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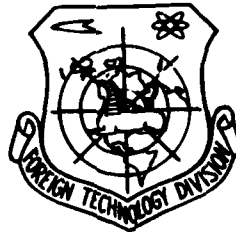
FOREIGN TECHNOLOGY DIVISION



PHASE TRANSFORMATION

by

E. Ciobanu



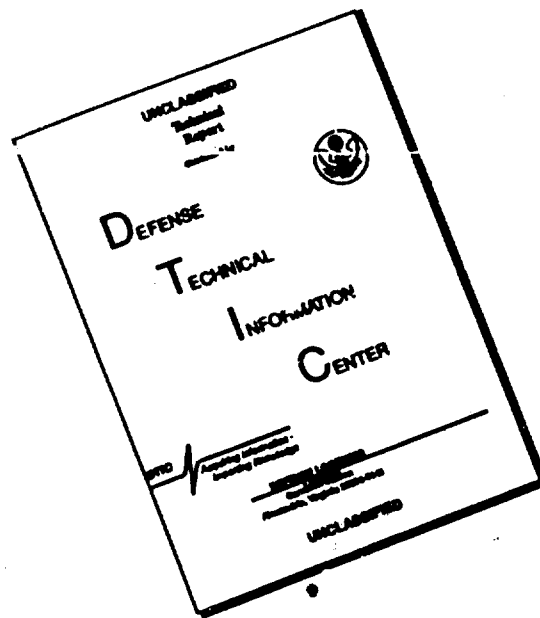
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13. ABSTRACT

equilibrium

A review is given of elementary thermodynamic theory of phase ~~equil~~ and phase transitions. The topics covered include phase transitions of the 1st and 2nd order, properties of the ~~crit~~ point, and the Clausius Clapeyron Equation. [AP0157745]

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PHASE TRANSFORMATIONS

Eleonora Ciobanu

1. Type I and II Phase Transformations

A phase represents the sum of all the homogeneous components within a thermodynamic system. Due to the absence of external forces, separation surfaces do not occur and no differences in composition properties exist. Within a phase, the parameters of state are the same for all volume elements, whose dimensions are large in comparison with the distances between atoms. For example, a gaseous mixture is a phase, provided the mixture has the same concentration throughout the volume.

The very same substance can be in equilibrium, whether within a single phase or multiple phases simultaneously, depending on the external conditions.

The transition of a substance from one phase into another is called phase transformation.

Phase transformations are of two types:

— Type I phase transformations are accompanied by a sudden variation of the internal energy and density. These transformations are associated with heat exchange between the substance and the medium, which represents the latent heat of transformation. Type I transformations are aggregation transformations of state, the transformations of allotropic states by crystals, and others.

— Type II phase transformations are accompanied by a sharp variation of the specific heat and of the expansion coefficient. Such a transformation is the transition of liquid helium in a super-fluid state. At low temperatures of $T = 2.2^\circ\text{K}$, and normal pressure in ${}^4_2\text{He}$ the so-called λ transformation occurs: the passage of liquid helium I into helium II. With an increase in pressure, the temperature of the λ transformation decreases. Superfluidity, which appears for liquid helium II, is the phenomenon of viscosity loss by flowing through very narrow capillary tubes (radius $\approx 10^{-5}$ cm). For this case, the coefficient of viscosity attains a value less than 10^{-11} poise. Another type II phase transformation is the passage, at the Curie point, of ferromagnetic substances into paramagnetic substances.

The temperature at which the passage from one phase into another occurs is called the transformation temperature. The following are type II transformation temperatures: melting temperature, boiling temperature, and sublimation temperature. These temperatures are pressure dependent. The value for the transformation temperature at normal pressure represents the transformation point. Thus, the melting point, boiling point, and sublimation point are characteristic of a substance in a pure state and are found in tabular form.

During type I transformations, the temperature remains constant (if the pressure is kept constant) and variations in volume and entropy occur. When the temperature remains constant, heat exchange occurs between the substance and the external medium. The heat exchanged per unit mass, during the transformation, bears the name of latent heat of transformation. In this fashion the latent melting heat (solidification); boiling heat (condensation), and sublimation heat are defined.

The graphic representation of the heat exchange between the body and the external medium, for a transformation which is produced with heat absorption, is given in Figure 1.

Q_2 — the heat exchange (the quantity of absorbed heat).

Q_1 — the quantity of heat absorbed until the start of the transformation.

$Q_2 - Q_1 = \Delta Q$ — is the total quantity of heat absorbed during the transformation.

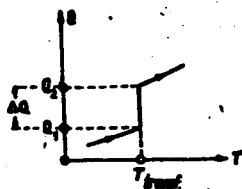


Figure 1.

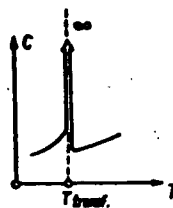


Figure 2.

$$\Delta Q = m\lambda \quad (1)$$

— m is the body mass

— λ is the latent transformation heat at a transformation temperature T .

The explanation for the latent absorption heat in a transformation of this type is simple. The transition from a phase with a specific density, into a phase of lower density requires a certain amount of energy, either for the destruction of the crystal network (melting), or for overcoming molecular cohesion and increasing the intermolecular spacing (vaporization). A quantity of energy equal to the potential energy of molecular interaction is absorbed. Since the total absorbed latent heat is equal to the potential energy of the cohesive forces, the intensity of the molecular thermal motion is not modified. For this reason, the temperature remains constant during the transformation. The increase in the amount of disordering within the system, due to these transformations, explains the entropy increase within the system:

$$\Delta S = \frac{m\lambda}{T}$$

For reverse phase transformations, the increase in molecular cohesion leads to a reduction in the molecular potential energy and the elimination of a certain quantity of heat. The average kinetic energy for the molecules remains the same, and the temperature stays constant during the transformation. This fact implies that, during type I transformations, the specific heat becomes infinite:

$$c_v = \lim_{T \rightarrow T_c} \left(\frac{dQ}{dT} \right) = \infty$$

In contrast to type I transformations, for type II the specific heat remains finite.

2. Phase Equilibrium

We shall study the particular case for the equilibrium between a liquid and a gaseous phase.

The perfect gas is an idealized limit of real gases. Real gases show a behavior analogous to perfect gases at very low pressures and elevated temperatures, but not at high pressures or low temperatures.

The perfect gas law states:

$$pv = RT \quad (2)$$

where: p — is the gas pressure;
 v — is the specific volume;
 R — is the specific gas constant;
 T — is the absolute temperature.

J. D. Van der Waals introduced a correction due to molecular interaction and due to the actual volume of the molecules, and obtained in 1862 the equation of state for real gases

$$\left(p + \frac{a}{v^2} \right) (v - b) = RT \quad (3)$$

where a and b are constants which depend on the nature of the gas.

The Van der Waals equation can be changed into the form

$$pv^3 - v^2(RT + pb) + av - ab = 0 \quad (4)$$

This third degree equation has three roots for the specific volume v , for p and T constant. For large T , two roots of the equation are imaginary. Thus, for a given pressure p , there is a single real value for the volume v . This case corresponds to the perfect gas. By representing the isotherms in the axis system (p, v) , equilateral hyperbolas are obtained. For small values of T , the three roots are real and for a given pressure value p , there are three values for the specific volume v . The Van der Waals isotherms in this region show both a maximum and a minimum value (Figure 3).

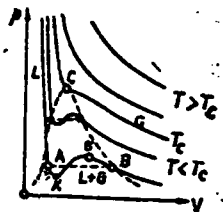


Figure 3.

The experimental isotherms, obtained by compressing a gas (CO_2 , for example), differ from the theoretical values. Thus, the segment AB, within which the maximum and minimum value must appear, is experimentally a straight-line segment. Gas liquefaction occurs in this region. The phenomenon occurs at a pressure called liquid vapor tension, which represents the liquids' saturated vapor pressure at the respective temperature. This region corresponds to the equilibrium state between the two phases: liquid and gaseous.

As the temperature increases, liquefaction occurs at higher pressures, which is explained by an increase of the liquid's vapor tension with temperature.

It was observed that, as long as the temperature increases, the region AB becomes narrower and for a specific temperature reduces to a point C. This is the critical point at which the gas transition occurs instantaneously.

Again, comparing the experimental isotherms with the Van der Waals isotherm, even in the equilibrium zone between the liquid and the gas, neither a maximum nor a minimum is obtained, although the regions AA' and BB' can be obtained experimentally. By slow heating of the purified liquid (without any vaporization centers) the portion AA' is obtained, corresponding to the super-heated liquid. Also, in the absence of condensation centers, the vapors can be compressed to a pressure which exceeds the vapor tension at the respective temperature. In this manner, the portion BB' is obtained, corresponding to a state of subcooled vapors. Both states (super-heated liquid and subcooled vapors) are unstable conditions,

and can only be maintained at very small perturbations. The region A'B' is completely unstable and cannot be obtained experimentally.

3. Properties of the Critical Point

By analyzing mathematically the critical point, it is observed that it possesses several unusual properties.

-- The coordinates of the critical point (p_c, v_c, T_c) verify the Van der Waals equation.

-- The tangent to the isotherm T_c , at the critical point, is horizontal, i.e.:

$$\left(\frac{\partial p}{\partial v}\right)_{T=T_c} = 0 \quad (5)$$

-- The critical point is the inflection point, i.e.:

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_c} = 0 \quad (6)$$

These three properties allow us to form a system of three equations (4), (5), (6). By resolving this system, the critical parameters are obtained (p_c, v_c, T_c) as a function of the constants a and b introduced by Van der Waals. Knowing from experience the critical values, the possibility arises for finding the constants a and b for the gas.

The substance behavior, in the vicinity of the critical point, proves that at this point the distinction between vapor and liquid disappears. We assume a system formed of two phases in equilibrium: a liquid and its saturated vapors. The variation of the specific volume with temperature is represented graphically, both for a vapor, as well as for a gas (Figure 4). An increase in temperature produces an increase in the liquid volume. The expansion coefficient is not constant (it increases with temperature), and the curve is concave upwards (AC).

The increase in temperature leads to an increase in the number of molecules leaving the liquid, and increases the density of the saturated vapor. Consequently,

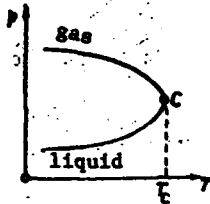


Figure 4.

the specific volume of the saturated vapor decreases (curve BC). The two curves cross at the point whose coordinates are (v_c, T_c) . At the critical point, the liquid's specific volume is the same as that of the saturated vapor. At this point, any distinction between liquid and vapor disappears.

The substance is in a state of opalescence, with the continuous appearance and disappearance of condensation centers in the vapor. In this state, the transition from the gaseous phase to the liquid phase occurs continuously, the latent heat of vaporization is zero, and the surface tension is zero.

The values of the critical parameters differ a great deal as a function of the nature of the substances, as indicated in the table below:

Substance	θ_c °C	p_c atm.
Nitrogen	-147.1	33.5
Hydrogen	-239.9	12.80
Air	-140.7	37.2
Helium	-267.9	2.26
Oxygen	-118.8	49.7
Neon	-228.65	26.86
Radon	104	62
Chlorine	144	76.1
Water	374.1	218.5
Carbon dioxide	31.1	73

Table derived from: "Tables of physical and chemical constants", G. W. Kaye, and T. H. Laby. Longmans, Green Co. London. New York. Toronto.

4. The Clausius-Clapeyron Equation

For type I transformations, the transformation temperature depends on the pressure. The curve which expresses this dependence for various transformations represents the equilibrium curve for the two phases of a substance. Mathematically, this dependence is expressed by the Clausius-Clapeyron equation.

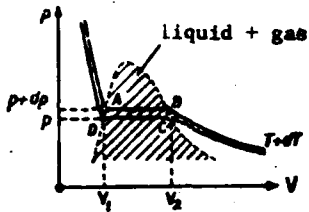


Figure 5.

This equation will be derived by thermodynamic methods for the case studied above relating to the equilibrium between a liquid and a gaseous phase.

In the transition to the liquid state region shown in the diagram (p, V) , the isotherms are horizontal. The volume modification is produced only by modifying the ratio between the quantity of liquid and gas, when the pressure is constant.

For each isotherm $T = \text{constant}$, the vapor tension varies. Therefore, $p = p(T)$.

By considering two very close isotherms T and $T + dT$ and the reversible cycle $ABCD$, the isotherm AB represents an expansion:

$$\Delta V = V_2 - V_1$$

The mechanical work necessary for this expansion measured by the area of the surface ABV_2V_1 is:

$$L_1 = (p + dp)(V_2 - V_1) \quad (7)$$

The heat transfer on mass m of substance, during this transformation, is:

$$Q_1 = m\lambda \quad (8)$$

where λ is the latent heat of transformation. The portion BC can be considered as an isochore $\Delta V = 0$, since the mechanical work is zero. The isotherm CD represents a compression during which the consumed mechanical work is:

$$L_2 = -p(V_2 - V_1) \quad (9)$$

equal to the area of the surface CDV_1V_2 .

The portion DA of the cycle can also be considered as the isochore, since the mechanical work is zero.

Since the cycle is considered reversible, its output is equal to that of the Carnot cycle, i.e.:

$$\eta = \frac{T + dT - T}{T + dT} \approx \frac{dT}{T} \quad (10)$$

using the general definition for the output:

$$\eta = \frac{L_1 + L_2}{Q_1} \quad (11)$$

where $L_1 + L_2$ represent the useful energy, and Q_1 is the energy used by the system. Taking into account (7), (8), (9), relation (11) becomes:

$$\eta = \frac{(p + dp)(V_2 - V_1) - p(V_2 - V_1)}{m\lambda} = \frac{dp(V_2 - V_1)}{m\lambda} \quad (12)$$

Introducing the specific volume $v = \frac{V}{m}$, the relation becomes:

$$\eta = \frac{dp(v_2 - v_1)}{\lambda} \quad (13)$$

Equating the output expressions (10) and (13), we obtain:

$$\frac{dp}{\lambda} (v_2 - v_1) = \frac{dT}{T} \quad \text{or:} \quad (14)$$

$$\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)}$$

This is the Clausius-Clapeyron equation.

From this equation, it is easy to establish the dependence of the transformation temperature upon pressure and the slope of the equilibrium curve.

For the particular case considered, $v_1 = v_L$ is the specific volume of the liquid phase; $v_2 = v_G$ is the specific volume of the gaseous phase.

$T = T_f$ is the boiling temperature

$\lambda = \lambda_v$ is the latent heat of vaporization at the boiling temperature.

From Equation (14), we obtain:

$$dT_f = \frac{T_f}{\lambda_v} (v_g - v_l) dp$$

Since in this case $v_g < v_l$, for any increase in pressure $dp > 0$, then $dT_f > 0$. Thus, the boiling point increases with pressure, a fact well known experimentally.

For equilibrium between the liquid and the solid phase (melting or solidification)

$v_1 = v_s$ the specific volume of the solid phase

$v_2 = v_L$ the specific volume of the liquid phase

$T = T_t$ the melting temperature.

Equation (14) yields:

$$dT_t = \frac{T_t}{\lambda_s} (v_s - v_L) dp$$

Since $v_L > v_s$ for $dp > 0$, then $dT_t > 0$, and the melting temperature increases with pressure.

For the case of sublimation, Equation (14) assumes the form:

$$dT_s = \frac{T_s}{\lambda_s} (v_s - v_g) dp.$$

and again the sublimation temperature rises with pressure.

The Clausius-Clapeyron equation leads to the determination of the slope of the equilibrium curves at any point, as long as the variation in volume and entropy is known for the transformation temperature.

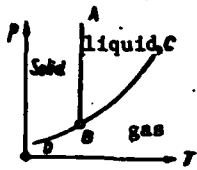


Figure 6.

Relation (14) gives the slope of the equilibrium curve between phases 1 and 2. λ and T are positive. Therefore, the sign of the curve's slope is determined by the sign of the volume's variation. For the equilibrium curve of a liquid gas, the slope is positive, as indicated in Figure 6 (curve BC).

The equilibrium curve between the solid and the liquid phase is a straight line (AB in Figure 6), which for the majority of substances has a positive slope.

There are a series of substances (Ge, Bi, Ga...B₂O₃, H₂O, etc.) for which the variation of the volume through melting is negative.

$$\Delta v = v_L - v_s < 0$$

For these substances, the melting curve has a negative slope.

The equilibrium curve of the solid phase with the gaseous phase, and the sublimation curve are given in Figure 6 by section DB.

The three equilibrium curves join into a point B called the triple-point, within which all three phases are in equilibrium. For water, for example, the triple-point is obtained at a temperature of 0.010°C at a pressure of 4.58 mm. Hg.

The curve for vapor tension has an upper limit denoted by the critical point C.

5. Conclusion

The thermodynamic method for studying systems in equilibrium is based upon the introduction of functions of state sufficiently adequate, denoted as thermodynamic potentials.

For processes produced at a constant temperature and pressure (a standard method of producing state transformations for units), the Gibbs thermodynamic potential function is introduced, which is defined by:

$$G = H - TS \quad (15)$$

where S is the entropy of the system and H the enthalpy.

$$H = U + pV \quad (16)$$

where U is the internal energy of the system.

Taking (16) into account, relation (15) becomes:

$$G = U - TS + pV \quad (17)$$

and:

$$U - TS = F \quad (18)$$

is the free energy of Helmholtz, and (17) becomes:

$$G = F + pV \quad (19)$$

By differentiating relation (18), one obtains:

$$dG = dF + pdV + Vdp \quad (20)$$

According to relation (18), we have:

$$dF = dU - Tds - SdT \quad (21)$$

Applying the 1st thermodynamic law:

$$TdS = dU + pdV \quad (22)$$

Relation (21) becomes:

$$dF = -pdV - TdS \quad (23)$$

Introducing Expression (23) into relation (20), we obtain:

$$dG = Vdp - SdT$$

Therefore:

$$\left(\frac{\partial G}{\partial p}\right)_{T-\alpha} = V \text{ si } \left(\frac{\partial G}{\partial T}\right)_{p-\alpha} = -S$$

for $p = \text{constant}$, $dG = -S dT$

for $T = \text{constant}$, $dG = V dp$.

When T and p are constant, $dG = 0$.

When a type I phase transformation occurs at a constant pressure, then the value for the Gibbs potential function for both phases is the same: $G_1 = G_2$.

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