ANALYSIS OF CERTAIN THERMODYNAMIC RELATIONSHIPS FOR EQUILIBRIUM PHASE TRANSITIONS OF THE FIRST KIND

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Based on the first and second laws of thermodynamics, given certain simplifications, we derived integral and theoretical equations for phase transitions, and these are applicable to a wide range of variations in temperature and pressure.

1. Derivation of Integral Equations to Evaluate Isobaric – Isothermal Phase Transitions

Let us use an equation of the general form

$$d(H-TS)-VdP+SdT+\delta A=0. \tag{1}$$

For an isobaric–isothermal transition

$$i=i_g \tag{2}$$

of a single mole of substance i (liquid, solid, or in solution) to the gaseous state i_g, Eq. (1) assumes the form

$$\Delta H-T\Delta S+A=0. \tag{3}$$

We will demonstrate that a universal evaluation of (2) is possible directly from this relationship, without resort to complex integration – which is not always possible in exact terms – of the Clapeyron–Clausius differential equations.

For the reversible isobaric–isothermal process (2) we will use the Van't Hoff procedure which, as will be shown below, offers greater potential than is generally assumed.

Since the choice of the pressures outside of the vessel (outside of the Van't Hoff box) is arbitrary according to this scheme, we assume these pressures to be equal to the equilibrium pressures of the substances in the vessel, thus eliminating the need for additional auxiliary work outside of the vessel in the case of isothermal conversion of the original pressures of the substance to the equilibrium pressures, prior to the reversible introduction of these materials into the vessel, and for the conversion of the equilibrium pressures of the substances to the original pressures, after they have been reversibly withdrawn from the vessel.

With equilibrium prevailing in the vessel, we can assume with an accuracy to the infinitesimals that the equilibrium will not be disturbed in the case of reversible isobaric–isothermal introduction of a single mole of substance into the vessel, nor by the simultaneous withdrawal from the vessel of a single mole of the vapors of this substance.

Hence we conclude that the parameters ΔH and ΔS in (3) are functions exclusively of the equilibrium molar parameters H_{T_i} and S_{T_i} of the substance i.

Having denoted the gaseous state with the subscript "g," and all other states with the subscript "k," we find that Eq. (3) assumes the form

$$(H_{Tg}-H_{T_k})-T(S_{Tg}-S_{T_k})+A=0. \tag{4}$$

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For convenience in studying Eq. (4), we will express it in terms of the standard parameters $H^0_{T_i}$ and $S^0_{T_i}$ at the temperature of the process under consideration, but with a pressure equal to unity.

We avoid indeterminacy in our analysis as we evaluate the work δA and A, treating these as specifically external work performed in addition to the work to overcome the forces of external pressure, which had been taken into consideration in the derivation of Eqs. (1), (3), and (4).

The work δA and A for process (2) may be equal to the work required to overcome the forces of terrestrial gravitation and the forces of surface tension.

With a reversible change in temperature and pressure of an individual substance retaining its aggregate state and position in space, we can assume quite accurately that $\delta A = 0$ and for a single mole of this substance we can impart to Eq. (1) the form

$$d(H_{Ti} - TS_{Ti}) - V_i dP_i + S_{Ti} dT = 0, \tag{5}$$

or after integration at T = const

$$H_{Ti} - TS_{Ti} = H^0_{Ti} - TS^0_{Ti} + \int_1^{P_i} V_i dP_i. \tag{6}$$

Since the reversible withdrawal of the vapors of substance i from the vessel is accomplished by the Van't Hoff method through an orifice with a semipermeable barrier, the pressure of the pure vapors beyond the confines of the vessel differs infinitesimally from the equilibrium vapor pressure P_{i_g} in the vessel at the level at which the material is withdrawn.

Proceeding from the concept of a fugacity factor γ and assuming at T = const, that $\gamma_i = 1$ when $P_{i_g} = 1$, we find

$$\int_1^{P_{ig}} V_i dP_i = RT \ln(\gamma_i P_{ig}). \tag{7}$$

The reversible introduction into the vessel of pure liquids and solids is accomplished through an orifice without semipermeable barriers, and these are positioned at the points of contact between these materials and the walls of the vessel.

The validity of introducing liquids into the vessel in this manner raises no doubts; consequently, accurate to the infinitesimals, the pressure P_{i_k} at which the liquid is reversibly introduced into the vessel is equal to the pressure of this material in the vessel at the level of its introduction, i.e.,

$$P_{i_k} = P + \rho gh = P + \frac{1}{V_{i_k}} mgh. \tag{8}$$

To prove the validity of the indicated introduction of solids, we should bear in mind that sublimation occurs at the surface of the solids and that it may move into the vessel in the manner of a piston, matching the translational velocity with the rate of "wear" of its surface during the sublimation process.

The static pressure overcome in this case by the solid is equal to the pressure P of the gas phase in the vessel at the surface of the solid, in which connection, accurate to the infinitesimals, we have

$$P_{i_k} = P. \tag{9}$$

Since with a change in pressure the molar volume V_{i_k} of the liquids and the solids changes only insignificantly, in many cases it can be assumed to be constant, thus yielding

$$\int_1^{P_{i_k}} V_i dP_i = V_{i_k}(P_{i_k} - 1). \tag{10}$$

However, for more precise calculations the parameter V_{i_k} should be treated in (10) as the integral mean.

Substituting solutions (6), (7), and (10) into Eq. (4), we find the general form of the function to calculate the equilibrium vapor pressure of the pure liquids and solids:

$$\ln(\gamma_i P_{ig}) - \frac{V_{ik}}{RT}(P_{i_k} - 1) = \frac{1}{R}(S^0_{Tg} - S^0_{Tk}) - \frac{1}{RT}(H^0_{Tg} - H^0_{Tk}) - \frac{A}{RT}. \tag{11}$$

If substance i evaporates in the vessel from a liquid solution, the reversible introduction of this substance into the vessel is accomplished through the orifice with the semipermeable barrier made of the same solution, but situated beyond the confines of the vessel.

When we place the external solution into a cylindrical vessel of great capacity – fitted out with a piston to develop a pressure difference which ensures the reversible penetration of the substance i through the semipermeable barrier – it is easy to prove that in this case the pressure P_{i_k} of the substance introduced into the evaporation vessel is also equal, accurate to the infinitesimals, to the total pressure of the solution in the evaporation vessel at the level of entry.

It follows from this sequence of the process that the parameters H_{T_k} and S_{T_k} must be replaced by the partial molar parameters $\overline{H}_{T_k}$ and $\overline{S}_{T_k}$, while the parameter V_{i_k} must be replaced by the molar volume $\overline{V}_{i_k}$ of the substance in the solution, in which connection function (11) assumes the form

$$\ln(\gamma_i P_{i\text{g}}) - \frac{1}{RT}\,\overline{V}_{i_\text{k}}(P_{i_\text{k}} - 1) = \frac{1}{R}\,(S^0_{T\text{g}} - \overline{S}^0_{T\text{k}}) - \frac{1}{RT}\,(H^0_{T\text{g}} - \overline{H}^0_{T\text{k}}) - \frac{A}{RT}\,. \tag{12}$$

The pressure P_{i_k} in Eqs. (11) and (12) varies with a change in the level at which the substances enter the vessel, but according to the law of the conservation of energy, the choice of this level cannot affect the equilibrium vapor pressure P_{i_g}.

This can be illustrated most clearly by an examination of the evaporation of a pure liquid. For such a liquid, with consideration of expression (8)

$$V_{i_\text{k}}(P_{i_\text{k}} - 1) = V_{i_\text{k}}(P - 1) + mgh. \tag{13}$$

However, the evaporation occurs at the surface of the liquid, so that as one mole of the liquid rises to that surface from the level at which it was introduced, work of opposite sign is performed, i.e.,

$$A' = mgh \tag{14}$$

as a part of the total work A.

Substituting solutions (13) and (14) into (11) proves that the terms mgh cancel each other out, thus offering the possibility of replacing (9) in (11), if we eliminate work such as (14) from the total work A.

In general form

$$dH_{Ti} = \frac{\partial H_{Ti}}{\partial T}\,dT + \frac{\partial H_{Ti}}{\partial P_i}\,dP_i.$$

Integrating this expression separately for the gaseous and condensed states when $H_{T_k} = U_{T_k} + P_{i_k}V_{i_k}$, $P_{i_k} = P$, and T = const, we find evaporation

$$\lambda_T = (H_{T\text{k}} - H_{T\text{g}}) = (H^0_{T\text{k}} - H^0_{T\text{g}}) - \int_1^{P_{i\text{g}}} \frac{\partial H_{T\text{g}}}{\partial P_i}\,dP_i + \int_1^{P} \frac{\partial U_{T\text{k}}}{\partial P_i}\,dP_i + V_{i_\text{k}}(P - 1). \tag{15}$$

If we neglect the effect of the pressure on the parameters H_{T_k} and U_{T_k}, formula (15) assumes the form

$$\lambda_T = (H^0_{T\text{k}} - H^0_{T\text{g}}) + V_{i_\text{k}}(P - 1). \tag{16}$$

These relationships are more complete than those obtained by the integration of the Clapeyron–Clausius equation, and we can prove this by looking at the differential form

$$d(H_{T\text{g}} - TS_{T\text{g}}) - d(H_{T\text{k}} - TS_{T\text{k}}) = 0 \tag{17}$$

of Eq. (4) when A = 0.

From (5) we have

$$d(H_{T\text{g}} - TS_{T\text{g}}) = V_{i\text{g}}dP_{i\text{g}} - S_{T\text{g}}dT, \tag{18}$$

$$d(H_{T\text{k}} - TS_{T\text{k}}) = V_{i\text{k}}dP_{i_\text{k}} - S_{T\text{k}}dT. \tag{19}$$

Substituting (18) and (19) into (17) and, in accordance with (4) and (16), for A = 0, making the substitution

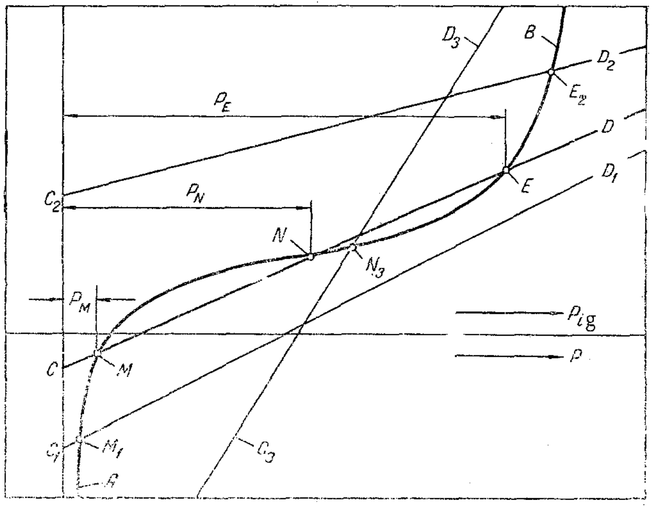

Fig. 1. Diagram of the graphic solution of Eq. (23). For the AB curve the ordinate values express those of the left-hand member of (23) for a change in P_{i_g}; for the family of lines CD the ordinate values express the values of the right-hand member of this equation for a change in P.

$$S_{T\text{k}} - S_{T\text{g}} = \frac{1}{T}(H_{T\text{k}} - H_{T\text{g}}) = \frac{\lambda_T}{T} \tag{20}$$

and the substitution $P_{i_k} = P$, we obtain

$$V_{i\text{g}}\frac{dP_{i\text{g}}}{dT} - V_{i\text{k}}\frac{dP}{dT} = -\frac{\lambda_T}{T}. \tag{21}$$

If the gas phase involves only one component, i.e., if $P = P_{i_g}$ and $A = 0$, Eq. (21) changes into the Clapeyron–Clausius equation

$$\frac{dP_{i\text{g}}}{dT} = -\frac{\lambda_T}{T(V_{i\text{g}} - V_{i\text{k}})}. \tag{22}$$

Hence we draw the conclusion that the contention of [1] to the effect that this equation is absolutely exact is valid only when $P = P_{i_g}$ and $A = 0$.

Equations (15), (16), (21), and (22) are suitable not only for the evaporation and sublimation processes for pure substances, but even for evaporation processes involving substances from solutions, when we replace the parameters $H^0_{T_k}$, $S^0_{T_k}$, and V_{i_k} by the parameters $\bar{H}_{T_k}$, $\bar{S}_{T_k}$, and $\bar{V}_{i_k}$.

The presence of the standard parameters H^0_T and S^0_T in (11) and (12) does not indicate that the true process (2) has been replaced by a standard process, because these parameters appeared on transition from the original equation (4) to Eqs. (11) and (12) as a result of the fact that the true parameters H_T and S_T have been expressed in terms of the standard parameters which we have adopted.

Generalizing the above, we conclude that the use of the Van't Hoff scheme to describe reversible processes permits us to find quite exact working integral equations and is of great methodological significance; in particular, it eliminates the need for the introduction of a concept of nonreal standard processes.

II. Investigating the Conditions of Complete Gasification for Real Substances and the Features Involved in Their Evaporation and Sublimation when a Plane Boundary of Separation Exists between These and the Gas Phase

Assuming $P_{i_k} = P$, according to the proved absence of any effect on the part of the choice of the level at which the substances are introduced into the vessel as regards the final solutions, in the case of $A = 0$, we impart to Eq. (11) the form

$$\ln(\gamma_i P_{i\text{g}}) = \frac{1}{RT}V_{i\text{k}}(P-1) + \frac{1}{R}(S^0_{T\text{g}} - S^0_{T\text{k}}) - \frac{1}{RT}(H^0_{T\text{g}} - H^0_{T\text{k}}). \tag{23}$$

The condition that the substance is stable only in the gaseous state, in particular the condition of liquid boiling, is governed by the inequality

$$P_{i\text{g}} > P.$$

From the graphic solution of Eq. (23) for $P = P_{i_g}$ and T = const, shown in Fig. 1, it follows that in accordance with the points M, N, and E at which the lines AB and CD are intersected, we have the possibility of three real roots P_M, P_N, and P_E, and the reality of these must be verified for each specific substance.

Initially the line AB for $\gamma_i \approx 1$ has the shape of a logarithmic curve, and then, in the high-pressure region, with $\gamma_i > 1$, it deviates upward from this curve.

The lines CD, C_1D_1, C_2D_2, and C_3D_3, respectively, have been plotted for the temperatures T, T_1, T_2, and T_3, shown conditionally as straight lines for V_{i_k} = const, but in actuality, as the parameter V_{i_k} diminishes with a rise in pressure, they deviate slightly downward from the straight lines.

The pressure range from zero to P_M corresponds to the stable existence of the substance only in the gaseous state, because in this interval Eq. (23) is valid only when $P_{i_g} > P$.

In the range from P_M to P_N Eq. (23) is valid only when $P_{i_g} < P$; consequently, the equilibrium existence of the substance in the gaseous and liquid form, or in solid form, if we consider sublimation, corresponds to this interval.

The existence of substances exclusively in the gaseous form corresponds to the pressure range from P_N to P_E, because in this interval $P_{i_g} > P$.

In the pressure range from P_E and higher we always find $P_{i_g} < P$, consequently, it is again possible for the substances to exist in equilibrium in the gaseous and liquid form, or in solid form in the case of sublimation.

It follows from this analysis that it is possible when T = const to achieve the boiling of the liquid in two ways: by dropping the pressure below P_M and by raising the pressure above P_N, however, the latter method is of little effect because of the slight differences between the properties of the liquid and the gas at very high pressures.

For sublimation this feature is most significant, since when $P_{i_g} > P$ the solid materials may lose strength in the high-pressure region.

These conclusions are not completely valid for any temperature. For example, for T_2 the line C_2D_2 has a single point E_2 of intersection with the curve AB, which indicates some possibility for the transition of the gaseous state into a liquid state, or directly into the solid state, but only at a very high pressure. At a temperature T_1 the line C_1D_1 also has only a single point. However, with a drop in temperature the rise in the line is increased in association with the increase in the first term of the right-hand member in Eq. (23); consequently, for a very low temperature T_3 (the line C_3D_3) the state of the substance will again be determined by three points M_3, N_3, and E_3, of which only point N_3 is shown in Fig. 1.

If we are dealing with a solid substance, its transition to the gaseous state in the interval between the points N_3 and E_3 may be explosive in nature and, in all probability, this is the manner in which the conditions are produced that lead to the destruction of cooling stars and their satellites when great pressures and low temperatures develop within their pores.

With a moderate pressure in the interval P_M-P_N we can assume that $\gamma_i \approx 1$, consequently, if the gas phase consists exclusively of the vapors of the substance, i.e., $P = P_{i_g}$, for T = const the equilibrium vapor pressure P_{i_g} remains constant because of the constancy of the standard parameters S_T^0 and H_T^0 in Eq. (23).

In the region of pressures exceeding P_E, we can no longer neglect the change in γ_i and with a rise in pressure for T = const an increase in P_{i_g} is entirely possible.

If $P_{i_g} < P$, i.e., if in addition to the vapors of the substance the gas phase contains other components, according to Eq. (23) the increase in P_{i_g} for T = const will be found to occur with a rise in the total pressure P not only in the region $P > P_E$, but also in the range P_M-P_N of moderate pressures.

For $P_{i_g} < P$ the concept of a critical pressure and a critical temperature as the only ones for which $\lambda_T = 0$ loses meaning, because the possibility of an isothermal increase in the parameter P_{i_g} with growth in the parameter P indicates there exists a unique critical pressure for each temperature, which follows from Eq. (15) for $\lambda_T = 0$.

As follows from Eq. (21), the condition $\lambda_T = 0$ is not a universal indicator of an absence of difference between the liquid and gas state of a real substance, because when $P_{i_g} < P$ and $\lambda_T = 0$ the molar volumes of the liquid and its vapors are not identical. Hence we conclude that when $P_{i_g} < P$ the condition $\lambda_T = 0$ indicates the possibility of a change in sign for the parameter λ_T with a further rise in the presence of the system.

Turning to an evaluation of the evaporation of the substances from liquid solutions, we note that unlike the parameters H_T^0 and S_T^0 which are exclusive functions of temperature, the partial molar parameters $\overline{H}_T^0$ and $\overline{S}_T^0$ are functions of the temperature and the concentration of the solution, in connection with which the binomial

$$\frac{1}{R}\,\overline{S}_{T\mathrm{k}}^0-\frac{1}{RT}\,\overline{H}_{T\mathrm{k}}^0 \tag{24}$$

in Eq. (12) for T = const is a variable quantity, and we know that it increases with reduction in the concentration of the solution.

While $P_{i_g} < P_{i_k} = P$ and at the initial instant $V_{i_k} \ll V_{i_g}$, the left-hand member of Eq. (12) initially increases with a rise in P for T = const, subsequently diminishing. When $H^0_{T_g}$ and $S^0_{T_g}$ = const this initially leads to a reduction in the binomial of (24); consequently, it leads to an increase in the concentration of the substance in the solution, i.e., to an increase in the solubility of the substance, and then to an increase in the binomial of (24), and consequently, to a reduction in the concentration of the substance in the solution, i.e., to a reduction in the solubility of the substance.

In view of the comparative smallness of the molar volume $\overline{V}_{i_k}$, the limit pressure is large – and the solubility of the substance begins to diminish when this limit pressure is exceeded; however, when $P_{i_g} \ll P$ it diminishes substantially, which can be seen from the left-hand member of (12).

III. Examining the Processes of Evaporation in the Case of a Distorted Liquid Surface

Let us initially examine the evaporation of a liquid in capillaries.

We accomplish the reversible isobaric–isothermal completion of this process by introducing one mole of liquid into the broad portion of the vessel at a depth h and by simultaneously withdrawing one mole of the vapors of the liquid at the level of its meniscus in the capillary with a vapor pressure P'_{i_g}.

If the liquid in the capillary is at a height $\pm h_\sigma$ with respect to its level in the wide portion of the vessel, during the evaporation of one mole of the liquid the work

$$A = mg\,(h \pm h_\sigma) \tag{25}$$

is performed in lifting the liquid from the level at which it was introduced to the meniscus in the capillary.

With a spherical meniscus, the following relationship is valid:

$$h_\sigma = \frac{2\sigma}{rg\rho} = \frac{2\sigma V_{i\mathrm{k}}}{rgm}. \tag{26}$$

Assuming the pressure of the gas phase at the liquid surface in the wide portion of the vessel to be equal to P and having substituted the values of (8), (25), and (26) into (11), we find

$$\ln(\gamma_i P'_{i\mathrm{g}}) = \frac{1}{RT}\,V_{i\mathrm{k}}(P-1) + \frac{1}{R}\,(S^0_{T\mathrm{g}} - S^0_{T\mathrm{k}}) - \frac{1}{RT}\,(H^0_{T\mathrm{g}} - H^0_{T\mathrm{k}}) \mp \frac{2\sigma V_{i\mathrm{k}}}{rRT}. \tag{27}$$

Subtracting (23) – found for a horizontal liquid surface – from (27) we obtain the Thomson equation

$$RT \ln \frac{P'_{i\mathrm{g}}}{P_{i_\mathrm{g}}} = \mp \frac{2\sigma V_{i\mathrm{k}}}{r}. \tag{28}$$

The resulting change in the vapor pressure P'_{i_g} for the liquid in the capillary in comparison with the vapor pressure P_{i_g} on the open horizontal liquid surface was made directly dependent on the sign of the surface curvature, without consideration of the forces generating the distortion.

To refine the possibilities of such generalization, let us consider the evaporation of a liquid drop, assuming, for purposes of simplifying the analysis, that in the evaporation vessel we find only a single spherical drop, in thermodynamic equilibrium with the gas phase.

In this case, we achieve a reversible isobaric–isothermal process (2) by drawing in from without one mole of liquid into the drop by means of a thin tube, and by simultaneously withdrawing from the vessel one mole of the liquid vapors, using the method described earlier.

Proceeding from Laplace's conclusion regarding the compressive effect of a convex film of liquid, we assume

$$P_{i_\mathrm{k}} = P + \frac{2\sigma}{r}. \tag{29}$$

Substituting (29) into (11) and assuming A = 0, since for this process, according to the scheme employed, the dimensions of the drop and its position in the vessel remain unchanged, we derive (27), i.e., we prove the validity of this generalization for the convex liquid surface.

In studying the evaporation of a liquid with a convex surface outside of the capillary we examine the spherical gas bubble inside the liquid.

Here we achieve a reversible isobaric–isothermal process (2) by using a thin tube to withdraw one mole of liquid vapors from the bubble beyond the confines of the vessel, while simultaneously introducing into the vessel – at some distance from the bubble – one mole of the liquid through the orifice in the vessel wall, which is at the same depth h at which the bubble is situated.

If the bubble represents the only gas phase in the closed vessel filled with a liquid, it is quite obvious that in achieving this process according to the scheme employed the dimensions of the bubble will not change and given a constant position of the bubble in the liquid we have A = 0.

When A = 0, substitution of (8) into (11) yields

$$\ln(\gamma_i P_{ig}) = \frac{1}{R} V_{ik}(P-1) + \frac{mgh}{RT} + \frac{1}{R}(S^0_{Tg} - S^0_{Tk}) - \frac{1}{RT}(H^0_{Tg} - H^0_{Tk}). \tag{30}$$

Since the parameter P_{i_g} in (30) is an exclusive function of the conventional static liquid pressure, and for h ≈ 0 this equation changes into (23), we draw the conclusion that the capillary pressure has no effect on the P_{i_g} of the gas in a bubble surrounded by the liquid.

The thermodynamic method of the reference solution requires no examination of the intermediate stages of the process, but since this result does not agree with current opinions, we find a need for a critical evaluation of the proof that the capillary pressure influences the pressure in the gas bubble, as follows from the equation

$$\sigma dF = PdV. \tag{31}$$

Substituting the values of $F = 4\pi r^2$ and $V = (4/3)\pi r^3$ into this equation, we obtain $P = 2\sigma/r$.

However, Eq. (31) serves only as a balance to the work performed in expanding the bubble, rather than as a balance to the total energy and, therefore, the validity of applying this equation to a bubble surrounded by a liquid is cast in doubt.

The need for the total energy balance in this case is clear if we take into consideration that the film, as it stretches out, does not become thinner as the bubble expands, but rather maintains its thickness, which is equal to the radius of the sphere of molecular attraction, in connection with which – given an increase in the bubble surface – the surface-tension layer must be replenished with new liquid molecules which, on entering that surface, significantly alter their thermodynamic state.

The experimental data on increasing the pressure in a soap bubble as its dimensions diminish, and the experiments which have been performed in connection with the introduction of gas bubbles into a liquid through a tube – confirming the increase in the pressure of the introduced gas with a reduction in bubble size – cannot be regarded as negating the validity of our conclusion to the effect that capillary pressure does not affect the pressure of the gas in a bubble surrounded by a liquid.

A soap-bubble film exhibits bilateral surface tension, in connection with which the rise in the pressure of the gas within the bubble can be explained exclusively by the compressive effect of the external convex surface-tension layer; however, in addition to this, we can agree that, on the whole, for such a film expression (31) is valid to some extent, since the film becomes thinner as it stretches out, there being no replenishment of new liquid molecules.

The rise in the pressure with a reduction in the dimensions of the bubble introduced into the liquid through a tube is not needed to produce a high pressure within the bubble itself, but to overcome the capillary forces in the tube, which increase as the tube diameter diminishes.

The cited examples are sufficiently convincing proof of the advantage of the proposed equations relative to the conventional equations of thermodynamics.

NOTATION

Δ denotes the finite change of the parameter;
H, S are, respectively, the enthalpy and entropy of the system under consideration;

V	is its total volume;
A	is the external work performed by the system, in addition to the usual work to overcome the pressure forces;
T	is the absolute temperature;
R	is the universal gas constant;
P	is the total pressure of the gas phase at the surface of the material;
P_{i_g}	is the equilibrium vapor pressure of the substance;
γ_i	is the fugacity factor;
P_{i_k}	is the total pressure in the evaporation vessel at the level at which the liquid and solid substances, and the substances in solution, are introduced into the vessel;
V_i	is the molar volume of the pure substance;
$\bar{V}_i$	is the molar volume of the substance in solution;
m	is the molar mass of the substance;
ρ	is its density;
g	is the acceleration of the force of gravity;
U_T	is the molar internal energy of the substance;
λ_T	is the molar latent heat of evaporation;
H_T, S_T	are, respectively, its molar enthalpy and entropy at the temperature and pressure of the process under consideration;
H_T^0, S_T^0	are the magnitudes of the parameters H_T and S_T at the temperature of the process, but at standard pressure equal to unity;
$\bar{H}_T, \bar{S}_T, \bar{H}_T^0, \bar{S}_T^0$	are the partial molar magnitudes for the indicated parameters at the actual concentration of the substance in the solution;
r	is the radius of surface curvature;
F	is its area;
h	is the vertical distance from the subject level to the surface of the liquid in the vessel;
h_σ	is the level of rise or descent of the liquid in the capillary;
σ	is the coefficient of surface tension;

Subscripts

g	denotes the gaseous state of the substance i;
k	denotes the liquid and solid state of the pure substance and the state of the substance in solution.

LITERATURE CITED

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