

## ABOUT "SURFACE GAS" of LIQUIDS And SOLIDS

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### Abstract

Many characteristics of fluids and solids it is possible to calculate, using notion about existence of "surface gas".

### Concept about surface gas of fluids and solids.

It helps to explain their many properties and to give the quantitative theory of these properties. Atoms or molecules, of which the solids or liquid consists, are capable to jump out of volume on a surface and freely enough to move on it, jumping from one potential hole in another, as a power barrier to such jumps small. If energy of activation of transition in surface gas large enough, the concentration of molecules in surface gas, accordingly, is small, and it is possible to consider it as ideal bivariate gas.

### Concentration of particles in surface gas.

Speed of transition of particles in surface gas:

$$V_1 = K_1 (C_0 - C) \quad (1),$$

where:  $C_0$  - surface concentration of particles of substance,  $1/\text{cm}^2$

$C$  - concentration of particles in surface gas.

Speed of condensation from surface gas in volume of substance:

$$V_2 = K_2 C \quad (2).$$

The balance is established quickly, since the process of condensation has no energy of activation:

$$V_1 = V_2 \quad (3).$$

(1) and (2) we shall substitute in (3) and we shall find:

$$C = \frac{K_1 C_0}{K_1 + K_2} \quad (4).$$

On the Arrhenius:

$$K_1 = K_1^0 e^{-\frac{E_1}{RT}}, K_2 = K_2^0, \text{ since } E_2=0 \quad (5),$$

where:  $E_1$  and  $E_2$  - energy of activation, accordingly, transition of a particle in surface gas and condensation in volume of substance, erg/mol.

(5) we shall substitute in (4) and at  $K_1^0 = K_2^0$  (particle same), we shall find:

$$C = \frac{C_0 e^{-\frac{E_1}{RT}}}{1 + e^{-\frac{E_1}{RT}}} \quad (6).$$

At  $E_1 \gg RT$  (6) will accept a kind:

$$C = C_0 e^{-\frac{E_1}{RT}} \quad (7).$$

Than closer to a condition fusing of a solid or boiling of a liquid, the below  $E_1$  and at  $E_1=0$  (6) will accept a kind:  $C=C_0/2$  that is obvious.

The energy of activation of carry of a particle in surface gas will be equal to the sum:

$$E_1 = Q - F \quad (8),$$

where:  $Q$  - energy necessary for break of connections with atoms of volume of substance at given temperature, cal/mol,

$F$  - specific free surface energy.

$Q_T$  we shall find from the following reasons. To break off connections in a liquid at given temperature, it needs to be heated up to temperature of boiling and to evaporate, then to cool of vapour up to initial temperature, but without condensation. To break off connections in a solid, it is necessary it to heat up to  $T_{mel}$  and melted. In the formed liquid of connections are so weakened, that they can be neglected as a first approximation and molecule or atoms to consider practically free. The formed liquid should be cooled up to initial temperature without crystallization in a solid. Thus it is necessary to notice, that the free specific surface energy is automatically taken into account also. Therefore as a first approximation (without cooling gas or liquid from temperature of phase transition up to initial temperature). For concentration of particles in surface gas such simplification is allowable:

$$Q_T = c_p M \Delta T + \lambda_0 \text{ cal/mol} \quad (9),$$

where:  $c_p$  - thermal capacity, cal/g-deg,

$M$  - molecular weight, g,

$\Delta T = T_{ph} - T$ , where  $T_{ph}$  - temperature of phase transformation, deg,

$\lambda_0$  - specific heat melting or evaporation, cal/mol.

Formally, we can attribute energy on (9) to one atom. Thus we shall take into account, that at an output in surface gas the atom has one degree of freedom, third of this energy therefore suffices, it and will be energy of activation:

$$E_1 = \frac{Q_T}{3} = 1/3 (c_p M \Delta T + \lambda_0) \quad (10).$$

Having substituted (10) in (7), we shall find:

$$C = C_0 \exp \left[ -\frac{1/3 (c_p M \Delta T + \lambda_0)}{RT} \right] \quad (11).$$

Expression (11) fairly far from temperature of boiling or melting, near to them it is necessary (10) to substitute in (6):

$$C = \frac{C_0 \exp \left[ -\frac{1/3 (c_p M \Delta T + \lambda_0)}{RT} \right]}{1 + \exp \left[ -\frac{1/3 (c_p M \Delta T + \lambda_0)}{RT} \right]} \quad (12).$$

It is easy to show, that:

$$C_0 = \left( \frac{dN_0}{M} \right)^{2/3} \quad (13),$$

where:  $C_0$  - surface concentration of particles of substance,  $\text{cm}^{-2}$ ,

$d$  - density of substance,  $\text{g/cm}^3$ ,

$N_0$  - Avogadro constant,  $\text{mol}^{-1}$ ,

$M$  - molecular weight, g.

### Surface tension.

Energy on the equation (10), come on one particle:

$$Q_0 = \frac{1}{3N_0} (c_p M \Delta T + \lambda_0) \quad (14).$$

Having multiplied number of particles on (13) on energy come on one particle on (14), we shall receive:

$$\sigma = \frac{4.2 \cdot 10^7 M}{3\sqrt[3]{N_0}} (c_p \Delta T + \lambda_0) \left( \frac{d}{M} \right)^{2/3} \text{ erg/cm}^2 \quad (15).$$

Expression (15) is possible to treat, how surface tension without account of surface gas, which does not bring in contribution in  $\sigma$ .

In the table 1 the calculated and experimental values of a surface tension for water and mercury are submitted at  $20^\circ\text{C}$  in  $\text{erg/cm}^2$ .

Table 1.

Substance	Is calculated on (15)	Tabulated value
Water	70	72.75
Mercury	444	472

For flying liquids to neglect concentration of atoms in surface gas it is impossible, since at change of a surface these atoms do not render influence, therefore results of account on (15) it appear overestimated. For example, for ethyl alcohol the calculated value on (15) 56.7 erg/cm<sup>2</sup>, and experimental 22.8 erg/cm<sup>2</sup>. It is obvious, that the effective concentration of particles on a surface influencing a surface tension, will be:

$$C_{eff} = C_0 - C \quad (18.1.16.),$$

where  $C$  is determined by expression (12). If it to substitute in (16) and to multiply by energy comes on one particle, we shall receive:

$$\sigma = \frac{4.2 \cdot 10^7 M}{3\sqrt[3]{N_0}} (c_p \Delta T + \lambda_0) \left(\frac{d}{M}\right)^{2/3} \left\{ 1 - \frac{\exp\left[-\frac{1/3(c_p M \Delta T + \lambda_0)}{RT}\right]}{1 + \exp\left[-\frac{1/3(c_p M \Delta T + \lambda_0)}{RT}\right]} \right\} \quad (17).$$

The known empirical expression, suitable for many liquids, looks so:

$$-\frac{d}{dT} \left[ \sigma \left(\frac{M}{d}\right)^{2/3} \right] \cong 2.12 \quad (18).$$

If to differentiate on temperature (15), as more simple, in comparison with adjusted (17), we shall receive the same result:

$$-\frac{d}{dT} \left[ \sigma \left(\frac{M}{d}\right)^{2/3} \right] = \frac{4.2 \cdot 10^7 c_p M}{3\sqrt[3]{N_0}} \cong 2.12 \quad (19).$$

### Evaporation heat.

Energy necessary for heating and evaporation for a liquid at temperature of boiling we shall find on a known ratio:

$$Q_{liq} = c_p^{liq} \Delta T_{liq} + \lambda_{ev} \quad (20),$$

where:  $c_p^{liq}$  - average thermal capacity of a liquid, cal/mol-deg,

$$\Delta T_{liq} = T_{boil} - T,$$

$\lambda_{tv}$  - evaporation heat at temperature of boiling, cal/mol.

Similarly for a solid:

$$Q_{sol} = c_p^{sol} \Delta T_1 + \lambda_{melt} + c_p^{liq} \Delta T_2 + \lambda_{ev} \quad (21),$$

где:  $c_p^{sol}$  - average thermal capacity of a solid, cal/mol-deg,

$$\Delta T_1 = T_{melt} - T,$$

$\lambda_{melt}$  - melting heat, cal/mol,

$$\Delta T_2 = T_{boil} - T_{melt}.$$

The formed gas as a result of processes (20) and (21) has superfluous energy:

$$Q_g = c_p^g \Delta T \quad (22),$$

where:  $c_p^g$  - average thermal capacity of gas, cal/mol,

$$\Delta T = T_{boil} - T.$$

If we shall take into account this circumstance, in result we shall receive for liquids:

$$\lambda_T^{liq} = (c_p^{liq} - c_p^g) \Delta T + \lambda_{ev} \quad (23)$$

and for solids:

$$\lambda_T^{sol} = c_p^{sol} \Delta T_1 + \lambda_{melt} + c_p^{liq} \Delta T_2 + \lambda_{ev} - c_p^g \Delta T \quad (24).$$

As thermal capacity of bodies depends on temperature, we have received approximate value evaporation heat. To have exact value, it is necessary to know experimental value of the expended integrated heat.

Comparison calculated on (23) and (24) and experimental values of evaporation heat of different substances at different temperatures is submitted in the table 2.

Table 2.

Substance	Temperature, °C	$\lambda$ tabular	$\lambda$ computed
CdCl <sub>2</sub>	568	41.2	41.1
Cs	28.7	18.82	19.9
FeCl <sub>3</sub>	304	16.5	16.6
H <sub>2</sub> O	0	10.77	10.80
H <sub>2</sub> O	25	10.51	10.53
H <sub>2</sub> Se	-65.7	5.34	5.61
Hg	-38.9	15.20	15.73
Hg	25	14.54	15.43
KBr	735	48.9	51.1

### Saturated vapor pressure.

It is obvious; that values determined on the equations (23) and (24) will be energies of activation of transition of particles from surface gas in a gas phase, accordingly for a liquid and solid. Therefore we shall arrange one more check of validity of the equation (23) for further use. We use tabular data for water (evaporation heat at 100°C 9717 cal/mol,  $c_p^{liq} - c_p^g = 9.971$  cal/mol-deg, 1 cal = 4.1858 joules). Results of comparison of account on (23) with the tabular data at different temperatures are submitted in the table 3.

Table 3.

Temperature, °C	Experimental evaporation heat, joule/g	The calculated evaporation heat, joule/g
0	2501	2492
5	2489	2480
10	2477	2469
15	2465	2457
20	2454	2446
25	2442	2434
30	2430	2423
40	2406	2399
50	2382	2376
100	2257	2260

The data of table 3. show that the equation (23.) is acceptable to rough accounts.

Let's consider that the surface gas is ideal bivariate gas and submits to the known equation of a gas condition:

$$PV = nRT \quad (25),$$

Number moles in surface gas:

$$n = \frac{1000C^{3/2}}{N_0} \quad (26).$$

In (25) let's substitute (26) and value gas constant  $R$ :

$$P = \frac{82TC^{3/2}}{N_0} \quad (27),$$

where the pressure is expressed in atmospheres. If in (27) let's substitute (12) and (13) with the account (23), we shall receive finally:

$$P = \frac{82Td}{M} \cdot \frac{\exp\left[-\frac{3\lambda_r^{liq}}{2RT}\right]}{1 + \exp\left[-\frac{3\lambda_r^{liq}}{2RT}\right]} \quad (28).$$

For solids it is necessary to take into account not (23), and (24).

References:

<http://www.new-physics.narod.ru>