COMMENTS ON AN ATTEMPT TO IMPROVE THE SCIENCE OF THERMODYNAMICS

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Attempts are constantly being made to "modernize" the fundamental concepts of classical thermodynamics or to solve certain complex problems using only elementary thermodynamic relations. And precisely because such attempts are undertaken by unacceptable means, as a rule, they are naturally doomed to failure. An example of such an attempt is the recent article by V. V. Revenko, "An analysis of certain thermodynamic relationships during equilibrium-phase transitions of the first kind," published in Inzhenerno-Fizicheskii Zhurnal, 16, No. 2 (1969).

In the first section of his article the author writes the equation for the isobaric–isothermal transition of one mole of matter (liquid or solid in solution) into the gaseous state in the form*

$$\Delta H - T\Delta S + \mathrm{A} = 0, \tag{1}$$

where A is the "entirely real external work performed apart from the work usually done in overcoming the forces of external pressure."

The author continues: "We will show that a universal evaluation (?) of the process is possible directly on the basis of this relation, without the need of complicated and not always exactly integrable differential equations of the Clapeyron–Clausius kind."

The author does not take the trouble to formulate the problem precisely, but one can guess from the wording in the text that he tries to analyze the conditions of phase equilibrium for two cases: 1) when the condensate phase is a pure substance while the coexisting gaseous phase is a mixture of vapors of this substance with extraneous gases not soluble in the condensate; and 2) when the condensate and the gaseous phase represent a multicomponent system.

It is not difficult to understand that the first case, under conditions further stipulated by the author, corresponds to the phase equilibrium of a single-component system with unequal pressures in both phases.

The author continues his deliberations in the following manner. Equation (1) is transformed into

$$(H_{\mathrm{TG}} - H_{\mathrm{TC}}) - T(S_{\mathrm{TG}} - S_{\mathrm{TC}}) + A = 0, \tag{2}$$

where the subscript G refers to the gaseous phase and the subscript C to the condensate phase.

There follows a far from irrefutable analysis of various phase transition modes in the given system, and a few transformations which have been made unwieldy by the use of exceptionally awkward and confused concepts and symbols.

As a result, the author arrives at "a general form of the relation for calculating the equilibrium tension of vapors of pure liquids and solids"

$$\ln(\gamma_i P_{i\mathrm{G}}) - \frac{V_{i\mathrm{C}}}{RT}(P_{i\mathrm{C}} - 1) = \frac{1}{R}(S^0_{\mathrm{TG}} - S^0_{\mathrm{TC}}) - \frac{1}{RT}(H^0_{\mathrm{TG}} - H^0_{\mathrm{TC}}) - \frac{A}{RT}, \tag{3}$$

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*Throughout, the numbering of the equations is ours.

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where γ_i is the volatility coefficient, P_{iG} is the equilibrium vapor tension of the condensate, and V_{iC} is the molar volume of a pure substance in the condensate state. The author subsequently takes P_{iC} to be identical to P, which is the total pressure in the gaseous phase; S^0_T and H^0_T are the steady-state entropy and enthalpy.

In considering this equation, one must note firstly that it is not original (equations of this form are found in many published works and even in the scientific literature on thermodynamics) and secondly that it is not "general" as the author claims. In his derivation the author has assumed without discussion that the gaseous phase in the equilibrium chamber is an ideal mixture. Finally, the said equation allows one to calculate the equilibrium vapor tension only for the case where the standard entropies of the condensate and of the gaseous phase have been determined independently. But this is possible only with the aid of the Third Law of thermodynamics so that the author's assertion that he succeeded in deriving "the design equations in integral form ... on the basis of the First and Second Law of thermodynamics ..." is mistaken. And that this can be done with the aid of the Third Law is a well-known fact.

Furthermore, the author finds an expression for the latent heat of evaporation $\lambda_T = (H_{TC} - H_{TG})$ which is "more complete than that derived by integrating the Clapeyron–Clausius equations" (apparently, here and in several subsequent equations, the minus sign before the parenthesis on the right-hand side has been omitted by misprint), namely

$$\lambda_T = (H^0_{TC} - H^0_{TG}) + V_{iC}(P - 1). \tag{4}$$

What then does Equation (4) represent? In its derivation the author has assumed, without proper discussion, that the vapor is an ideal gas; the author disregards the dependence of the internal energy of the condensate phase on the pressure, even though the contribution by this component may sometimes amount to 20 or 30% and even though it can easily be accounted for. In this way, the applicability of Eq. (4) becomes severely limited. The author also does not mention, in connection with Eq. (4), that for its use it is necessary to know the standard enthalpy H^0_{TG} of the gas. In tables of the ideal-gas thermodynamic functions of substances only the quantity $H^0_{TG} - H^0_{0G}$ is shown, i.e., for practical calculations it is necessary also to know the heat of sublimation (or evaporation) at 0°K.

Continuing his analysis, V. V. Revenko writes Eq. (2) for A = 0 in differential form:

$$d(H_{Tr} - TS_{TG}) - d(H_{TC} - TS_{TC}) = 0, \tag{5}$$

and then for each phase

$$d(H_{TG} - TS_{TG}) = V_{iG}dP_{iG} - S_{TG}dT \tag{6}$$

$$d(H_{TC} - TS_{TC}) = V_{iC}dP_{iC} - S_{TC}\,dT, \tag{7}$$

where V_{iG} is the molar volume of the vapor of the i-th component, and, after substituting into (5), the author obtains the expression

$$V_{iG}\frac{dP_{iG}}{dT} - V_{iC}\frac{dP}{dT} = -\frac{\lambda_T}{T}. \tag{8}$$

On one hand, this equation reflects the well-known fact that the equilibrium pressure of saturated vapors and its change as a function of temperature under unequal phase pressures differ from the usual equilibrium values under equal phase pressures. At the same time, however, by using this equation without any comments whatsoever the author can only lead the reader into confusion. Indeed, a two-phase single-component system under unequal phase pressures has not one but two degrees of freedom and, therefore, if the derivatives dP_{iG}/dT and dP/dT are to have an unambiguous meaning, one must use one of the degrees of freedom, i.e., one must specify some character of the process.

Having derived Eq. (8), V. V. Revenko asserts without any proof that the evaporation of a substance from its solution is described satisfactorily by the equation

$$\frac{dP_{iG}}{dT} = -\frac{\lambda_T}{T(V_{iG} - \overline{V}_{iC})}, \tag{9}$$

where $\overline{V}_{iC}$ is the partial volume of the component in the liquid state.

It is not difficult to show that this equation contradicts known statements concerning the thermodynamics of solutions (see, for example, V. A. Kirillin and A. E. Sheindlin, The Thermodynamics of Solutions, Gosenergoizdat (1956)). Many similar "findings" are contained in the article.

The author proceeds to discuss certain applications of his "theory." In particular, he considers this theory universal enough to be used as a basis for formulating even "the conditions which cause the fissure of cold stars."

In Section 3 of his article, devoted to a study of evaporation processes at a curved liquid surface, V. V. Revenko admits that "his results (considering, specifically, the formation of a gas bubble while the liquid boils) do not conform to contemporary views on the subject" and he anticipates his critics' objections. He does it unadroitly, moreover, as follows. He writes the equation of energy change in the surface layer of a bubble incorrectly: $\sigma dF = PdV$ (where σ is the coefficient of surface tension and F, V are respectively the surface area and the volume of a bubble) and then, having derived from it the naturally incorrect expression $P = 2\sigma/r$, he views it critically.

There is no need to consider the author's remaining arguments in greater detail. We will merely quote his concluding statement: "The examples given here confirm convincingly enough the advantage which the proposed equations have over the conventional equations of thermodynamics."

It is impossible to agree with this. In our opinion, the entire article does not measure up to criticism as far as both the substance of the problem and the style of its exposition are concerned (one should note, above all, the amazing carelessness in the formulation of the problems at hand and also the incredible confusion of concepts and symbols used in the analysis).