compounds. The low value of ΔE_r^b shows that very few hydrogen bonds are broken as the molecules are moved from the bulk liquid to the surface. The very high value for the entropy difference (entropy of vaporization of surface molecules), nearly 100 J/K/mol, is due to the great degree of order of the surface molecules, as compared with the molecules in the vapor. In fact, low values of ΔS_s^b, high values for ΔS_{vs}^b, and low values for ΔE_r^b are decisive for indicating a high degree of orientation of surface molecules. (The Trouton constant is elevated, indicating some degree of structure in the liquid.)

The straight-chain alcohols are unique, in that the surface molecules are packed tightly together through their entire length. Therefore the London forces change very little in moving them from the liquid. In fact, the surprise is not that little energy is needed to form the surface layer, but that so much energy is needed.

The low value for surface entropy, high entropy difference, and low internal energy ratio for 2-methyl-2-propanol show that it too is hydrogen-bonded to the surface, contrary to the conclusion of Good [4].

Table 6
Surface thermodynamic properties: alcohols

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
CH_3OH	337.9	1.966	8.00	4.67	35.21	96.2	0.144
C_2H_5OH	351.5	2.301	10.9	6.13	38.56	98.8	0.172
$n\text{-}C_3H_7OH$[a]	370.5	2.71	14.7	8.15	41.44	97.1	0.212
$n\text{-}C_4H_9OH$	390.3	3.073	16.8	9.62	43.29	94.1	0.240
$n\text{-}C_5H_{11}OH$	411.1	3.228	18.2	10.72	44.36	89.7	0.262
$n\text{-}C_6H_{13}OH$	430.5	3.462	21.0	12.51	44.50	82.4	0.306
$(CH_3)_3OH$[b]	355.4	2.766	16.08	8.48	39.07	93.9	0.235
(Recalculated, assuming all surface areas are same as for CH_3OH)							
CH_3OH	337.9	1.966	8.00	4.67	35.21	96.2	0.144
C_2H_5OH	351.5	(1.81)	(8.57)	(4.82)	38.56	(101.1)	(0.135)
$n\text{-}C_3H_7OH$	370.5	(1.76)	(9.53)	(5.29)	41.44	(103.3)	(0.138)
$n\text{-}C_4H_9OH$	390.3	(1.72)	(9.39)	(5.39)	43.29	(101.5)	(0.135)
$n\text{-}C_5H_{11}OH$	411.1	(1.60)	(9.03)	(5.31)	44.36	(98.9)	(0.130)
$n\text{-}C_6H_{13}OH$	430.5	(1.54)	(9.31)	(5.54)	44.50	(94.1)	(0.135)

[a] Ref. [28].
[b] Ref. [29].

Table 7
Surface thermodynamic properties: hydrogen compounds of groups 15 and 16

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
H_2O	373.15	3.518	11.5	7.82	40.66	97.5	0.208
H_2O_2	423.3	4.15	11.6	9.04	47.6	101	0.206
$(CH_2OH)_2$	470.5	4.38$_5$	11.9	10.01	50.46	95.3	0.215
H_2S[a,b]	212.8	2.60	21	7.07	18.68	67	0.418
H_2Se	232.1	2.84	15	6.28	19.9	70	0.35
H_2Se	232.1	2.84	(20)	(7.48)	19.9	(66)	(0.42)
H_2Te	271.0	3.62	32	12.3	23.64	55	0.575
H_2Te	271.0	3.62	(20)	(9.04)	23.64	67	(0.42)
NH_3	239.8	2.426	19.8	7.174	23.31	77.4	0.336
N_2H_4[c]	386.7	4.07	21.6	12.42	41.8	86.5	0.322
$(CH_2NH_2)_2$	390.1	4.23	20.8	12.34	37.98	76.6	0.355

[a] Ref. [20].
[b] Ref. [30].
[c] Ref. [31].

3.7. Hydrogen compounds of groups 15 and 16 (Table 7)

As expected, the values for H_2O, H_2O_2, and 1,2-ethane-diol deviate considerably from those of "normal" liquids, and the pertinent thermodynamic constants, ΔS_s^b, ΔS_{vs}^b, and ΔE_r^b are almost as low as for the alcohols, and, more importantly, are almost identical for all three compounds. We conclude that the situation of surface molecules is the same. The thermodynamic data are close to those of the alcohols and water. Therefore we assume that one –OH group is pointed toward the interior molecules. This will be considered later.

We might expect the corresponding nitrogen compounds to show similar behavior. However, they behave almost normally, in that the molar surface entropy is close to 20 J/K/mol. Yet ΔS_{vs}^b is slightly elevated. Therefore the surface molecules are oriented to some extent. One concludes that the molecules in the bulk liquid are also slightly ordered, but there is little change in moving molecules to the surface.

The slopes of the surface tension curves for H_2Se and H_2Te are surely in error. If one assumes ΔS_s^b of 20 J/K/mol then all the calculated values are nearly normal for these almost nonpolar liquids. The surface tension of these substances needs to be redetermined. It would be very instructive to have surface tension data for PH_3, AsH_3, and SbH_3, to see if they behave like the group 14 tetrahydrides.

3.8. Straight-chain amines (Table 8)

One might expect these primary amines to form hydrogen bonds, and therefore have a low ΔS_s^b. The data show mixed behavior. ΔS_s^b and ΔE_r^b are low for the first couple of members, but increase steadily. ΔS_{vs}^b starts high and then decreases as the chain length increases. When $C_6H_{13}NH_2$ is reached, the results are virtually the same as for $n\text{-}C_7H_{16}$, indicating "normal" behavior. One concludes that there is a small amount of hydrogen bonding for the first members of the series, but this virtually disappears when $C_6H_{13}NH_2$ is reached.

Table 8
Surface thermodynamic properties: amines

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
CH_3NH_2	266.82	2.54_3	15.9	6.78	25.60	80.0	0.290
$C_2H_5NH_2$	289.7	2.80	18.9	8.27	27.6	76.4	0.328
$n\text{-}C_3H_7NH_2$	320.37	3.12	20.4	9.67	29.55	71.8	0.360
$n\text{-}C_4H_9NH_2$	350.15	3.35	21.3	10.80	31.81	69.5	0.374
$n\text{-}C_5H_{11}NH_2$	377.4	3.56_5	22.0	11.87	34.02	68.1	0.384
$n\text{-}C_6H_{13}NH_2$	405.9	3.55_5	24.5	13.48	36.54	65.5	0.406

Table 9
Surface thermodynamic properties: aldehydes, nitro compounds, nitriles

Compound	T_b (K)	ΔG_s^b (kJ/mol)	ΔS_s^b (J/K/mol)	ΔH_s^b (kJ/mol)	ΔH_v^b (kJ/mol)	ΔS_{vs}^b (J/K/mol)	ΔE_r^b (kJ/mol)
CH_3CHO	293.4	2.633	16.9	7.60	25.76	70.9	0.330
CH_3CH_2CHO	347.93	4.74	16.5	10.48	31.5	74.0	0.366
CH_3NO_2	374.4	3.068	21.6	11.16	33.99	69.5	0.361
$C_2H_5NO_2$	387.22	3.32	19.5	10.77	36.2	78.6	0.330
$n\text{-}C_3H_7NO_2$	404.33	3.52	19.3	11.32	38.47	75.8	0.322
$n\text{-}C_4H_9NO_2$	425.92	3.56	20.6	12.3	40.6	74.7	0.333
CH_3CN	354.80	2.70	15.9	8.34	29.75	68.0	0.331
C_2H_5CN	371.3	2.84	18.5	9.71	31.81	67.2	0.338
$n\text{-}C_3H_7CN$	390.8	3.14	18.8	10.4	33.68	67.4	0.344
$n\text{-}C_4H_9CN$	414.4	3.31	19.3	11.32	35.9	67.7	0.349

3.9. Very polar molecules (Table 9)

The only deviation is the low value of ΔS_s^b for ethanenitrile and the two aldehydes. (Unfortunately there is a great lack of data for the latter group.) The other indicators show normal behavior for these liquids. This is contrary to the deduction of Duncan–Hewitt, who calculated a high degree of order for surface molecules of ethanenitrile, with the dipoles oriented 21° from the plane of the surface [15]. We need more surface tension data and more accurate data for these types of very polar molecules, which do not engage in hydrogen bonding.

4. Summary

For the first time, true molar values have been calculated for surface thermodynamic functions: free energy, entropy, and enthalpy. This allows comparison with other molar thermodynamic quantities, such as enthalpy and entropy of vaporization, and can be combined with the latter data to make deductions as to surface structure. Calculations are made for several homologous series and groups of similar compounds, which permit important deductions to be made about the arrangement of surface molecules of liquids. The truly spherical molecules, the rare gases, form a separate grouping, and the group 14 tetrahydrides are in this same category, possibly because they are in free rotation at the boiling point. This agrees with the previous finding of Myers that the boiling points of these two classes of substances behave in a similar manner. A low value for the molar surface entropy, ΔS_s^b, shows that there is an increase in order in going from the bulk liquid to the surface. This is also indicated by a high value for the entropy of vaporization of surface molecules. Straight-chain alcohols are standing on end, with the OH group pointed toward the surface, so all have surface areas very close to that of CH_3OH. The situation is quite similar for H_2O, H_2O_2, and $(CH_2OH)_2$. The very high values for the Trouton constant (entropy of vaporization) of the hydroxy compounds indicates a fair degree of order (association) for the molecules in the liquid. This will be considered later. Some other classes of liquids show a high value for the entropy change in going from the bulk liquid to the vapor, even though the molar surface entropy is in the normal range. In this case we judge that there is some structure of molecules in the bulk liquid, which does not change significantly on moving them to the surface.

5. The cause for the high surface tension of water

It has been known for a long time that water has a very high surface tension. The usual explanation is that water is very polar and has high forces of attraction between the molecules. But the dipole moment of water has a medium value; many molecules are much more polar. The present work gives the reason for water's high surface tension. This can be seen from Table 10. The first column gives the values for the molar surface free energy of a few liquids which boil somewhat near room temperature. It is evident that the molar surface free energy of water is not at all high. This is the free energy involved in moving a mole of molecules to the surface. But surface tension is surface free energy per unit area. So we must divide the molar surface tension by the area of one mole of molecules (third column) in order to obtain the surface tension as usually measured. Water

Table 10
Contributions to surface tension of liquids

Compound	ΔG_s^b (J/mol)	V_b (cm^3/mol)	A_s^b (cm^2/mol) $\times 10^9$	ΔG_u^b (J/cm^2) $\times 10^7$	γ (mN/m)
H_2O	3518	18.79	0.597	58.9	58.9
H_2O_2	4151	26.2	0.745	55.7	55.7
CH_3OH	1966	42.7	1.023	19.05	19.04
C_2H_5OH	2300	61.24	1.312	17.5	17.5
n-C_3H_7OH	2811	81.75	1.59	17.7	17.7
n-C_4H_9OH	3073	102.1	1.84	16.7	16.65
$(CH_2OH)_2$	4385	63.38	1.35	32.6	32.65
NH_3	2426	24.98	0.722	33.6	33.60
n-C_6H_{14}	3073	140.9	2.29	13.4	13.43
n-C_7H_{16}	3145	163.5	2.52	12.5	12.45
CH_3CN	2703	57.4	1.26	21.5	21.50
C_2H_5CN	2840	78.6	1.55	18.3	18.30
n-C_3H_7CN	3140	99.3	1.81	17.3	17.31

ΔG_s^b = molar surface free energy; V_b = molar volume; A_m^b = molar surface area; ΔG_u^b = surface free energy per unit area = surface tension = γ (measured surface tension, γ included only to check my calculations).

Table 11
Entropy changes during vaporization of liquids

Substance	T_b (K)	ΔH_v^b (kJ/mol)	ΔS_v^b (J/mol/K)	ΔS_s^b (J/mol/K)	ΔS_{sv}^b (J/mol/K)
H_2O	373.15	40.66	109.0	11.53	97.5
H_2O_2	423.3	47.6	112	11.5	100
CH_3OH	337.9	35.21	104.2	8.00	96.2
C_2H_5OH	351.5	38.56	109.7	10.9	98.8
n-C_3H_7OH	370.5	41.44	111.8	12.37	99.5
n-C_4H_9OH	390.3	43.29	110.9	13.1	97.8
$(CH_2OH)_2$	470.5	50.46	107.2	11.95	95.25
n-C_6H_{14}	341.9	28.85	84.38	23.3	61.1
n-C_7H_{16}	371.6	31.77	85.50	24.8	60.7
NH_3	239.8	23.31	97.21	19.8	77.4
CH_3CN	354.8	29.75	83.9	15.9	68.0
C_2H_5CN	371.3	31.81	85.7	18.5	67.2
n-C_3H_7CN	390.8	33.68	86.2	18.8	67.4
CH_3NO_2	374.4	33.99	91.0	21.6	69.4
$C_2H_5NO_2$	387.2	36.2	93.5	19.5	74.0
CH_3CHO	293.4	25.76	87.8	16.9	70.9
C_2H_5CHO	347.9	31.5	90.5	16.5	74.0

ΔH_v^b = enthalpy of vaporization (interior molecules); ΔS_v^b = entropy of vaporization (interior molecules); ΔS_s^b = molar surface entropy (interior to surface); ΔS_{sv}^b = entropy of vaporization (surface molecules).

has a very low molar volume, hence a very low area for one mol of molecules, and hence a very high surface tension. It is clear that the high surface tension for water is due to the fact that it consists of very small molecules which are tightly packed. Hydrogen peroxide has a slightly higher molar surface free energy, but also a slightly higher molar surface area, so its surface tension is very close to that of water. 1,2-Ethanediol has a higher molar surface free energy, but a much higher molar area, so it has a much lower surface tension. In contrast, ammonia, which consists of small molecules, has a very low surface tension, because the molecules are not densely packed, mostly due to a much lower attraction between the molecules. The effect of size of molecules on surface tension can be seen by comparing the values for the normal alkanes and for the nitriles. This can be seen most clearly in comparing water and butanenitrile. The latter has about the same molar surface free energy, but much

higher surface area per molecule. In Table 6 a calculation was made assuming all alcohols had the same surface area per molecule. If this were true then the surface tension would be proportional to the molar surface free energy. Instead it decreases as molecules get larger. This suggests that only a fraction of the alcohol molecules are attached to the surface by a hydrogen bond.

6. Details of the vaporization process

It is now clear that evaporation of a liquid occurs in two phases. First the molecules in the bulk liquid move to the surface, and then these surface molecules escape into the vapor phase. The usual value for the enthalpy of vaporization is the amount of heat necessary to move molecules from the interior of the liquid to the vapor phase. The present research

gives the molar entropy change for moving molecules from the interior to the surface. Therefore we can calculate the entropy change for evaporation of surface molecules, given the symbol ΔS_{vs}^b. Table 11 gives the data for the substances in Table 10. The first item of note is the very high entropy of vaporization of the surface molecules from the associated liquids. The values are all very close. This is due to the fact that the molecules are highly oriented, on end, sticking out from the surface, including hydrogen peroxide. The value for ammonia is slightly elevated, indicating some structure of surface molecules. Thus, from surface tension data one can determine if molecules on the surface are oriented. The surface entropies are low, because the molecules in the interior, somewhat oriented, are going to the surface, where they are highly oriented. Water and hydrogen peroxide, in the bulk liquid, are much more oriented than methanol.

The situation with "normal" liquids is quite different. Although almost entirely disordered in the bulk, they go to somewhat higher disorder on the surface, and thus to a much higher surface entropy. Consequently the entropy of vaporization of the surface molecules is much lower than that for the hydrogen-bonded liquids, which have highly oriented molecules on the surface.

Finally, it is clear that if we wish to understand the behavior of molecules on the surface of liquids, we need to obtain high-quality surface tension data for some liquids which have already been measured and also to obtain data for many new substances. It is also clear that this method of analysis provides a way to evaluate the quality of surface tension data, especially within a homologous series.

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