COMPRESSIBILITY OF PARAHYDROGEN PHASES ON SATURATION LINE

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Introduction

Today in many cases (in particular, for the rocket engineering needs) hydrogen is stored in a liquid state. And it is important high concentration of paramolecule (>95%) in the liquid phase, because of spontaneous transition of ortohydrogen into parahydrogen is accompanied by 0,5 kDj/kg heat yield. This leads to the large hydrogen losses on the evaporation during the storage. It is actual the development of the analytical state equations of the saturation line (binodale) for two coexisting phases (liquid and vapor). This problem consist in the existence only one theoretically grounded form of the equation presentation – the virile one in a form of the decomposition of the undimensions compressibility coefficient Z ($Z = pV/RT = p/\rho RT$) into the endless degree row:

$$Z(\rho,T) = 1 + B(T)\rho + C(T)\rho^2 + \ldots, \qquad (1)$$

where Z decomposition is carried out by the variable value ρ - the fluid density (kg/m3); B(T) and C(T) – the second and third virial coefficients, corresponding to contributions of the double and triple collisions of molecules in Z accordingly; T - absolute temperature, K.

However great difficulties take place during the solution of the theoretical equation. They are connected with the calculation of the member of the endless virial row. That is why the empirical method is used in most cases for the development of the state equations. Great but final number of members is used instead of the endless row. The form of the polynomial elements is chosen arbitrarily and they include many constants with incomprehensible physical meaning.

Obviously, the optimal solution of this task is us of the "half - empirical" method. It may by determined by the next way: 1) the state equation must be constructed on the base of some most verified correlation (one or twoconstant "rules"), 2) the exact thermodynamics correlation connecting this "rules" together must be used and 3) equation must have a rational form, that is must be obtained in a reserved form, have a compact look and minimum of constants and besides they be the known criterions of the thermodynamicall similarity.

Results and discussion

Classification of the most exact criterions of similarity and few-constant correlation (by the main point, the local "laws of the corresponded states", or ZCS) is adduced in monograph "Thermodynamics" by Putilov: "Under the first ZCS it is understood usually the assertion, that for thermodynamically similar substances the corresponding states exist as such, in which at the equality of the conducted temperatures ($\tau = T/T_{cr}$) and conducted pressures ($\pi = p/p_{cr}$) the conducted volumes ($\varphi = V/V_{cr}$) of the substance are equal. Under the second law it is understood the assertion, that the conducted pressure of the saturated vapor for the similar substances is the universal function of the conducted temperature (Van-der-Waal's "rule"). The third law is the analogous assertion about the densities of the saturated vapor and liquid (this is given expression by the Mattias's "law" of diameters"). The fourth law confirms, that entropy of the vapor formation is the universal function of the conducted temperature (it is more accurate definition of Truton's rule).

Van-der-Waal's correlation is one of the most known rule and connects the with conductive temperature logarithm of the phases conducted pressure on the binodale:

$$\lg\pi = f(1 - \tau^{-1}), \qquad (2)$$

where the value of the undemensions coefficient f for the pure substances is about 3,05.

Mattias's law of "the straight – forward – forward diameter" for the phases on the saturation line is the most known:

$$(\rho' + \rho'')/2 = \rho_{cr}\,[1 + a(1 - \tau^{-1})], \qquad (3)$$

where a – constant, which is equal to 1 for many substances ($a \approx 1$). This rule is sufficiently exact and is used often at the development of the state equation on the binodale. The final form of the Truton's rule progress is the Vatson's correlation for the latent heat of the vapor formation in dependence upon the conducted temperature:

$$H_2/H_1 = [(1 - \tau_2^{-1})/(1 - \tau_1^{-1})]^n \qquad (4)$$

where H_i – latent heat of vapor formation (Dj/kg), n – Vatson's parameter, and besides it is recommended [2] to count n = 0,38 (for parahydrogen n = 0,237). The adduced above rules

have only one strong point – critical one. Obviously, it is necessary to take into consideration that binodale is a limited by two point: the critical and triple. That is why for the entry of Vatson's correlation it is more correctly to use not two conducted temperatures τ_1 and τ_2, but only one undimensions temperature (standardized):

$$\theta = (T - T_{tr})/(T_{cr} - T_{tr}), \quad (5)$$

which is equal to zero for the triple point and is equal to one for the critical one ($0<\theta<1$). The term of standardized temperature was firstly introduced into thermodynamically calculations by Bawer and Siurdan [1]. The use of the standardized temperature allows writing Vatson's correlation more compactly:

$$H(\theta) = H_{tr}\,(1 - \theta)^n, \quad (6)$$

where H – the maximum of the latent heat of vapor formation (at t of triple point T_{tr}).

And the rule of the " straight – forward" diameter with standardized temperature will be written in a form:

$$(\rho' + \rho'')/2 = \rho_{cr}\,[1 + m(1 - \theta)], \quad (7)$$

m - undimensions simplex, Van–der-Waals's correlation may be easy written not in adduced temperature form, but in a standardised temperature one, if take into account, that:

$$\tau = \tau_{tr} + \theta(1 - \tau_{tr}), \quad (8)$$

where τ – adduced temperature of the triple point: $\tau = T/T_{tr}$.

During the use of the half-empirical method it is necessary to take into consideration two factors. Firstly, theoretically grounded state equation is determined as a function of the compressed coefficient Z. That is why Kaitte's-Mattias's "straight –forward' rule may be written through the compression of the phases as:

$$1/Z' + 1/Z'' = (2/Z_{cr})[1 + m(1 - \theta)](\tau/\pi), \quad (9)$$

where Z_{cr} – the known criterion of the thermodynamical similarity characterizing the critical strong point on the line of the fluid saturation. Secondly, the "half – empirical" method assumes the use the exact thermodynamical correlation. For example, it must include the coexisting phases on the binodale: $\mu'(p,T) = \mu''(p,T)$. This equality may by presented in a look of the Klapeiron's – Klauzius's equation:

$$\partial p/\partial T = (S'' - S')/(V'' - V')T, \quad (10)$$

And from it the difference of the coefficients of the phases compressibility on the binodale may be determined:

$$Z'' - Z' = H/[T^2 \partial(\ln p)/\partial T]. \quad (11)$$

A new rule as a synthesis of two mentioned above ones may be obtained, if to fulfil the logarithmically differentiation of the Van-der-Waals correlation and to substitute in it the value of the latent heat vapor formation H from the Vatson's correlation:

$$Z'' - Z' = \Delta Z_{tr}\,(1 - \theta)^n. \quad (12)$$

This "half – empirical" rule is "two – parameters" correlation and includes new constant: $\Delta Z_{tr} = Z''_{tr} - Z'_{tr}$. It reflects the properties in a triple point; n is a degree exponent from Vatson's correlation.

Thus, on the basis of the exact thermodynamical expression for the equality of the chemical potentials of the coexisting phases (formulas by Klapeiron – Klauzius) and on the basis of the standardized Vatson's and Van-der-Waals's correlations the new one – parameter rule has been syntheses. It includes the new criterion of the thermodynamical similarity ΔZ_{tr} characterizing the second strong point on the saturation line - the triple one.

$$\begin{cases} 1/Z'' + 1/Z' = (2/Z_{cr})[1 + m(1 - \theta)](\tau/\pi) \\ Z'' - Z' = \Delta Z_{tr}\,(1 - \theta^{\alpha})^n. \end{cases} \quad (13)$$

Solution of thus equation system may be presented in a generalization form:

$$Z_s = 0{,}5\{1 + \sqrt{[1 + (B/A)^2]}\} \pm 0{,}5B, \quad (14)$$

where A and B – undimensions complexes; accordingly $A = Z_{cr}/[1 + m(1 - \theta)^n](\tau/\pi)$ and $B = \Delta Z_{tr}\,(1 - \theta^{\alpha})^n$, Z_s – compressed coefficient of fluid on the saturation line, and besides for the saturated vapor in this expression the symbol is (+) and $Z_s \equiv Z''$, and for the saturated liquid in this expression the symbol is (–) and $Z_s \equiv Z'$.

Solution the put task allowed no obtain the generalized dependence for the compressed coefficient of the fluid on the binodale in the next look:

$$Z_s(\theta) = F(\theta, Z_{cr}, \Delta Z_{tr}, m, n, \tau_{tr}, \ln(\pi_{tr})^{-1}), \quad (15)$$

That is as function of one variable - the standardized temperature θ, including six constant – two criterions of thermodynamical similarity: undimensions complexes Z_{cr} and ΔZ_{tr}, three numbers of similarity: undimensions simplexes m, τ_{tr}, $\ln(\pi_{tr})^{-1}$and two parameters - degree index n, α.

For parahydrogen: $T_{cr} = 32{,}98$K, $T_{tr} = 13{,}9$K, $\tau_{tr} = 0{,}402$, $p_{tr} = 0{,}0704$ bar, $p_{cr} = 12{,}93$ bar

One can obtain $Z_{cr} = 0{,}3059$, $\Delta Z_{tr} = 0{,}9956$ calculated these constant for parahydrogen in accordance to inquiry date.

This equation allows to calculate the parahydrogen phase compression on the binodale, that is for $0 \le \theta \le 1$ with sufficient for technical calculations accuracy.