SOME FEATURES OF THE CRITICAL POINT

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A characteristic relation is derived for the critical point. Some features of the critical point are brought out by an examination of the entire condensate-state region of a substance.

The critical state of a substance has been the subject of many studies. Both experimental and theoretical strides toward an understanding of the nature of the condensate state have contributed a great deal to our formulation of concepts pertaining to the critical point. In turn, a better understanding of the critical point may serve as guidance for exploring other regions of the condensate state. This explains the heightened interest in studies concerning the critical state of a substance.

We consider the following derivatives:

$$\left(\frac{\partial H}{\partial \ln V}\right)_p = \frac{C_p}{\alpha}, \tag{1}$$

$$\left(\frac{\partial H}{\partial \ln V}\right)_T = \frac{V}{\beta}\,(\alpha T - 1). \tag{2}$$

Since

$$\left(\frac{\partial H}{\partial V}\right)_p = \left(\frac{\partial H}{\partial V}\right)_T + \left(\frac{\partial H}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p,$$

hence the following equality holds true at the critical point

$$\left(\frac{\partial H}{\partial V}\right)_p = \left(\frac{\partial H}{\partial V}\right)_T, \tag{3}$$

and, with (1), (2) taken into account:

$$\left(\frac{\partial H}{\partial \ln V}\right)_p = \left(\frac{\partial H}{\partial \ln V}\right)_T = \frac{C_p}{\alpha} = \frac{\alpha T}{\beta}\,V. \tag{3a}$$

At the critical point, the same relative change in volume under constant pressure or under constant temperature produces the same change in enthalpy. Since Eq. (3) applies to the critical point only, it may serve as a characteristic and one definition of the critical state.

On the basis of known experimental data for argon, graphs have been plotted representing the logarithmic derivatives of enthalpy as functions of the temperature over the entire range of condensate state. The data pertaining to the solid state and the melting point of this substance are referred to atmospheric pressure, and the critical point is approached along the saturation curve.

According to the diagram, the spread between the two derivatives, measured along the vertical axis, is maximum at the absolute zero temperature and decreases with rising temperature until it becomes zero at the critical point. The same value of both derivatives (1) and (2) at the critical point is for argon 2360 kJ/mole. Thus, on the basis of the derivatives analyzed here, the critical point appears as the antipode of the absolute zero point and vice versa.

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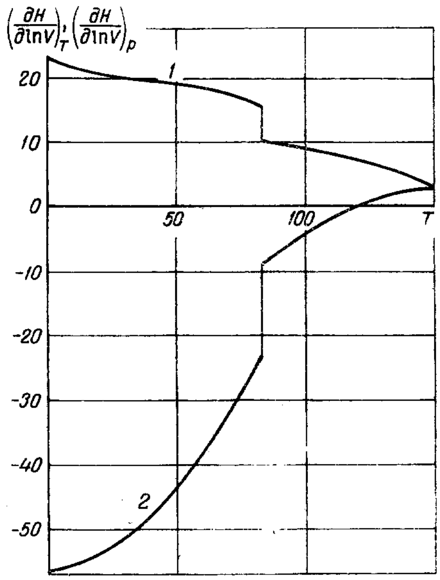

Fig. 1. Derivatives $(\partial H/\partial \ln V)_p$ (1) and $(\partial H/\partial \ln V)_T$ (2) as functions of the temperature T (°K), for argon. Units of the axis of ordinates 10^{-3} kJ/kmole.

The trend of the curves, which represent the variation of the said derivatives for all substances, leads one to the following conclusion: if at the absolute zero temperature the absolute value of derivative (2) is higher than or equal to the value of derivative (1), then both derivatives in the process of their variation with temperature pass through a point where

$$\left|\left(\frac{\partial H}{\partial \ln V}\right)_p\right| = \left|\left(\frac{\partial H}{\partial \ln V}\right)_T\right|. \tag{4}$$

At temperature T_E, the same relative change in volume due to cooling of the substance or due to compression of the substance by external pressure will be accompanied by the same absolute change in enthalpy. For argon this temperature T_E coincides, within experimental accuracy, with the melting temperature.

There exists a unique relation between the critical temperature and the T_E temperature which is due only to the sign difference between relations (3a) and (4). Only an examination of many substances and their diverse properties, however, will explain to what extent this formal correlation is significant.

NOTATION

T	is the temperature;
p	is the pressure;
V	is the molal volume;
H	is the molal enthalpy of a substance;
α	is the thermal volume expansivity;
β	is the isothermal compressibility;
C_p	is the molal heat capacity under constant pressure.