

# Results of investigation of first-order phase transitions

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Universal equations are presented for the general law and for the  $p$ - $T$  equilibrium curve with two empirical constants. They account well for the experimental data on the main forms (vaporization, sublimation, melting) of the first-order phase transitions in various substances.

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First-order phase transitions are described by the Clapeyron-Clausius equation

$$\frac{dp}{dT} = \frac{r}{\Delta v} \frac{1}{T} = \frac{\Delta s}{\Delta v} , \quad (1)$$

where in the general case  $r$  is the thermal energy,  $\Delta v$  is the difference between the volumes of the phases, and  $\Delta s$  is the entropy difference.

In investigations of the liquid–vapor phase transition, the quantity  $r/\Delta v$  is regarded as a generalized parameter called the specific vaporization energy.<sup>[1]</sup> Physically,  $r/\Delta v$  is the energy consumed to the formation of a unit phase-volume difference. On the basis of the experimental, we seek the dependence of  $r/\Delta v$  on the temperature and pressure on the equilibrium line. The use of two parameters in place of the temperature alone offers greater possibilities, although the sought dependence turns out here to be an implicit form of the temperature. It has turned out<sup>[2]</sup> that

$$\frac{r}{\Delta v} = \frac{r_0}{\Delta v_0} \left( \frac{T_0}{T} \right)^n \left( \frac{p}{p_0} \right)^c , \quad (2)$$

where  $r/\Delta v$ ,  $p$ ,  $T$  and  $r_0/\Delta v_0$ ,  $p_0$ ,  $T_0$  are the specific energy, pressure, and temperature on the saturation line and at the triple point, respectively, while  $n$  and  $c$  are empirical constants of the individual substance.

From (1) and (2) we have

$$p = \left\{ p_0^{1-c} + \frac{1-c}{n} \frac{r_0}{\Delta v_0} \frac{1}{p_0^c} \left[ 1 - \left( \frac{T_0}{T} \right)^n \right] \right\}^{\frac{1}{1-c}} . \quad (3)$$

For the critical point we obtain from (3)

$$\frac{1-c}{n} \frac{r_0}{\Delta v_0} \frac{1}{p_0^c} = \frac{p_{cr}^{1-c} - p_0^{1-c}}{[1 - (T_0/T_{cr})^n]}$$

and consequently

$$p = \left\{ p_0^{1-c} + \frac{(p_{cr}^{1-c} - p_0^{1-c}) [1 - (T_0/T)^n]}{[1 - (T_0/T_{cr})^n]} \right\}^{\frac{1}{1-c}} \quad (4)$$

The constants  $n$  and  $c$  are calculated most reliably from (4) by using the experimental  $p$  and  $T$  and a computer. The values of the constants  $n$  and  $c$  for the liquid-vapor phase transitions, according to experiments for 98 substances (including still unpublished data) lie in a narrow range, from 0.6 to 1.1 for  $c$  and from  $-2.8$  to  $2.8$  for  $n$ . A definite connection exists between the constants of all the substances (in first-order approximation, the dependence of  $c$  on  $n$  is close to linear<sup>[3]</sup>), and (2) and (4) can in principle be expressed in terms of one constant.

A generalized parameter is also  $\Delta s/\Delta v$  with the earlier form of the relation (2). In fact, if

$$\frac{\Delta s}{\Delta v} = \frac{\Delta s_0}{\Delta v_0} \left(\frac{T_0}{T}\right)^m \left(\frac{p}{p_0}\right)^k, \quad (5)$$

then we obtain from (5) and (1) the equation

$$p = \left\{ p_0^{1-k} + \left(\frac{1-k}{1-m}\right) \frac{\Delta s_0}{\Delta v_0} \frac{T_0}{p_0^k} \left[ \left(\frac{T_0}{T}\right)^{m-1} - 1 \right] \right\}^{\frac{1}{1-k}},$$

which coincides with (3) at  $k=c$ ,  $m-1=n$ , and the obvious equality  $r_0 = \Delta s_0 T_0$ .

Calculations have shown that Eq. (4) is capable of accounting well for the experimental  $p$ - $T$  liquid-vapor curves of a great variety of substances (elements, simple and complex inorganic and organic compounds) under tremendous variations of the pressure on the saturation line ( $p_{cr}/p_0$  amounts to  $10^6 - 10^9$ ), and the accuracy is higher (to hundredths of 1%) the more accurate the experiment. The last feature of (4) has made it possible to show<sup>[4]</sup> that He<sup>4</sup> has two liquid-vapor  $p$ - $T$  curves separated by the  $\lambda$  transition.

Using (3) or (4), we can now represent the expression for the specific vaporization energy (2) as a function of the temperature only.

Equation (4) (expressed in the appropriate form) also approximates well the experimental  $p$ - $T$  curves of sublimation,<sup>[4]</sup> melting (37 substances, including anomalous melting),<sup>[3]</sup> and apparently of polymorphic transitions into the solid phase. Each of the aforementioned process and chosen substances is characterized by its own values of  $c$  and  $n$  and by different relations between them. The accuracy of the approximation, the limits of variation of the pressure on the saturation, and the characteristics of the employed substances are the same as for the liquid-vapor phase transition.

Thus, the equation of the liquid-vapor  $p$ - $T$  curve (3) or (4), and consequently

also the expressions (2) and (5) for the general relation, turned out to be a universal solution for the main forms of first-order phase transitions. Individual features of the substance are reflected in these equations by the thermodynamic parameters at the triple point (and additionally at the critical point), and by two empirical interrelated constants.

<sup>1</sup>M. K. Zhokhovskii, *Izv. Timirzaevskoi Sel'skokhoz. Akad.*, No. 4, 1967.

<sup>2</sup>M. K. Zhokhovskii, *Izmeritel'naya tekhnika*, No. 10, 1975.

<sup>3</sup>M. K. Zhokhovskii, *Izmeritel'naya tekhnika*, No. 4, 1967.

<sup>4</sup>M. K. Zhokhovskii, *Izmeritel'naya tekhnika*, No. 11, 1974.