

## 2.4 Stability of Phases

The stable equilibrium state of a system may be homogeneous for a given set of values of the intensive variables. But, there is no reason to suppose that it remains homogeneous for every set of values of these intensive variables.

It is possible that for a given set of values of these variables, the single phase becomes intrinsically unstable and spontaneously separates into two homogeneous parts (phases) which are in mutual equilibrium with each other.

Therefore, the problem of stability arises on two distinct levels: (a) *intrinsic* stability of a single homogeneous state (a phase), and (b) *mutual* stability of two co-existing phases of a system.

### 2.4.1 Intrinsic Stability of Homogeneous States

The basic extremum principle of thermostatics is that  $dS = 0$  and  $d^2S < 0$  (i.e., entropy maximum principle), or,  $dE = 0$  and  $d^2E > 0$  (i.e., energy minimum principle) or the equivalent extremum principles in terms of the various thermostatic potentials. The first part of this condition, namely, that the entropy is extremum, has been exploited so far but the second part of the condition, namely, the entropy is a *maximum* remains to be used. The latter decides whether or not a state of equilibrium is also state of *stable* equilibrium.

We illustrate the derivation of the condition(s) for intrinsic stability by studying a fluid; the corresponding conditions for a magnet can be written down from the well known analogy between fluids and magnetic systems.

#### •Intrinsic Stability of a Homogeneous Fluid

Since  $dE = TdS - PdV + \mu dN$ , and since the energy  $E(S, V, N)$  is a minimum in stable equilibrium,

$$(\partial^2 E / \partial S^2) = (\partial T / \partial S) > 0$$

and

$$(\partial^2 E / \partial V^2) = -(\partial P / \partial V) > 0$$

Therefore,

$$C_v = T(\partial S / \partial T)_{V,N} > 0 \tag{2.1}$$

and <sup>1</sup>

$$\kappa_T = -(1/V)(\partial V / \partial P)_{T,N} > 0 \tag{2.2}$$

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<sup>1</sup>Since, in general,  $C_p > C_v$ , (2.1) implies that  $C_p > 0$ .

The conditions (2.1) and (2.2) for intrinsic stability are special cases of a general principle known as

*Le Chatelier's Principle:* "If a system is in stable equilibrium, then any spontaneous change of its parameters must bring about processes which tend to restore the system to equilibrium". Suppose, the temperature  $T$  of the system  $A$  has increased spontaneously above that of its surroundings separated from it by a diathermal wall. Then, a process of heat transfer from  $A$  (which is at a higher temperature) to its surroundings must take place. This would lead to a decrease in the energy of  $A$  (i.e.,  $\Delta E < 0$ ). But, the stability condition expressed by Le Chatelier's principle requires that this process, induced by the original temperature increase, is such that the temperature is again decreased (i.e.,  $\Delta T < 0$ ), so that  $\Delta E$  and  $\Delta T$  must have the same sign and, hence,  $C_V > 0$ , which is the stability condition we have derived earlier from thermostatics. I leave it as an exercise to verify that this condition (2.2) for intrinsic stability is also consistent with Le Chatelier's principle.

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Solve problem 2.2.

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### •Intrinsic Stability of a Magnetic State

Drawing analogy between fluids and magnets, we know that the isothermal magnetic susceptibility  $\chi_T$  is the analogue of  $\kappa_T$  while the specific heats  $c_M$  and  $c_H$  are the analogues of  $c_V$  and  $c_P$ , respectively. Therefore, the conditions for the intrinsic stability of magnetic systems are

$$c_M > 0, \quad c_H > 0, \quad \chi_T > 0. \quad (2.3)$$

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Solve problem 2.3.

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### •General Conditions for the Intrinsic Stability

Generalizing our observations in the preceding sections we conclude that for the intrinsic stability of a homogeneous state (phase) the response functions must be positive. However, it is worth emphasizing that these conditions were derived considering small variations in temperature, volume, etc. and, therefore, the states satisfying these conditions are certainly in "local equilibrium". But, a state which satisfies these conditions need not be the state of "global equilibrium" of the system. More detailed discussions on this point will be presented later in section 2.5.

## 2.4.2 Mutual Stability of Coexisting Phases

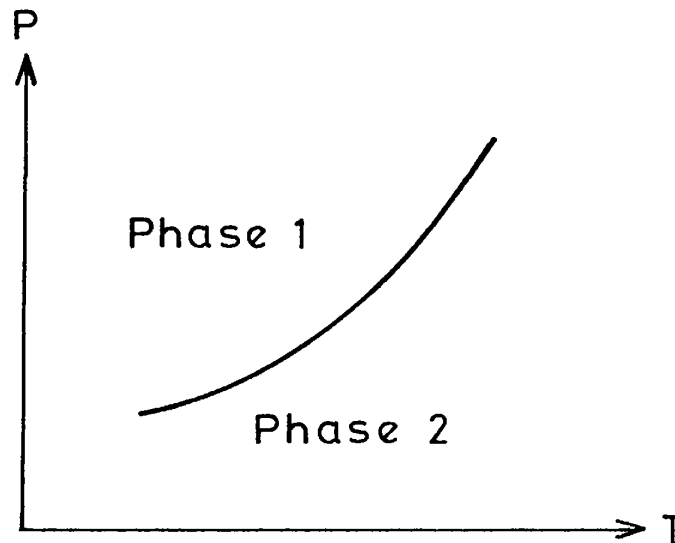
If the criteria for the intrinsic stability of a phase are not satisfied the homogeneous system breaks up into two or more coexisting phases and, thus, becomes inhomogeneous. This spontaneous separation is called a *first order phase transitions*; the reason for this choice of terminology will become clear a little later in this chapter. Instead of abstract discussion we develop the theory for a fluid system; we can later generalize the results for any arbitrary system through analogy.

### •Two Coexisting Phases

Since the two phases coexisting in equilibrium may be regarded as two substances which can exchange heat, volume and matter, we must have

$$T_1 = T_2; \quad P_1 = P_2; \quad \mu_1 = \mu_2$$

where  $T_1, P_1, \mu_1$  and  $T_2, P_2, \mu_2$  are the temperatures, pressures and chemical potentials, respectively, of the two phases.



**Fig.2.4:** Phases 1 and 2 coexist along the continuous curve.

But, because of the Gibbs-Duhem relation, only two of these three intensive variables are independent. Suppose we take  $T$  and  $P$  as the independent variables. Then, denoting the common temperature and common pressure by  $T$  and  $P$ , i.e.,  $T_1 = T_2 = T$  and  $P_1 = P_2 = P$ , the condition for

equilibrium is

$$\mu_1(P, T) = \mu_2(P, T) \quad (2.4)$$

Equation (2.4) implies that on the  $P - T$  plane two phases cannot coexist in mutual equilibrium at all  $P$  and  $T$ . Since  $\mu_1(P, T)$  and  $\mu_2(P, T)$  are two different two-dimensional surfaces in the  $(\mu, P, T)$  space, equation (2.4) describes the curve of their intersection and the two phases can coexist only along this curve (see fig.2.4). Thus, if either the temperature or the pressure for the two-phase equilibrium is given the other is completely determined.

Now recall that, from the definition of the Gibbs potential  $G = E - TS + PV$  and the Euler relation  $E = TS - PV + \mu N$  for a single-component simple fluid, the *molar Gibbs potential*  $g = G/N$  is identical with  $\mu$ . In fact, because of this relation, the chemical potential is sometimes referred to as the molar Gibbs potential. From now onwards, we shall use  $\mu$  and  $g$  interchangeably in our discussions in this section. The condition (2.4) can also be written as

$$g_1(P, T) = g_2(P, T) \quad (2.5)$$

The two curves in fig.2.5(a) represent the molar Gibbs potentials of the two phases as functions of temperature at a given fixed pressure  $P_0$ . Since, entropy  $s = -(\partial g / \partial T)_P$  must be positive, the slope of the  $g(T)$  curve has to be negative as in fig.2.5(a). The point of intersection of the two curves satisfies the condition (2.5); the temperature  $T_0$  corresponding to this intersection is the temperature at which the two phases can coexist in equilibrium provided the common pressure of the two phases is the given pressure  $P_0$ . At any other temperature (for the given pressure  $P_0$ ) only one or the other of the two phases can exist in equilibrium. Since the stable equilibrium state corresponds to the lowest value of  $g$  for a given  $T$  (and  $P$ ), in fig.2.5(a) the phase labelled by 1 is stable at  $T < T_0$  and the phase labelled by 2 is stable at  $T > T_0$ . Similarly, a section through the  $g$ -surfaces in a plane of constant temperature is shown in fig.2.5(b); the slope of the  $g(P)$  curve is positive as  $v = (\partial g / \partial P)_T$  must be positive.

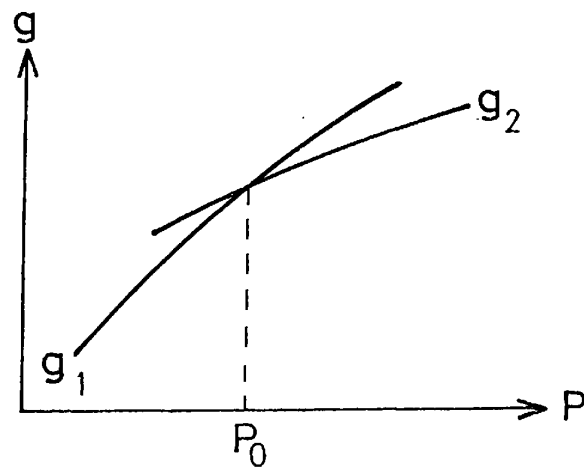
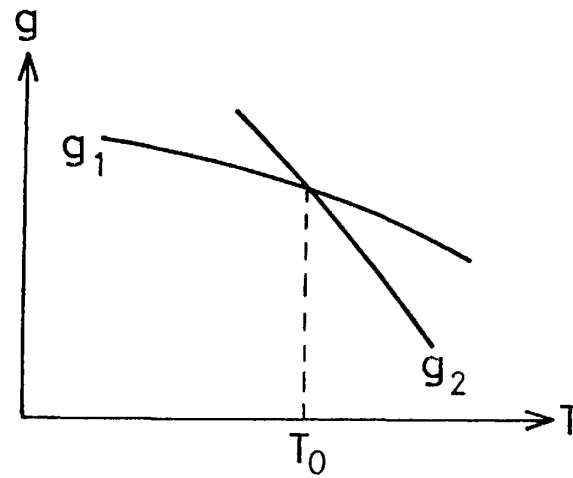
Since in fig.2.5(a) at the point of intersection  $T = T_0$ ,

$$(\partial \mu_1 / \partial T)_{P_0, T_0} > (\partial \mu_2 / \partial T)_{P_0, T_0}$$

and since  $s = -(\partial \mu / \partial T)_P$ , we have  $T_0 s_1 < T_0 s_2$ , i.e.,

$$q = T_0(s_2 - s_1) > 0$$

where  $q$  is the latent heat of the transition.



**Fig.2.5:** A section through the  $g$  surfaces in a plane of (a) constant pressure; (b) constant temperature.

If the phase transition is between the liquid and gaseous phases the latent heat is called the heat of vaporization; if the transition is between the solid and the liquid phases the latent heat is called the heat of fusion whereas for

transitions between the solid and gaseous phases the corresponding latent heat is called the heat of sublimation.

Thus, if you prepare a cup of tea, you first heat the water up to its boiling temperature near  $100^\circ\text{C}$ . From then on all additional heat is used to transform liquid water into vapour while the temperature remains constant. Only when all the liquid has evaporated, which takes much more energy than to heat it to 100 degrees, does the temperature rise further and may start a fire. Thus put the boiling water quickly over your tea leaves and thank Nature for having invented latent heat.

### Clausius-Clapeyron Equation

As stated before, at the two-phase coexistence  $P$  and  $T$  are not independent of each other. Suppose, we treat  $T$  as the independent variable and  $P$  to be a function of  $T$ . Then, taking derivatives with respect  $T$  of both sides of equation (2.4) we get

$$(\partial\mu_1/\partial T)_P + (\partial\mu_1/\partial P)_T(dP/dT) = (\partial\mu_2/\partial T)_P + (\partial\mu_2/\partial P)_T(dP/dT) \quad (2.6)$$

But, from the Gibbs-Duhem relation we have

$$(\partial\mu/\partial T)_P = -(S/N) = -s \quad (2.7)$$

and

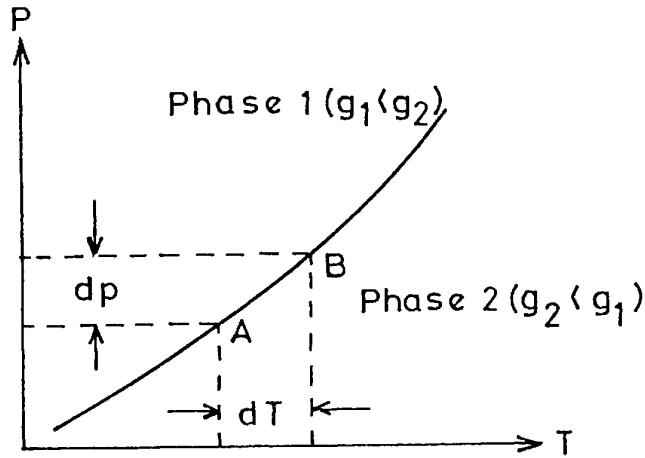
$$(\partial\mu/\partial P)_T = (V/N) = v. \quad (2.8)$$

Substituting (2.7) and (2.8) into (2.6) we get

$$(dP/dT) = [(s_1 - s_2)/(v_1 - v_2)] = q/[T(v_2 - v_1)] \quad (2.9)$$

where  $q = T(s_2 - s_1)$  is the latent heat of the transition. The equation (2.9) is called the Clausius-Clapeyron equation. Thus, the Clausius-Clapeyron equation can be interpreted as follows: consider any point  $(P, T)$  on the phase equilibrium curve on the  $P - T$  plane. Then, the Clausius-Clapeyron equation relates the slope of the phase-equilibrium curve at this point to the entropy change  $\Delta s$  and the volume change  $\Delta v$  of the substance in crossing the line at this point, i.e., in undergoing a change of phase at this temper-

ature and pressure.



**Fig.2.6:** Derivation of the Clausius-Clapeyron equation.

In order to gain further insight into the physical significance of the Clausius-Clapeyron equation let us focus our attention on fig.2.6.

$$g_1(T, P) = g_2(T, P) \text{ at point } A \quad (2.10)$$

and

$$g_1(T + dT, P + dP) = g_2(T + dT, P + dP) \text{ at point } B \quad (2.11)$$

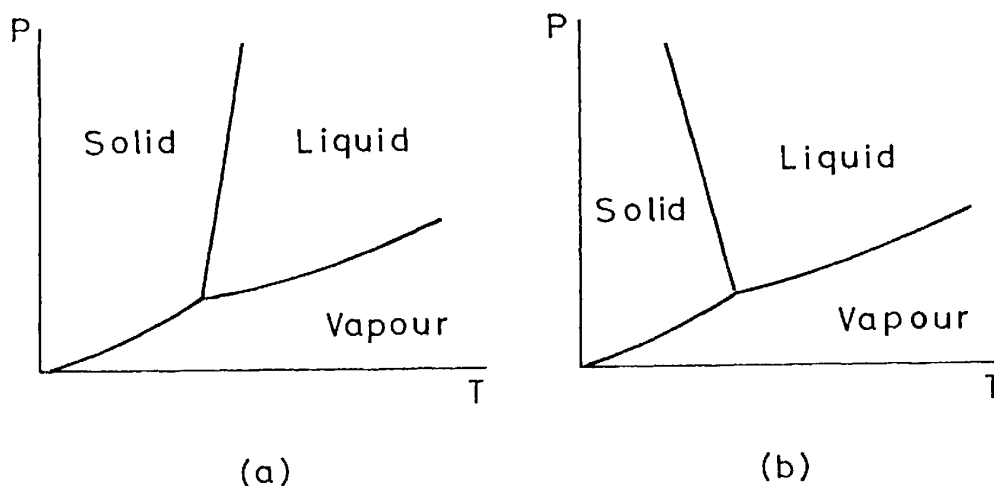
Expanding equation (2.11) around  $(T, P)$  and using equation (2.10) we get

$$\begin{aligned} & (\partial g_1 / \partial T)_P dT + (\partial g_1 / \partial P)_T dP \\ & = (\partial g_2 / \partial T)_P dT + (\partial g_2 / \partial P)_T dP \end{aligned}$$

which leads to the equation (2.6) as  $\mu$  and  $g$  are identical. It gives the change in the pressure of the phases in equilibrium when the temperature changes, i.e., the rate of change of pressure with temperature along the curve of two-phase equilibrium in the  $P - T$  plane.

Now consider the specific case of the liquid-vapour phase transition in a fluid. Since the molecular volume of the gas is always larger than that of the liquid, and heat is absorbed in the passage from the liquid to the vapour phase, we have  $(dT/dP) > 0$ , i.e., the boiling point always rises

with the increase of pressure, a well known empirical fact. In contrast to this, the melting point of a solid may rise or fall with the increase of pressure depending on whether the specific volume of the liquid is larger or smaller than that of the solid (see fig.2.7).



**Fig.2.7:** Phase diagrams of (a) typical substances which expand on melting (b) water which expands on freezing.

### Saturated Vapour Pressure of a Solid: An Application of the Clausius-Clapeyron Equation

From the Clausius-Clapeyron equation we have

$$(dP/dT) = L_{sg}/[T(v_g - v_s)]$$

where the subscripts  $s$  and  $g$  refer to the solid and gaseous phases, respectively, and  $L_{sg}$  is the molar latent heat of sublimation;  $v$  being the mole-specific volume. Consider very low temperature and pressure. At very low pressure we can use the ideal gas law for the gaseous phase, i.e.,  $Pv_g = \mathcal{R}T$ . Moreover, since the density of solids is much greater than that of the vapour,  $v_g - v_s \simeq v_g$ . Therefore,

$$(dP/dT) \simeq L_{sg}/(Tv_g) = (L_{sg}P)/(\mathcal{R}T^2)$$

and, hence,

$$P \propto \exp[-L_{sg}/(\mathcal{R}T)]$$



Moreover,

$$L_{sg} = (\epsilon_g - \epsilon_s) + P(v_g - v_s)$$

where  $\epsilon_g - \epsilon_s$  is the change in the internal energy caused by the transfer of one mole from the solid to the gaseous phase. But,  $P(v_g - v_s) \simeq Pv_g = \mathcal{R}T$  which is negligibly small compared to  $\epsilon_g - \epsilon_s$  provided the temperature is sufficiently low. Therefore,  $L_{sg} \simeq (\epsilon_g - \epsilon_s)$  and, finally,

$$P \propto \exp[-(\epsilon_g - \epsilon_s)/(RT)] \quad (2.12)$$

The equation (2.12) has been found to be in excellent agreement with experimental data for many substances.

### •Three Coexisting Phases

In order that three phases with intensive variables  $(T_1, P_1, \mu_1)$ ,  $(T_2, P_2, \mu_2)$  and  $(T_3, P_3, \mu_3)$  coexist in mutual equilibrium we must have  $T_1 = T_2 = T_3 = T$ ,  $P_1 = P_2 = P_3 = P$ ,  $\mu_1 = \mu_2 = \mu_3 = \mu$ , or, equivalently,

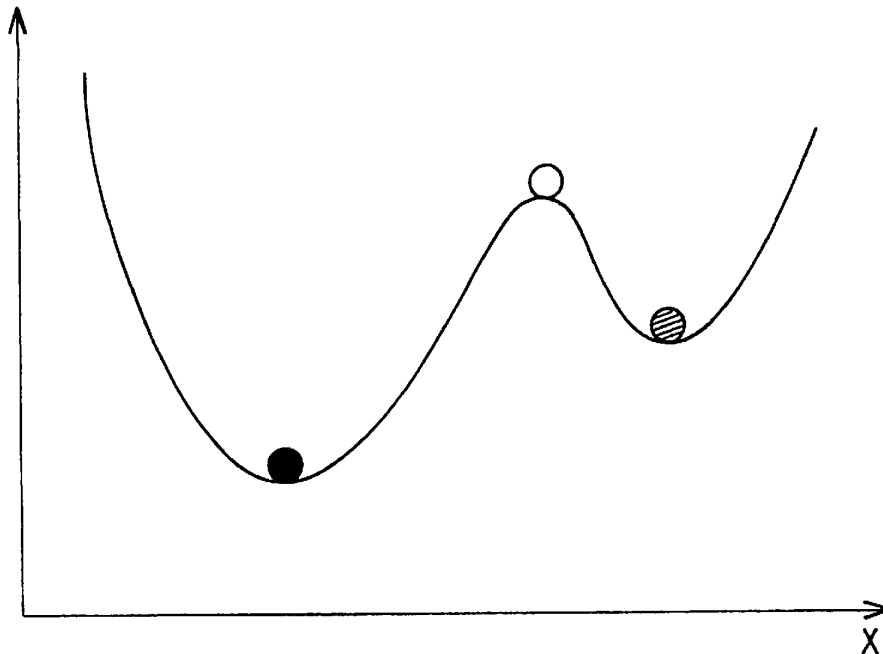
$$\mu_1(P, T) = \mu_2(P, T) = \mu_3(P, T) \quad (2.13)$$

Since the intersection of the planes  $\mu_1(P, T)$  and  $\mu_2(P, T)$  is a curve, that between  $\mu_2(P, T)$  and  $\mu_3(P, T)$  is another curve and that between  $\mu_3(P, T)$  and  $\mu_1(P, T)$  is yet another curve, these curves of intersection meet at a special point described by the equation (2.13). This special point where all the three phases coexist simultaneously in mutual equilibrium is called the *triple point* (see fig.2.1).

## 2.5 Stable, Metastable and Unstable States

The concepts of stable, unstable and metastable states are very familiar in mechanics. Consider, for example, a particle sitting at rest in a groove inside a wire which has the shape shown in fig.2.8. All the locations of extrema of this curve, shown in fig.2.8, can be regarded as positions of equilibrium for the particle. However, the particle is in *unstable* equilibrium when at the maximum of the curve, as any infinitesimal perturbation in its position takes it away from the top of the potential "hill" thereby lowering its gravitational potential energy. On the other hand, the position of the left minimum is identified as the state of *stable* equilibrium because the gravitational potential energy has a *global* minimum in this position. Note that the positions of both the minima correspond to *local* minima of the gravitational potential energy of the particle and, therefore, both these states are stable against infinitesimal perturbations in the corresponding positions, but the

right minimum does not correspond to the *global* minimum of the potential energy and, hence, identified as *metastable*.

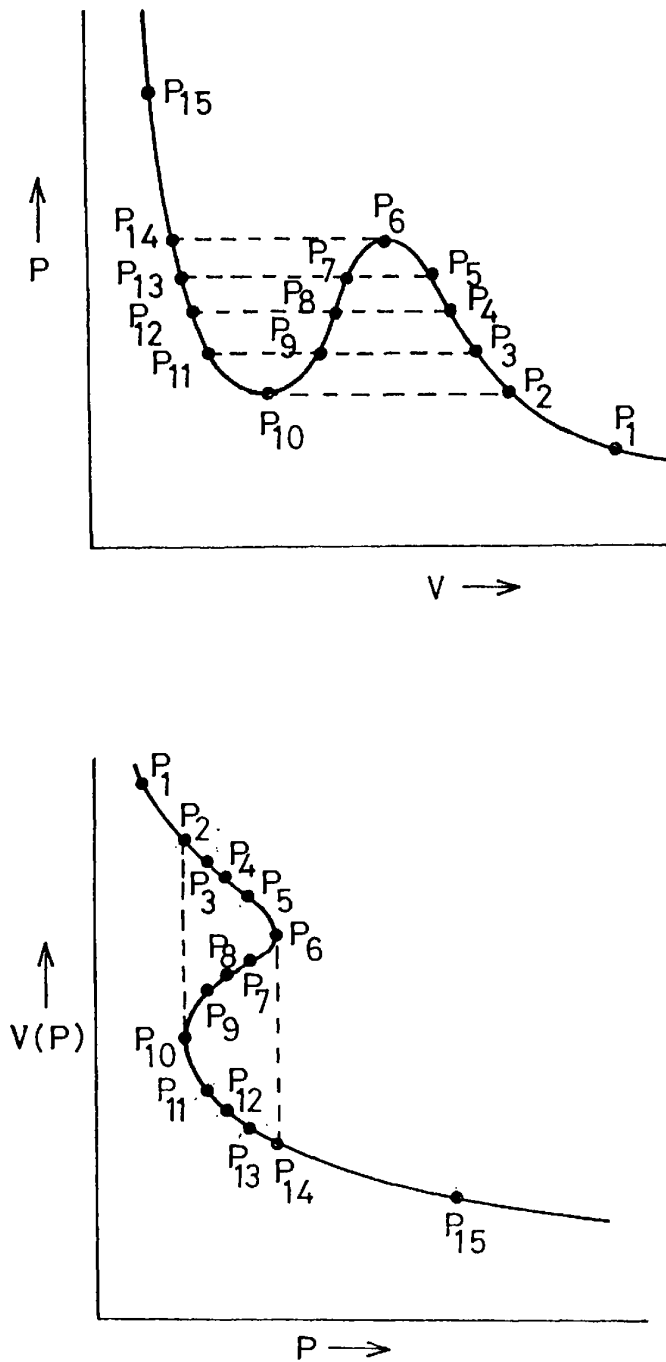


**Fig.2.8:** Concepts of stable, unstable and metastable states.

As explained in chapter 1, the thermostatic states of equilibrium of a system corresponds to the extrema of the appropriate thermostatic potentials. As the conditions of intrinsic stability were derived in section 2.4 from *local* stability analysis, these are satisfied by both stable and metastable thermostatic states. In other words, a state with all positive response coefficients may still be metastable rather than being stable.

Supercooled liquids, supersaturated solutions, etc. are examples of metastable states in real physical systems. However, in this section we investigate the metastability and instability in the Van der Waals fluid and its magnetic counterpart (a Curie-Weiss magnet); the metastable and unstable branches of the isotherms in these model systems are artefacts of approximations

made in their derivations which will be presented in chapter 10.



**Fig.2.9:** (a) A typical isotherms of the Van der Waals fluids below  $T_c$  on (a) the  $P - V$  diagram, (b) the  $V - P$  diagram.