NEW TEMPERATURE DEPENDENCE OF VAPOR PRESSURE (REFERENCE DATA)

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Calculations of material and thermal balances of chemical-technological processes are the basis for the development of chemical equipment and technological processes optimal modes.

At the same time, information on the density, viscosity, mass and heat transfer, surface tension, diffusion, critical parameters, heat of change in the aggregate state (heats of evaporation, sublimation, melting) of individual substances and their mixtures is required.

The saturated vapor pressure, being a specific natural property of the substance, is related to its other properties. Therefore, all the physical properties listed above are calculated using the dependence of the saturated vapor pressure on temperature.

At present, hundreds and thousands of different substances are used in the coal-chemical, by-product coking, metallurgical, petrochemical industries, as well as in basic organic synthesis, for the production of inorganic substances, dyes, plastics, medicines, etc. They are used within the continuous temperature range from close to absolute zero to thousands of degrees and pressure range from a deep vacuum to hundreds of MPa.

In connection with this, the development of a quantitative method to calculate the vapor pressure dependence within a wide range of temperatures and pressures is an actual interindustry problem.

The experimentally determined vapor pressures are always in a certain interval and are always discrete, that is why it is necessary to have an equation giving a continuous description of the vapor pressure dependence on temperature within the entire interval P_j^H– T. A set of equations which differ by structure is proposed, an absolute majority of which describe the vapor pressure using polynomials of different degrees. Among them the Antoine equation was found to be the most useful. Nevertheless, in the theoretical and practical analysis of chemical-technological processes, the Antoine equation must be specified by introducing additional parameters or by narrowing the range of substances and P_j^H–T interval. In this paper, we attempt to establish the dependence of the vapor pressure on temperature using the parameters of the intermolecular interaction potentials in the form of the energy of the system deviated from the equilibrium of the intermolecular attraction and repulsion forces and the self-energy of the molecules.

It is suggested to use the value b_j to estimate the energy barrier that a molecule must overcome in order to exceed the forces of intermolecular attraction and "escape" from the liquid phase to the gaseous one. Moreover, let us assume that the molecules are distributed symmetrically (for example, normally) or asymmetrically (according to Maxwell) relative to some average value m_j with dispersion s_j^2. Actually, the increase in temperature which

occurs due to an external or internal source of heat, increases the energy of the molecules; thus $m_{ji} = c_j \cdot t_u$, where c_j – the dimensionless coefficient.

It is obvious that with the increasing temperature the average self-energy of the molecules m_j approaches the energy barrier b_j, and increases the number of molecules j that can pass from liquid to gaseous phase and, thereby, increase the rate of the direct process. The rate of the reverse process is determined by the achieved content of the j-substance in the gas phase, which is usually estimated by the actual partial pressure P_j.

At the constant temperature t_u (u = 1, 2, ..., n), sufficient amount of liquid and sufficient contact time of the phases the value of P_j is increased and, as a consequence, the rate of the reverse process increases. When it becomes equal to the rate of the direct process, there is an equilibrium between the liquid and gaseous states of the j-substance to which the equilibrium partial pressure corresponds.

Thus it should be assumed that:

1. The partial pressure of saturated vapor, as the maximum possible content of the j-substance in the gas phase at a given temperature, reflects the degree of disequilibrium of the intermolecular forces of attraction and repulsion in the liquid, which itself depends on the size, composition, structure and properties of the substance molecules.

2. The ratio of the forces of intermolecular interaction and the molecules self-energy determines the temperature dependence $P_{ju}{}^H$ and independence from the content of other substances in the gaseous phase.

On the basis of the above mentioned assumptions concerning the mechanism of vaporization, an integral expression is obtained:

$$\int_{t_1}^{t_n} \frac{b_i}{(b_j - c_j \cdot t)^2} \cdot dt = \int_{P_{j1}^H}^{P_{jn}^H} \frac{dP_j^H}{P_j^H}$$

The solution is the dependence:

$$P_j^H = P_{j0}^H \cdot e^{\frac{1}{b_j - c_j \cdot t}}$$

where $P_{j0}{}^H$ is the vapor pressure of the j-substance achieved as the temperature rises to 0°C. A review of instrumental methods and published results showed that the Stall Tables remains the most complete and reliable source of actual data about the dependence of the vapor pressure on temperature.

These results involve the temperature interval from the absolute zero to the critical points at which the vapor pressure curve breaks down and includes data on 336 inorganic and 1300 organic substances.

We processed this data and summarized them in two reference manuals, which differ in the completeness of the information.

Examples of this information presentation are given below.

1n Al Aluminium

|	0	1
0	1.284E+003	1.333E-001
1	1.421E+003	6.667E-001
2	1.487E+003	1.333E+000
3	1.555E+003	2.666E+000
4	1.635E+003	5.332E+000
5	1.684E+003	7.998E+000
6	1.749E+003	1.333E+001
7	1.844E+003	2.666E+001
8	1.95E+003	5.332E+001
9	2.056E+003	1.01325E+002

$$f(t) := a \cdot e^{\frac{t}{b-c \cdot t}}$$

$$S := \sqrt{\frac{S2}{n-3}}$$
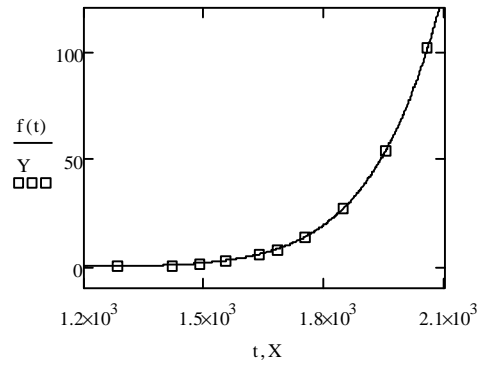
n = 1E+001
S = 3.80628258E-001
a = 2.035E-015
b = 1.67663241E+001
c = −1.78521256E-002

2n AlB$_3$H$_{12}$ Aluminium borohydride

|	0	1
0	-5.22E+001	6.667E-001
1	-4.29E+001	1.333E+000
2	-3.25E+001	2.666E+000
3	-2.09E+001	5.332E+000
4	-1.34E+001	7.998E+000
5	-3.9E+000	1.333E+001
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7	2.81E+001	5.332E+001
8	4.59E+001	1.01325E+002
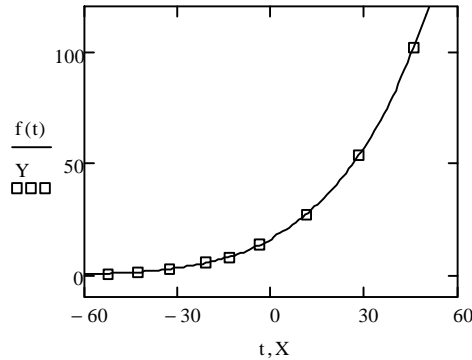
$$f(t) := a \cdot e^{\frac{t}{b-c \cdot t}}$$

$$S := \sqrt{\frac{S2}{n-3}}$$

n = 9E+000
S = 1.72503128E-001
a = 1.615E+001
b = 2.09625413E+001
c = −8.78395353E-002

3n AlBr$_3$ Aluminium bromide

|	0	1
0	8.13E+001	1.333E-001
1	1.038E+002	6.667E-001
2	1.18E+002	1.333E+000
3	1.34E+002	2.666E+000
4	1.506E+002	5.332E+000
5	1.617E+002	7.998E+000
6	1.761E+002	1.333E+001
7	1.998E+002	2.666E+001
8	2.27E+002	5.332E+001
9	2.563E+002	1.01325E+002
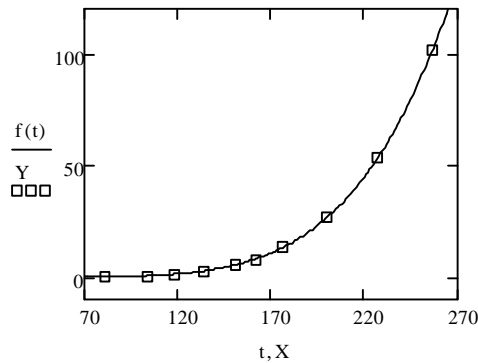
$$f(t) := a \cdot e^{\frac{t}{b-c \cdot t}}$$

$$S := \sqrt{\frac{S2}{n-3}}$$

n = 1E+001
S = 1.88367485E-001
a = 1.13575E-004
b = 7.16569193E+000
c = −4.50259423E-002

4n AlCl$_3$ Aluminium chloride

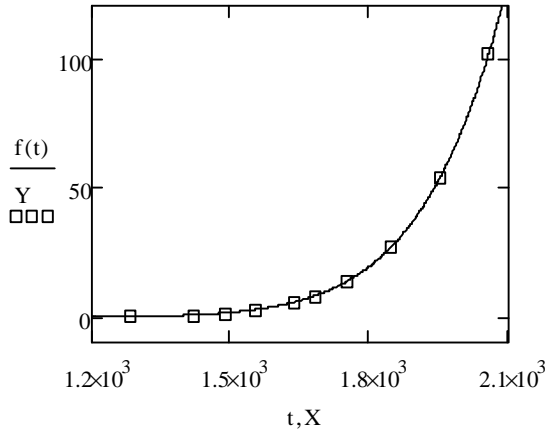|	0	1
0	1E+002	1.333E-001
1	1.164E+002	6.667E-001
2	1.238E+002	1.333E+000
3	1.318E+002	2.666E+000
4	1.399E+002	5.332E+000
5	1.454E+002	7.998E+000
6	1.52E+002	1.333E+001
7	1.618E+002	2.666E+001
8	1.716E+002	5.332E+001
9	1.802E+002	1.01325E+002
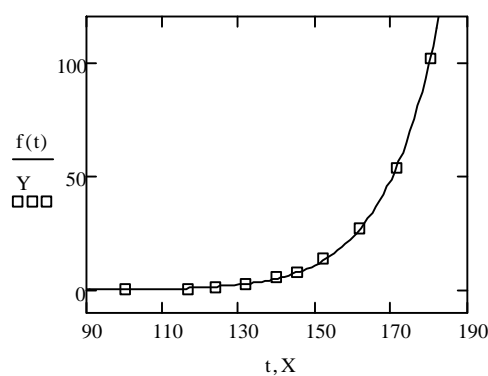
$$f(t) := a \cdot e^{\frac{t}{b-c \cdot t}}$$

$$S := \sqrt{\frac{S2}{n-3}}$$

n = 1E+001
S = 3.63350841E-001
a = 5.6943E-006
b = 8.21210709E+000
c = −1.4337498E-002

$$f(t) := a \cdot e^{\frac{t}{b - c \cdot t}}$$

$$t := -273 \, .. \, 2350$$

$$S := \sqrt{\frac{S2}{n - 3}}$$

$$n = 1E+001$$

$$S = 3.80628258E-001$$

$$a = 2.035E-015 \qquad b = 1.67663241E+001 \qquad c = -1.78521256E-002$$

$$a1 = 1.65E-015 \qquad b1 = 1.39719367E+001 \qquad c1 = -1.27515183E-002$$

$$a2 = 2.75E-015 \qquad b2 = 2.32865612E+001 \qquad c2 = -2.12525304E-002$$

$$\text{augment}\left(Y, YR, \overrightarrow{|Y - YR|}\right) =$$

	0	1	2
0	1.333E-001	2.284811E-001	9.51811E-002
1	6.667E-001	9.02393961E-001	2.35693961E-001
2	1.333E+000	1.65476901E+000	3.21769014E-001
3	2.666E+000	2.98869675E+000	3.22696751E-001
4	5.332E+000	5.75662514E+000	4.24625143E-001
5	7.998E+000	8.43263267E+000	4.34632665E-001
6	1.333E+001	1.3695212E+001	3.65211973E-001
7	2.666E+001	2.67104719E+001	5.04718723E-002
8	5.332E+001	5.34399742E+001	1.1997424E-001
9	1.01325E+002	1.01796521E+002	4.71521412E-001

$$\sum_{i=0}^{n-1} \left(Y_i - YR_i\right)^2 = 1.0141451E+000$$

$$\max\left(\overrightarrow{|Y - f(X)|}\right) = 4.71521412E-001$$