- Consider the transition of a solid to liquid at constant T.
  - The solid phase is distinct from the liquid phase.
  - The solid phase has a well defined crystalline structure.
  - Thus the environment of a molecule in that solid is different from the environment of a molecule in a liquid.
  - In a liquid (or in a amorphous solid such as a glass), long range molecular order is absent.
  - Note that an amorphous solid does not have a sharp phase transition and thus is not distinct from the liquid phase.
- A phase transition occurs at a sharp temperature.
  - However this temperature depends on pressure.

- A phase transition is accompanied by an enthalpy change.
- Two phases can coexist in any proportion at the transition temperature for a particular pressure.
  - At other temperatures at the same pressure (or other pressures at the same temperature) only one phase or the other is stable.
  - The vapour-liquid coexistence curve may be thought of as dividing the (p, T) plane into two regions (see Figure 24.1).
    - In one region, the liquid is the stable phase.
    - In the other region, the gas is the stable phase.
  - A phase transition may also be considered in the (v, T) plane (see Figure 24.2).
    - At constant temperature a gas can be compressed until condensation occurs.

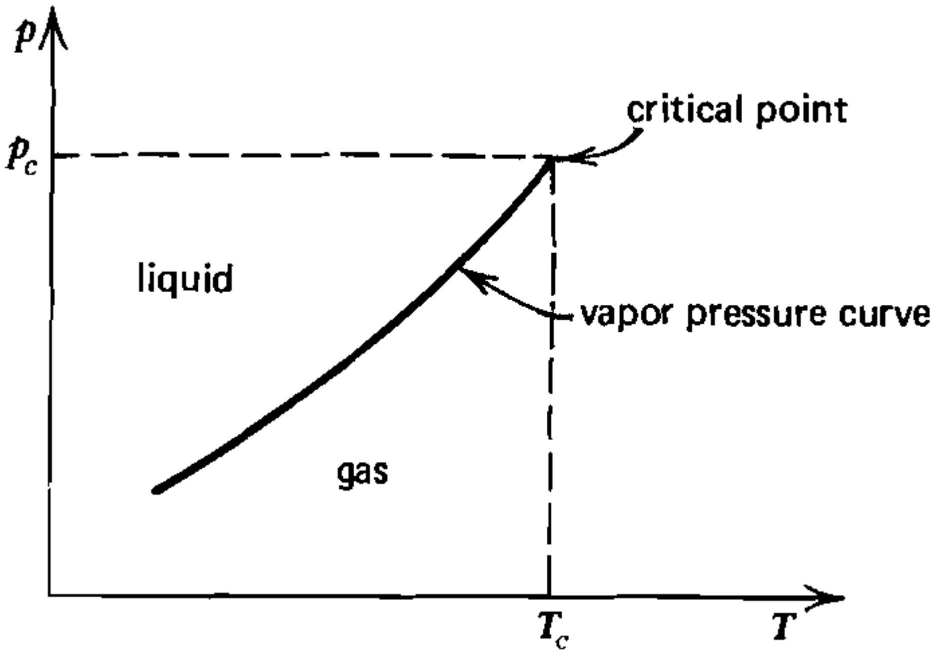


Figure 24.1 Schematic diagram of a vapor pressure curve.

transition is easily appreciated when the (V, T) plane is examined (see Fig. 24.2). Suppose that a gas with volume V_a is compressed at constant temperature until condensation begins, which occurs at $V = V_G$. As the system is compressed further, the amount of gas in the system decreases while the amount of liquid increases. When $V = V_L$, the substance is entirely converted to liquid. Consider the point D in Fig. 24.2. Let the fractions of gas and liquid at D be x and $1 - x$. Then the total volume of the system is

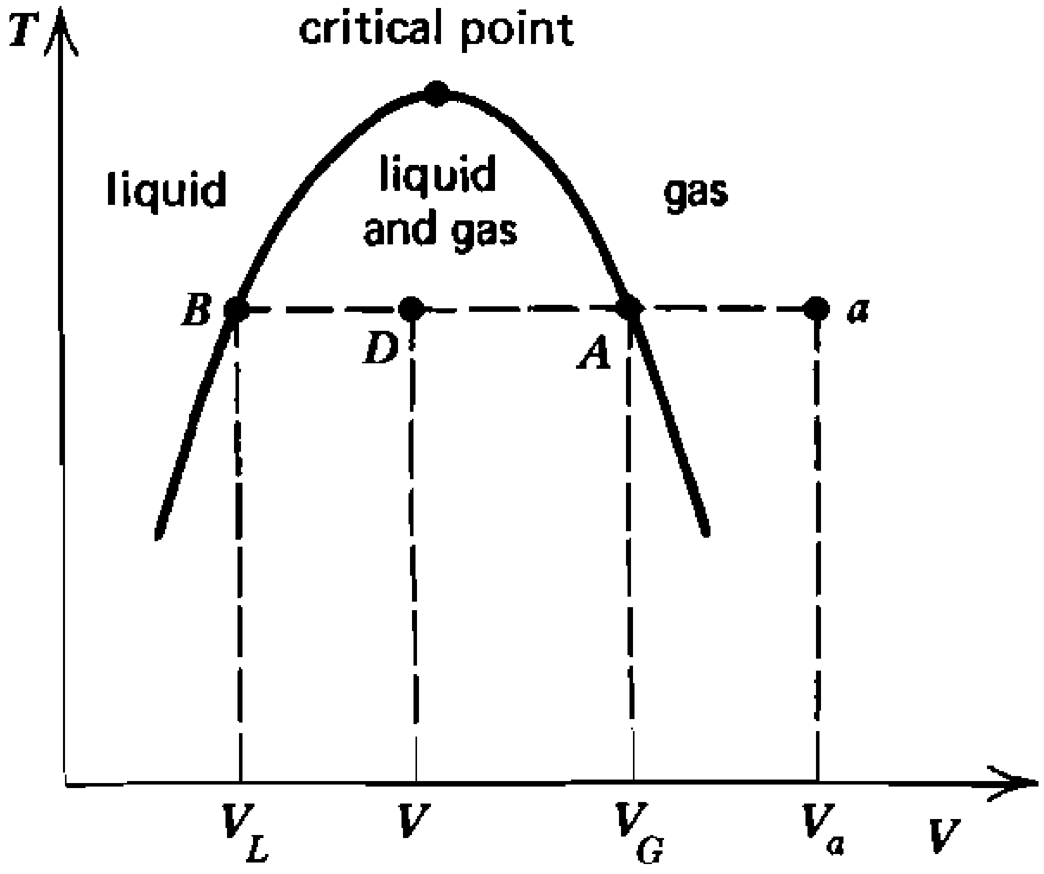


Figure 24.2 Schematic diagram of the coexistence region of liquid–gas equilibrium in the (V, T) plane. The line *aADB* represents the condensation path described in the text.

- Condensation will occur when the volume reaches V_G, the volume of the gas at the pressure equal to the vapour pressure.
- As the gas is compressed further, more liquid appears.
- The volume decreases until the volume reaches V_L, the volume of the liquid at the vapour pressure.
- The proportion of substance is each phase is determined by the lever rule.
- Let x be the mole fraction in the gas phase.
- Then $1 - x$ is the mole fraction in the liquid phase.
- The total volume of the system is:

$$V = xV_G + (1 - x)V_L$$

- This may be rearranged to:

$$x = \frac{V - V_L}{V_G - V_L}$$

$$1 - x = \frac{V_G - V}{V_G - V_L}$$

- The mole ratio of gas to liquid is:

$$\frac{x}{1-x} = \frac{V - V_L}{V_G - V} = \frac{\text{length } BD}{\text{length } AD}$$

- In both (T, V) and (p, V) planes, coexistence of two phases defines an area.
  - This is a consequence of coexistence requiring that the phases have the same pressure and temperature, but not the same density.

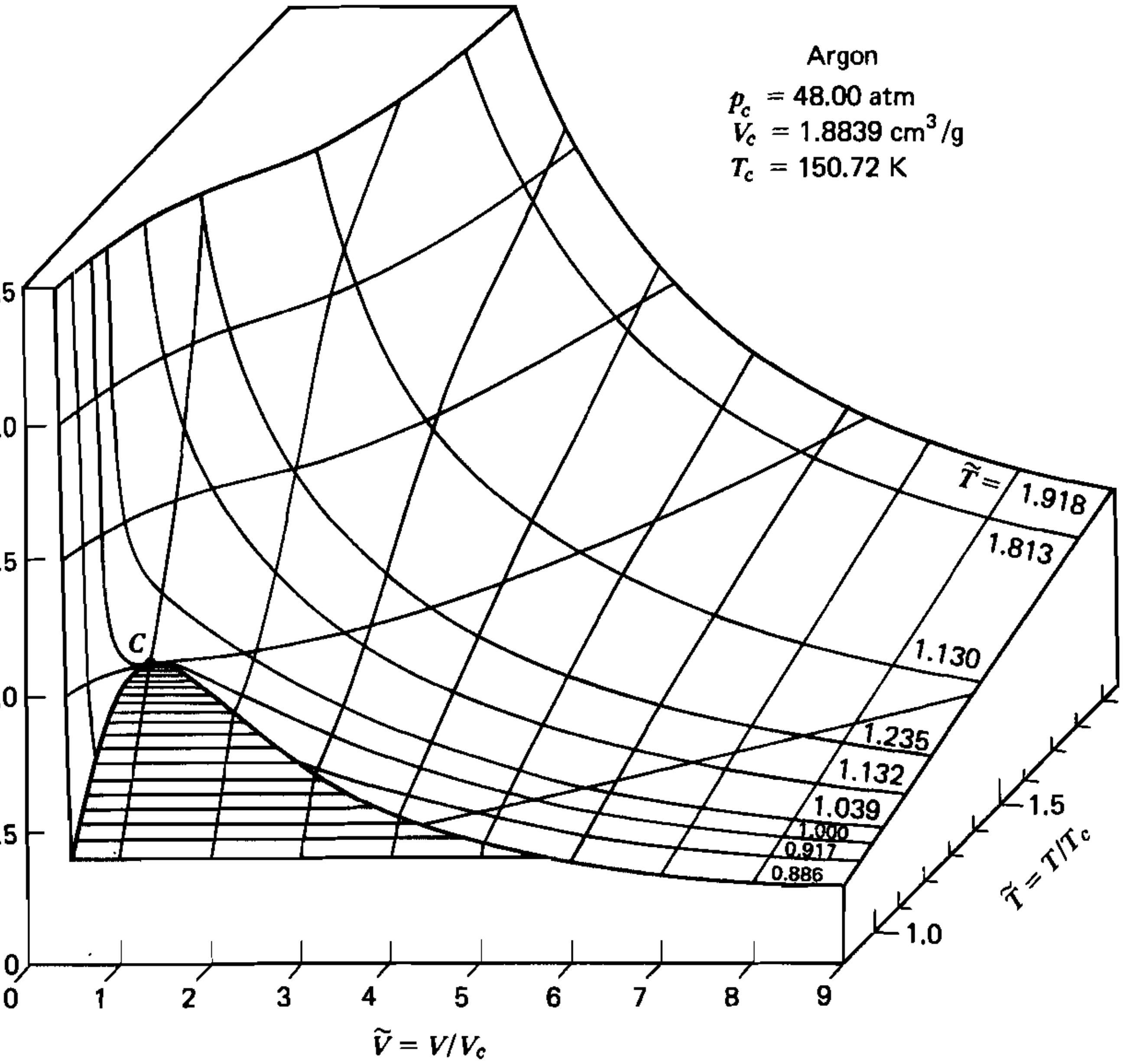


Figure 24.3 Part of the (p, V, T) surface of argon, showing lines of constant p, V, and T.

- Consider the (p, V, T) surface shown in Figure 24.3.
- Note that at the critical point, the density of the liquid phase converges to that of the gas phase in both the (p, V) plane and the (V, T).
- The existence of the critical point is indicative that there is no fundamental difference between liquid and gas.
  - In both liquid and gas, the local structure around a molecule has a spherical symmetry.
  - Thus both phases are isotropic.
- If two phases exist and the internal symmetries are different (at least one is anisotropic), then a critical point does not exist.
  - The densities could become equal, but the phases can be distinguished on the basis of internal symmetry.

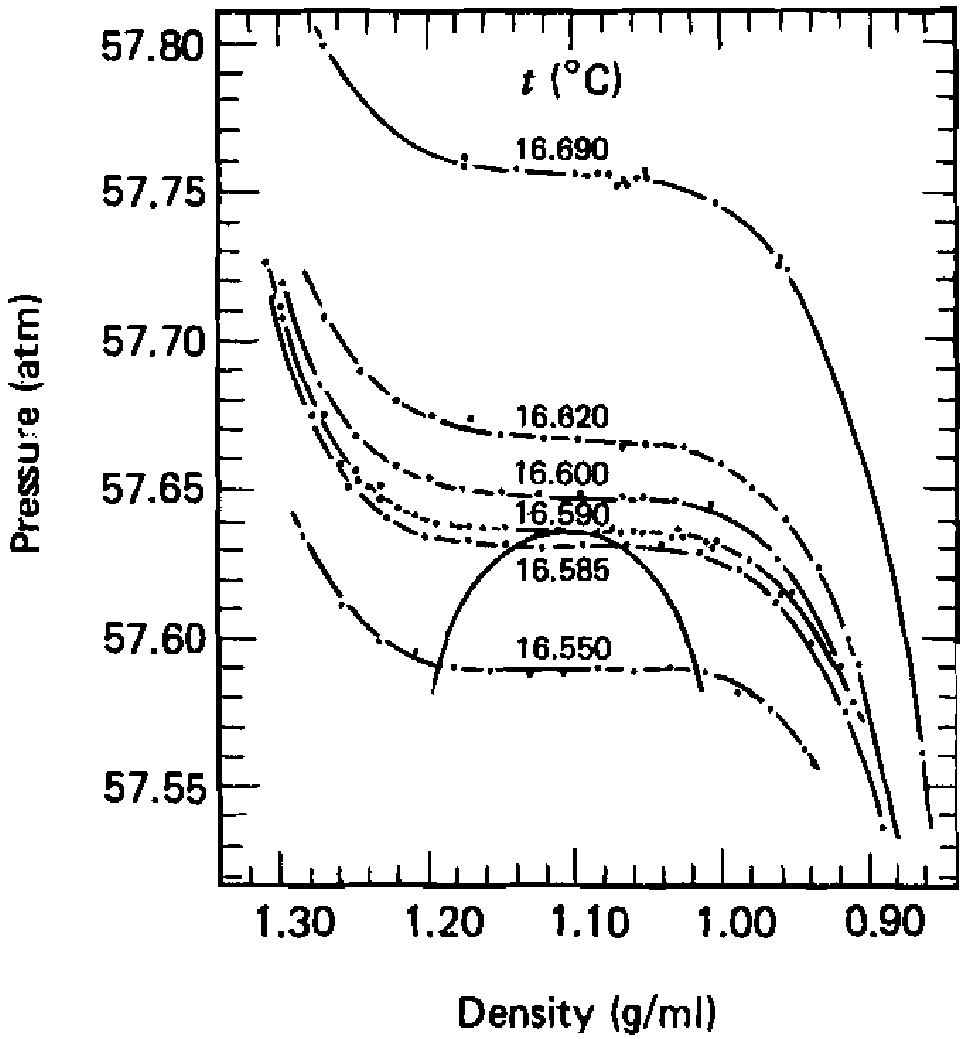
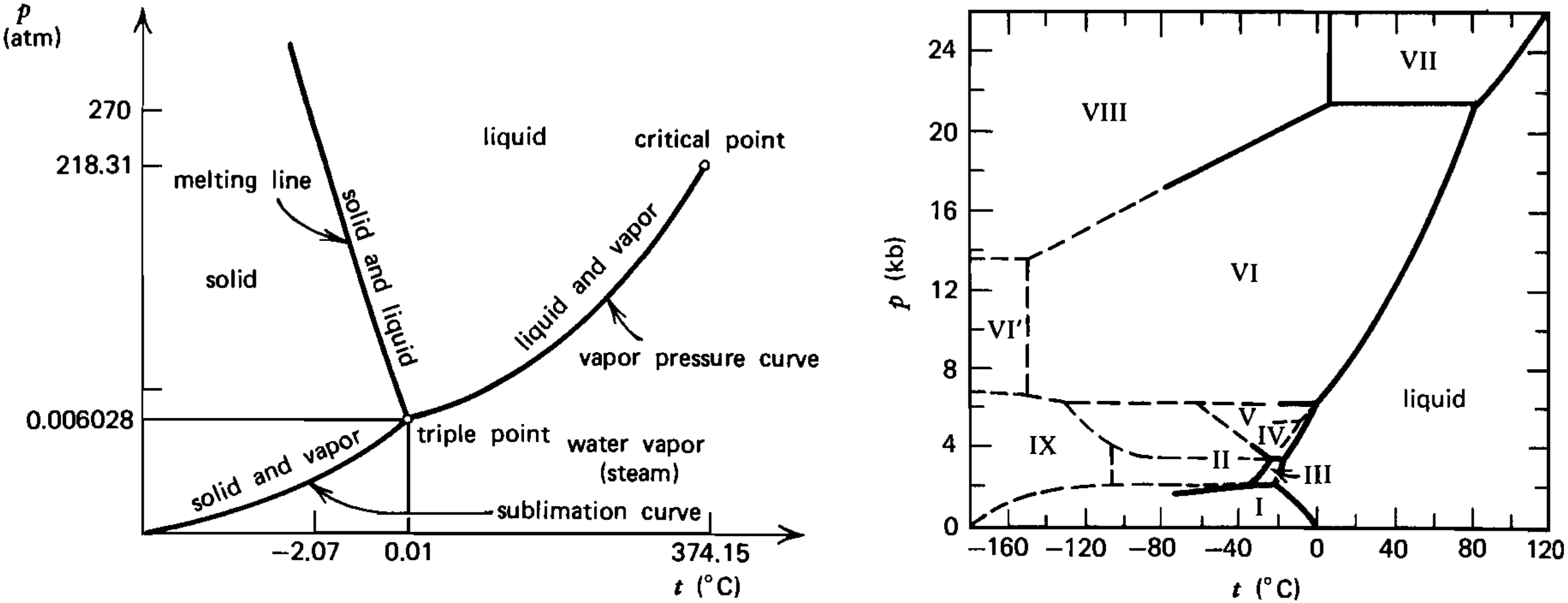


Figure 24.4 Experimental pressure against density isotherms in the critical region of xenon. From H. W. Habgood and W. G. Schneider, *Can. J. Chem.* **32,** 98 (1954).



(a) *(b)*

Figure 24.5 Phase diagrams for water. (*a*) Low-pressure ice–water vapor–liquid equilibrium. From J. Kestin, *A Course in Thermodynami* (Blaisdell, Waltham, Mass., 1966). (*b*) High-pressure equilibria among various forms of ice. From B. Kamb, in E. Whalley, S. Jones, ar L. Gold (Eds.), *Physics and Chemistry of Ice* (University of Toronto Press, Toronto, 1973).

- In a phase, a particular symmetry property either exists or does not exist.
- It is a property of all molecules of the phase as a whole.
- It cannot be partially present.
- Different crystalline of a particular substance forms are different phases.
- Usually, different crystalline forms have different densities.
- They can coexist along certain (p, T) curves in the (p, T) plane.
- If a coexistence curve is crossed, there will be a spontaneous phase transition and one crystal form will change into the other accompanied by an enthalpy change.

- Most phase transitions, liquid-gas, solid-gas, liquid-solid and some crystal-crystal phase transitions involve a discontinuous change in density across the coexistence curve.
  - This discontinuity in density is accompanied by discontinuities in entropy, internal energy, and specific heat.
  - Such phase transitions are phase transitions of the first kind and are known as first-order phase transitions.
- In principle, it is possible to have a change in the type of symmetry without discontinuities in density, entropy, or internal energy.
  - Consider the case of a tetragonal crystal with unequal edges a and c and $c > a$.

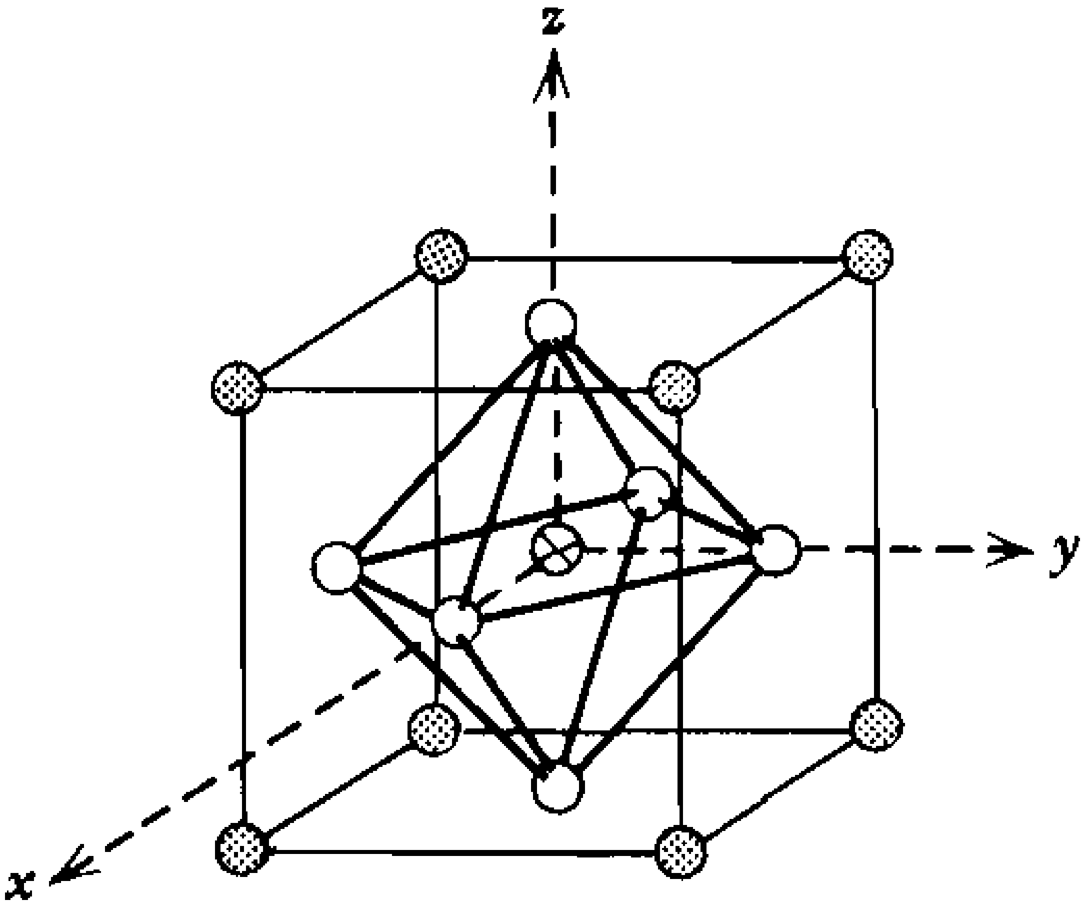
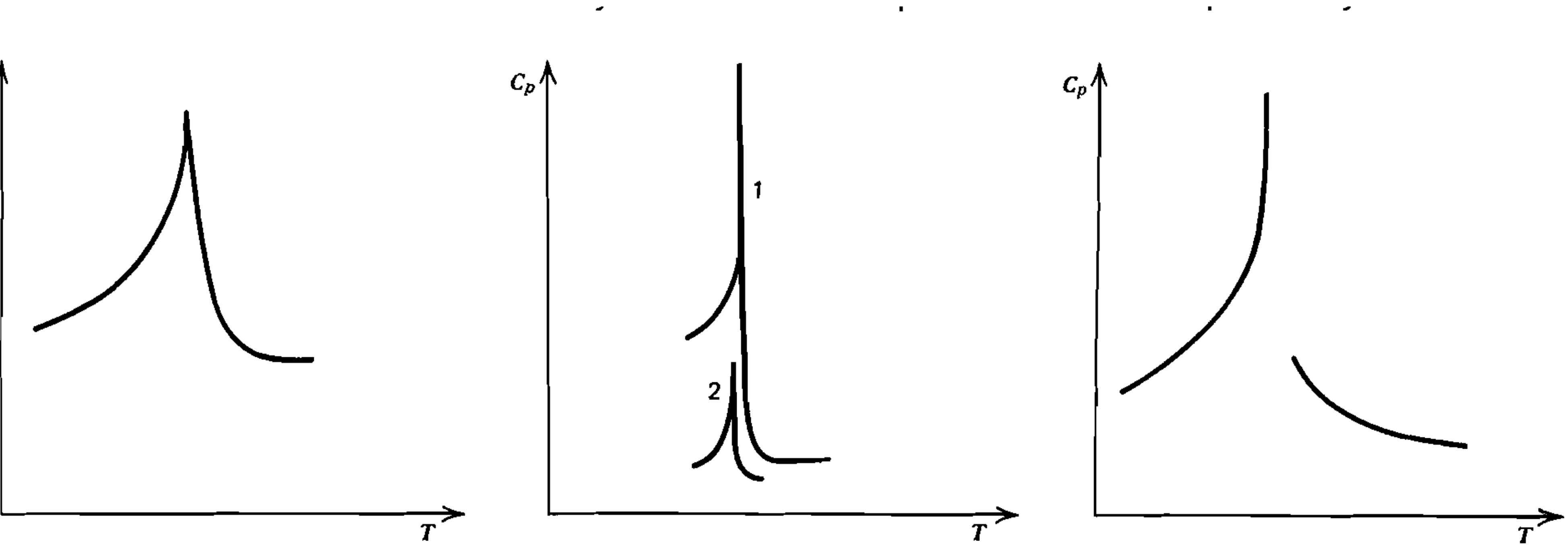


Figure 24.6 Schematic diagram of the unit cell of the cubic pero skite structure with the B ion at the center: ●A, ⊗B, ○O. The ge eral chemical formula is ABO_3.

- These edges change with length with temperature, but at different rates such that:

$$\left(\frac{\partial a}{\partial T}\right)_p > \left(\frac{\partial c}{\partial T}\right)_p$$

- Then there exists some temperature at which $a = c$ and the symmetry has become cubic.
- In this case, the change in symmetry is not accompanied by a discontinuous change in the thermodynamic properties of the crystal.
- This is an example of a transition of the second kind or a second-order transition.
- Second order transitions are not common, but have been observed for perovskites (ABO_3)



4.7 Some schematic heat capacity versus temperature curves near transition points. (*a*) Order–disorder transition in a binary alloy.
id–gas transition; curves 1 and 2 are approximately to scale for argon and helium, respectively. (*c*) Order–disorder transition in a
the curve is for nickel chloride hexahydrate.

Thermodynamics of Phase Equilibria in One-Component Systems

- When two phases of a one component system are in equilibrium, their chemical potentials, temperatures, and pressures are equal.
- Consider a phase transition of the first kind.
  - For each (T, p) at which liquid and gas coexist,

    $$\mu^L(T, p) = \mu^G(T, p)$$

    .
  - If the equations of state are known, then this can be used to determine the pressure as a function of temperature.
  - Usually, the equations of state of both phases are not known.

- Note that
$$d\mu^L(T,p) = d\mu^G(T,p)$$
at all points on the coexistence curve.
- Therefore, for two phases to remain in equilibrium, a change in the chemical potential of one must be matched by a change in chemical potential of the other.
- But the system is a one-component closed system.
$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dp$$
$$= -s dT + v dp$$
- Thus:
$$= -s_L dT + v_L dp = -s_G dT + v_G dp$$

- This may be rewritten as:

$$\left(\frac{dp}{dT}\right)_{\sigma} = \frac{s_L - s_G}{v_L - v_G}$$

- But:

$$s_G - s_L = \Delta s_{vap} = \frac{\Delta h_{vap}}{T_{vap}}$$

  and thus:

$$\left(\frac{dp}{dT}\right)_{\sigma} = \frac{\Delta h_{vap}}{T_{vap}\Delta v_{vap}}$$

- This may also be applied to the coexistence of liquid and solid phases:

$$\left(\frac{dp}{dT}\right)_{\sigma f} = \frac{\Delta h_{fus}}{T_{fus}\Delta v_{fus}}$$

- This means that pressure and temperature measurements can be combined with density measurements to determine the entropy and enthalpy of a phase change.
- It is also possible to determine the sign of $(dp/dT)_\sigma$.
  - ΔH_{vap} and Δv_{vap} are always positive.
    - Therefore $(dp/dT)_\sigma > 0$ and boiling temperature increases with pressure.
  - ΔH_{fus} is always positive, but Δv_{fus} may be either positive or negative.
    - The sign of the slope of the coexistence curve is determined by the sign of Δv_{fus}.
- Consider vaporization of liquid at low pressure.
  - If the pressure is low enough, the gas phase may be treated as obeying the perfect gas equation of state.

- At this low pressure, the molar volume of the gas phase is much greater than the molar volume of the condensed phase.
  - Thus: $\Delta v_{vap} \equiv v_G$.
- Then

$$\left(\frac{dp}{dT}\right)_\sigma = \frac{\Delta h_{vap}}{T v_G} = \frac{\Delta h_{vap}\ p}{RT^2}$$

- This is the Clausius-Clapeyron equation.
- The variables p and T may be separated:

$$\frac{dp}{p} = \frac{\Delta h_{vap}}{RT^2} dT$$

- This may be integrated directly if the dependence of Δh_{vap} on T is negligible.

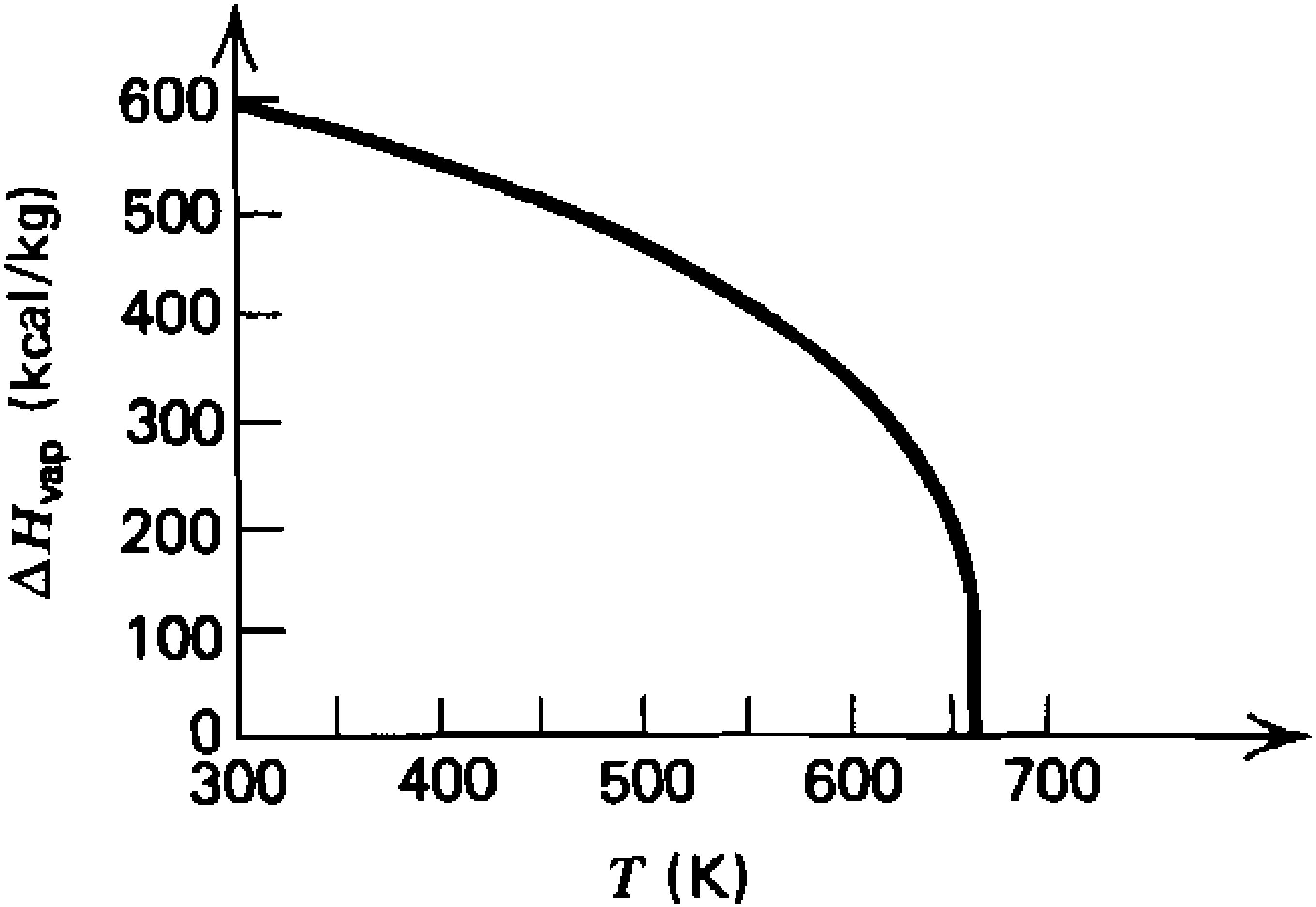


Figure 24.8 The heat of vaporization of water as a function of temperature. From J. Kestin, *A Course in Thermodynamics* (Blaisdell, Waltham, Mass., 1966).

- Upon integration this yields:

$$\ln\left[\frac{p_2(T_2)}{p_1(T_1)}\right]_\sigma = -\frac{\Delta h_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

- This means that the heat of vaporization may be determined from measurements of vapour pressure at two temperatures.
- Consider three phases of a pure substance at equilibrium.
  - Denote these phases as 1, 2, and 3.
  - Since the three phase are at equilibrium,

$$\mu^{(1)} = \mu^{(2)}$$

$$\mu^{(1)} = \mu^{(3)}$$

$$\mu^{(2)} = \mu^{(3)}$$

- Corresponding to this are three Clausius-Clapeyron equations:

$$\left(\frac{dp_{12}}{dT}\right)_{\sigma_{12}} = \frac{\Delta h_{12}}{T\Delta v_{12}}$$

$$\left(\frac{dp_{13}}{dT}\right)_{\sigma_{13}} = \frac{\Delta h_{13}}{T\Delta v_{13}}$$

$$\left(\frac{dp_{23}}{dT}\right)_{\sigma_{23}} = \frac{\Delta h_{23}}{T\Delta v_{23}}$$

- Two of these are independent.
- In p, T space, the coexistence of these phases is shown in Figure 24.9.
- The three phases coexist at the triple point.

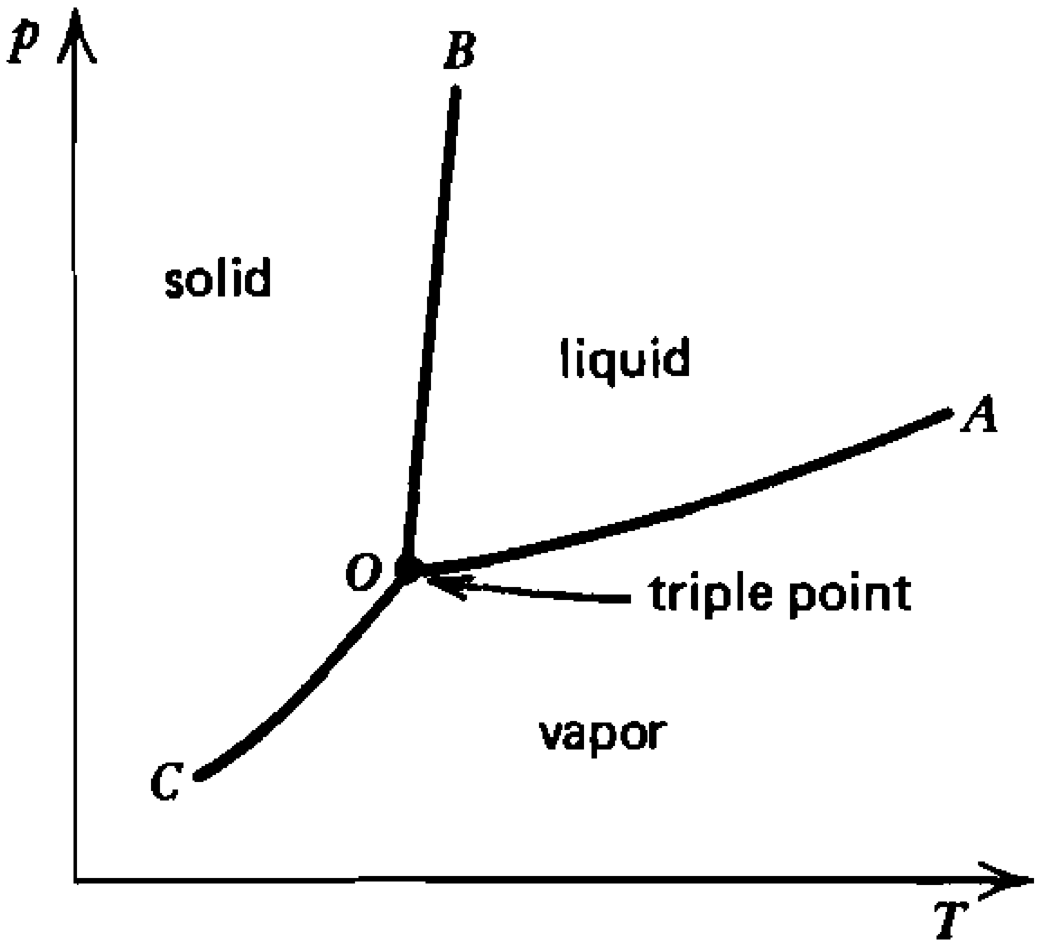


Figure 24.9 Schematic diagram showing the triple point and the equilibrium of solid, liquid, and vapor.

- Each coexistence curve is described by the appropriate Clausius-Clapeyron equation.
- For any (p, T) point not on a coexistence line only one phase is stable and p and T may be varied independently of each other.
- If two phases coexist, then p depends on T.
- If three phases coexist, then there are no independent variables and p and T are completely defined for that substance.
- This may be summarized in the Gibbs phase rule.
    - Left f be the number of independent variables and P be the number of phases.
    - The Gibbs phase rule for a one-component system is is $f = 3 - P$.

- Now consider a multicomponent system with C components in P coexisting phases in equilibrium.
- A component is a chemical species with a concentration that can be varied independently of all other species concentrations.
  - There may be more chemical species present than there are components, since some species may be in chemical equilibrium with other species.
- To characterize a multicomponent system completely, temperature, pressure, and mole fractions must be determined for each of the C components in the P phases.
  - This would imply $C + 2$ variables for each phase and $P(C + 2)$ variables in total.
  - However not all these variables are independent.

- Mole fractions in each phase must add to unity.
  - Therefore, there are $C - 1$ independent mole fractions in each phase and this removes P degrees of freedom from the entire system.
- The fact that P phases are equilibrium imposes a further constraints.
  - The chemical potential of each component is equal in all phases, imposing $C(P - 1)$ constraints.
  - The temperature and pressure is uniform in all phases, imposing $2(P - 1)$ constraints.
- Therefore:

$$f = P(C + 2) - P - 2(P - 1) - C(P - 1)$$

$$f = C - P + 2$$

- When the general form of the Gibbs phase rule, $f = C - P + 2$, is applied to a one component, three phase system, it gives $f = 0$.
- This means that there will never be a quadruple point in a one component system since that would involve a negative number of degrees of freedom.
- This also means that for three phases in equilibrium, p and T are uniquely determined.
- Now consider heat capacity in a multicomponent system.
- The constraint of coexistence of phases is different from the constraint of constant volume or constant pressure.
  - Heat capacity under this constraint, c_σ, will be affected by heat of the phase change.
  - Consider the first law of thermodynamics: $đq = du - đw$.

- Therefore:

$$c_\sigma = \left(\frac{đq}{dT}\right)_{\text{phase equilibrium}}$$

$$\left[\left(\frac{du}{dT}\right) - \left(\frac{đw}{dT}\right)\right]_{\text{phase equilibrium}}$$

- In a liquid-vapour transition, only pV work is done.
- Therefore:

$$c_\sigma = \left(\frac{du}{dT} + p\frac{dv}{dT}\right)_{\text{vapour pressure curve}}$$

- Define $c_{\sigma L}$ and $c_{\sigma G}$ as the heat capacities of the coexisting liquid and vapour.

- Since the two phases are in equilibrium,

$$p_L = p_G = p_\sigma$$

$$T_L = T_G = T_\sigma.$$

- Then

$$c_{\sigma L} = \left(\frac{du_L}{dT}\right)_\sigma + p_\sigma \left(\frac{dv_L}{dT}\right)_\sigma$$

$$c_{\sigma G} = \left(\frac{du_G}{dT}\right)_\sigma + p_\sigma \left(\frac{dv_G}{dT}\right)_\sigma$$

- Therefore:

$$c_{\sigma G} - c_{\sigma L} = \left[\frac{d}{dT}(u_G - u_L)\right]_\sigma + p_\sigma \left[\frac{d}{dT}(v_G - v_L)\right]_\sigma$$

- The latent heat of vaporization per mole is:

$$\Delta h_{vap} \equiv h_G - h_L = u_G - u_L + p_\sigma (v_G - v_L)$$

- Therefore:

$$\frac{d\Delta h_{vap}}{dT} = \left[\frac{d}{dT}(u_G - u_L)\right]_\sigma + p_\sigma \left[\frac{d}{dT}(v_G - v_L)\right]_\sigma$$

$$+(v_G - v_L)_\sigma \frac{dp_\sigma}{dT}$$

$$= c_{\sigma G} - c_{\sigma L} + (v_G - v_L)_\sigma \frac{dp_\sigma}{dT}$$

- But from the Clausius-Clapeyron equation:

$$\frac{dp_\sigma}{dT} = \frac{\Delta h_{vap}}{T}$$

- Therefore:

$$c_{\sigma G} - c_{\sigma L} = \frac{d\Delta h_{vap}}{dT} - \frac{\Delta h_{vap}}{T}$$

- If the temperature is low, then $c_{\sigma L} \approx c_{pL}$.
- Therefore at low temperature, the heat capacity of saturated vapour will be:

$$c_{\sigma G} = c_{pL} + \frac{d\Delta h_{vap}}{dT} - \frac{\Delta h_{vap}}{T}$$

- Consider the case of water vapour in equilibrium with liquid water at 100° C.
    - The thermodynamic properties are well characterized.

- They are:
    - Δh_{vap} = 40.67 J mol^{-1}.
    - $d\Delta h_{vap}/dT$ = -47.93 J K^{-1} mol^{-1}
    - c_{pL} = 75.86 J K^{-1} mol^{-1}
- On this basis, $c_{\sigma G} = -80.91$ J K^{-1} mol^{-1}.
- This means that if saturated water vapour is compressed, the temperature increases more rapidly than the (p, T) coexistence curve.
- This means that the final temperature would not be on the coexistence curve, but rather in the region of the phase diagram where gas is the stable phase.
- Therefore, to maintain coexistence, sufficient energy would need to be removed to bring the system back to the coexistence curve.

Critical Point

- There exists a critical temperature T_c, above which gas and liquid are indistinguishable.
- Consider the constraints of coexistence in equilibrium:

$$p_1 = p_2$$

$$T_1 = T_2$$

$$\mu_1(p_1, T_1) = \mu_2(p_2, T_2)$$

$$p_1 = p_1(v_1, T_1)$$

$$p_2 = p_2(v_2, T_2)$$

which gives five equations for the six variables, p_1, T_1, v_1, p_2, T_2 and v_2.

- This leaves a relation between two variables to be considered such as the relation between p and T along a coexistence line.
  - If there exists a p and T where v_1 and v_2 for the two phases are equal and the symmetry of the two phases is identical, then there exists a critical point.
  - No critical point exists if there is no temperature for which $v_1 = v_2$ along the coexistence curve.
  - No critical point exists if there is a temperature for which $v_1 = v_2$ along the coexistence curve, but the lattice symmetries are different.
  - This means that conditions of equilibrium and the equations of state are an incomplete description of the system.
  - A complete description would involve a description of the symmetry of each phase.

- Consider the gas-liquid critical point.
- The critical isotherm at T_c has a point in the (p, v) plane where the curve is horizontal and also has an inflection point.
- Mathematically these are:

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

for the horizontal tangent and

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

for an inflection point.

- This may then be used to explore fluid properties at and near the critical point.
- Recall that:

$$\kappa_T = \left[-\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \right].$$

- For any real substance $(\partial v / \partial p)_T < 0$.
- At the critical point:

$$\lim_{T \to T_c, v \to v_c} \left[-\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \right] = \infty$$

  and κ_T becomes positive and infinite.
- Consider $(\partial u / \partial v)_T$ as a finite quantity.

- Recall:

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

- Since T and p are finite, $(\partial p/\partial T)_v$ is finite.
- Along the gas-liquid coexistence line:

$$\left(\frac{\partial p}{\partial T}\right)_\sigma = \frac{s_G - s_L}{v_G - v_L}$$

- At the critical point:

$$\lim_{T\to T_c, v\to v_c}\left(\frac{\partial p}{\partial T}\right)_\sigma = \left(\frac{\partial s}{\partial v}\right)_{T=T_c}$$

- But:

$$\left(\frac{\partial p}{\partial T}\right)_{\sigma, critical\ point} = \left(\frac{\partial p}{\partial T}\right)_{v=v_c}$$

and $(\partial p/\partial T)_v$ is always a finite quantity.

- Therefore $(\partial p/\partial T)_{\sigma,T=T_c}$ is finite.
- Using the cyclic rule:

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v$$

it follows that:

$$\lim_{T\to T_c, v\to v_c}\left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p\right] = \infty$$

- The Clausius-Clapeyron equation may be written as:

$$\Delta h_{vap} = T(v_G - v_L)\left(\frac{\partial p}{\partial T}\right)_\sigma$$

- Since at the critical point, $(\partial p/\partial T)_\sigma$ is finite and $v_G = v_L$,

$$\lim_{T\to T_c} \Delta h_{vap} = 0$$

- It may also be shown that:

$$\left(\frac{d\Delta h_{vap}}{dT}\right)_{T=T_c} = -\infty$$

(See Figure 24.8).

- A fluid near the critical point has peculiar properties.
  - Densities converge toward each other as:

    $$(\rho_L - \rho_G) = |T - T_c|^{\beta}$$

    where the critical exponent $\beta = 0.326 \pm 0.002$ (See Figure 24.10 and 24.11)
  - There is a thermal anomaly at the critical point.
  - At the critical density,

    $$c_V(T) \rightarrow \infty$$

    regardless of from which direction T_c is approached.
  - The critical exponents, δ, α, and γ are used to describe the behaviour of other thermodynamic properties near the critical point.

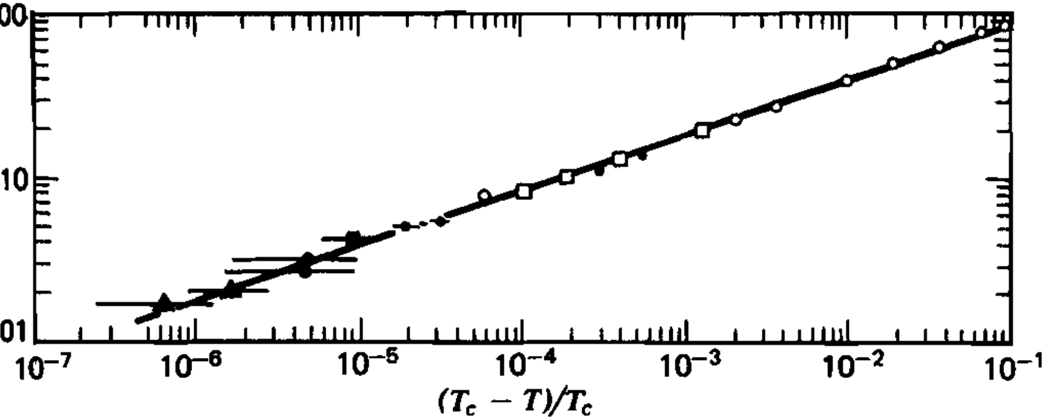


Figure 24.10 The dependence of $\rho_L - \rho_G$ on $T - T_c$ near T_c for CO_2. From P. Heller, *Rep. Prog. Phys.* **30** (II), 731 (1967).

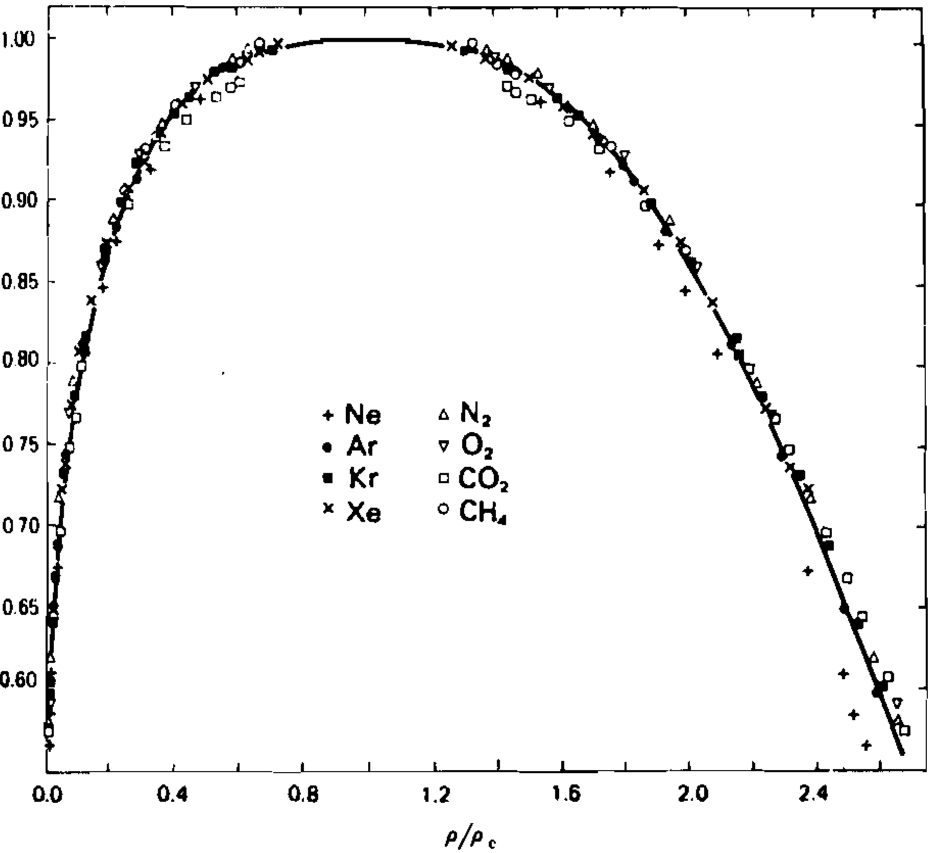
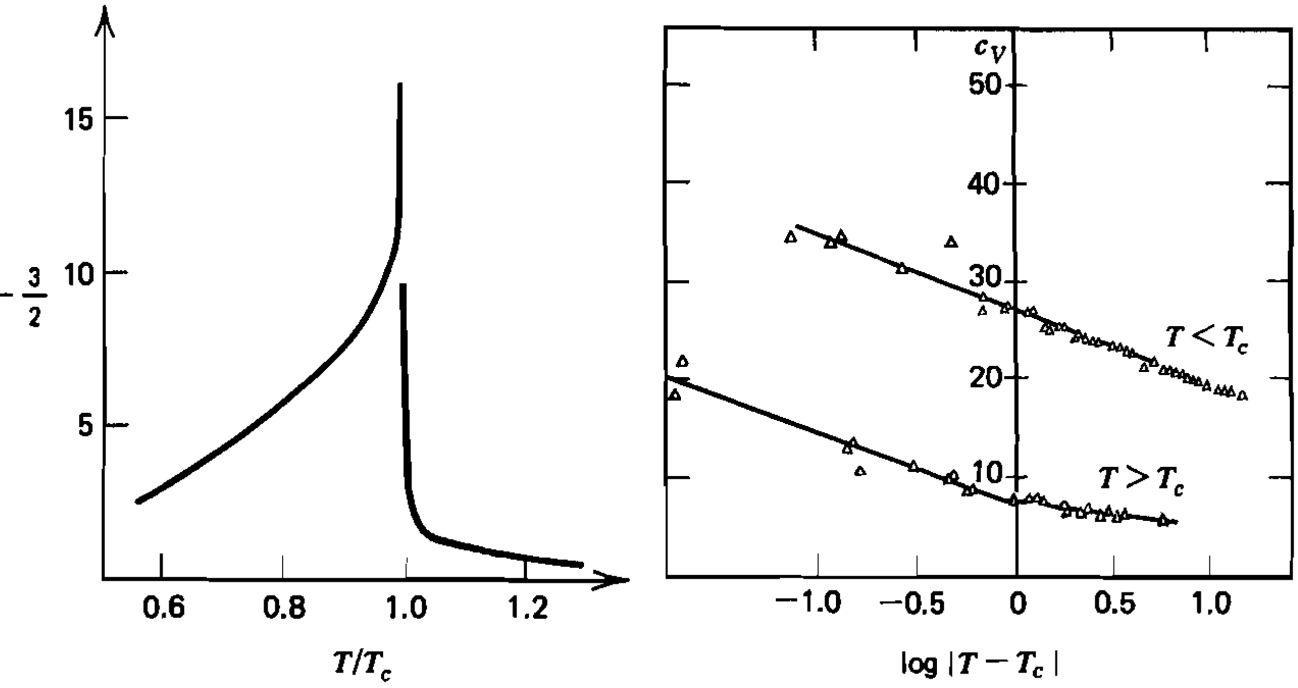


Figure 24.11 The liquid–gas coexistence curve for simple substances. The curve is a composite of data for Ne, Ar, Kr, Xe, N_2, O_2, CO_2, and CH_4. Note the use of the reduced variables T/T_c and ρ/ρ_c. From E. A. Guggenheim, *J. Chem. Phys.* **13,** 253 (1945).



(a)

(b)

Figure 24.12 (*a*) Schematic diagram of the constant-volume heat capacity of argon near the critical point. (*b*) Variation of the constant-volume heat capacity of argon along the critical isochore. The data show that the variation of c_V near T_c is logarithmic. From P. A. Egelstaff and J. W. Ring [data of M. I. Bagatskil, A. V. Voronel, and B. G. Gusak, *Zh. Eksperim. i Teor. Fiz.* **43,** 728 (1962); *JETP* **16,** 517 (1963)], in H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (Eds.), *Physics of Simple Liquids* (North Holland, Amsterdam, 1968).

- For chemical potential:

$$(\mu - \mu_c) \propto |\rho - \rho_c|^{\delta-1}(\rho - \rho_c)$$

where $\delta = 4.80 \pm 0.02$.

- For heat capacity at constant volume:

$$c_V(T) \propto |T - T_c|^{-\alpha}$$

where $\alpha = 0.110 \pm 0.003$

- For the variation of density with chemical potential:

$$\left(\frac{\partial \rho}{\partial \mu}\right)_T = \rho^2 \kappa_T \propto |T - T_c|^{\gamma}$$

where $\gamma = 1.239 \pm 0.002$.

- These relationships hold for all fluids at the critical point.
- The exponents are the same for all fluids.
- This is due to the short range interactions and the fact that there are fluctuations.
- The mathematical properties are the same.
- This is an area that is explored by techniques of statistical mechanics.
- There are no simple equations of state that will account for this behaviour at the critical point and behaviour far from the critical point.

Phase Transitions Viewed as Responses to Thermodynamic Instabilities

- Chemical potential of a pure substance depends on only (p, T).
- The functional forms are different for different phases.
- The stable phase is the phase with the lowest chemical potential at some (p, T).
- If more than one phase has the lowest chemical potential, then those phases coexist in equilibrium at that (p, T).
- The phases with the higher chemical potentials are unstable.
- A system will spontaneously move to the stable phase (or phases) at that (p, T).
- Consider the development of a thermodynamic instability.

- This may be considered in the context of the equilibrium properties of a one-component system in term of $u(s, v)$.
- This may be represented as a surface in (u, s, v) space (Figure 24.13)
- Each point of the surface represents an equilibrium state of the system.
- Derivatives at each point on the surface may be defined:

$$\left(\frac{\partial u}{\partial s}\right)_v = T$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -p$$

- These define tangents parallel to the s and v axes.

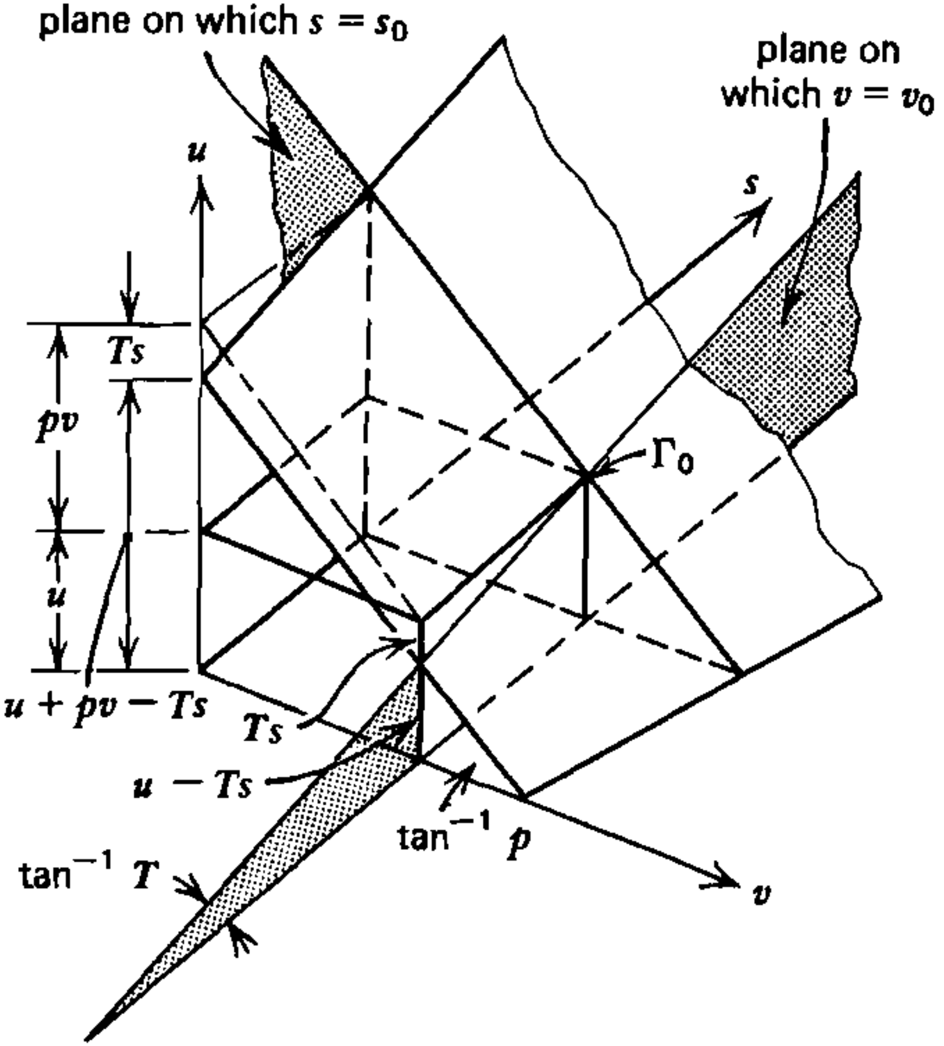


Figure 24.13 The tangent plane to the thermodynamic surface. Drawing courtesy of Prof. J. A. Beattie.

- Consider some point Γ_0 defined by (u_0, s_0, v_0) on the surface and the tangent plane that passes through it.
- The equation of that plane is:

$$u = u_0 + T_0(s - s_0) - p_0(v - v_0)$$

- Consider the plane $v = v_0$ which is parallel to the (u, s) plane and passes through Γ_0.
- This plane will intersect the tangent plane along the line:

$$u = u_0 + T_0(s - s_0)$$

- This line will intersect the u axis at:

$$u = u_0 - T_0 s_0 \equiv a_0$$

- Similarly the $s = s_0$ plane will intersect the tangent plane along the line:

  $$u = u_0 - p_0(v - v_0)$$

  which intersects the u axis at:

  $$u = u_0 + p_0 v_0 \equiv h_0$$

- The tangent plane intersects u axis at:

  $$u = u_0 - T_0 s_0 + p_0 v_0$$

- A one component system of fixed mass has definite values of $u(s, v)$ regardless of the number of phases present.
- Each phase has a $u(s, v)$ surface.

- Consider such a system at the triple point.
- Γ_3^S represents $u(s, v)$ of the solid at the triple point.
- Similarly Γ_3^L and Γ_3^G represents $u(s, v)$ of the liquid and gas phase respectively at the triple point.
- A tangent plane for each of the three surfaces can be constructed through the triple point.
- These tangent planes intersect the u axis at g_3^S, g_3^L, g_3^G.
- But g can be identified with the Gibb's free energy.
- Therefore g is the chemical potential.
- At the triple point, the chemical potential of all three phases is the same and

$$g_3^S = g_3^L = g_3^G$$

- Also, at the triple point $T_3^S = T_3^L = T_3^G$ and $p_3^S = p_3^L = p_3^G$.
- This means that there is a common tangent plane for Γ_3^S, Γ_L^3, and Γ_3^G and that these three points form a triangle on that plane.
- This region of the common tangent plane is referred to as the derivative surface.
- A point representing three phases in equilibrium is determined by:

$$u = x_S u_S + x_L u_L + x_G u_g$$

$$s = x_S s_S + x_L s_L + x_G s_G$$

$$v = x_S v_S + x_L v_L + x_G v_G$$

- Consider liquid and vapour coexistence for a one component system with fixed mass.
- The derived surface consists of a set of lines that are tangent to both Γ_2^L and Γ_2^G which represents coexisting liquid and vapour.
- These point of tangency approach each other and meet at the critical point.
- As the $u(s, v)$ surface for each phase approaches Γ_2^L or Γ_2^G, its curvature becomes negative.
- Negative curvature coincides with instability.
- The derived surface spans the region of instability (see Figure 24.14).
- Consider a homogeneous pure substance isolated in volume v with energy u and entropy s.

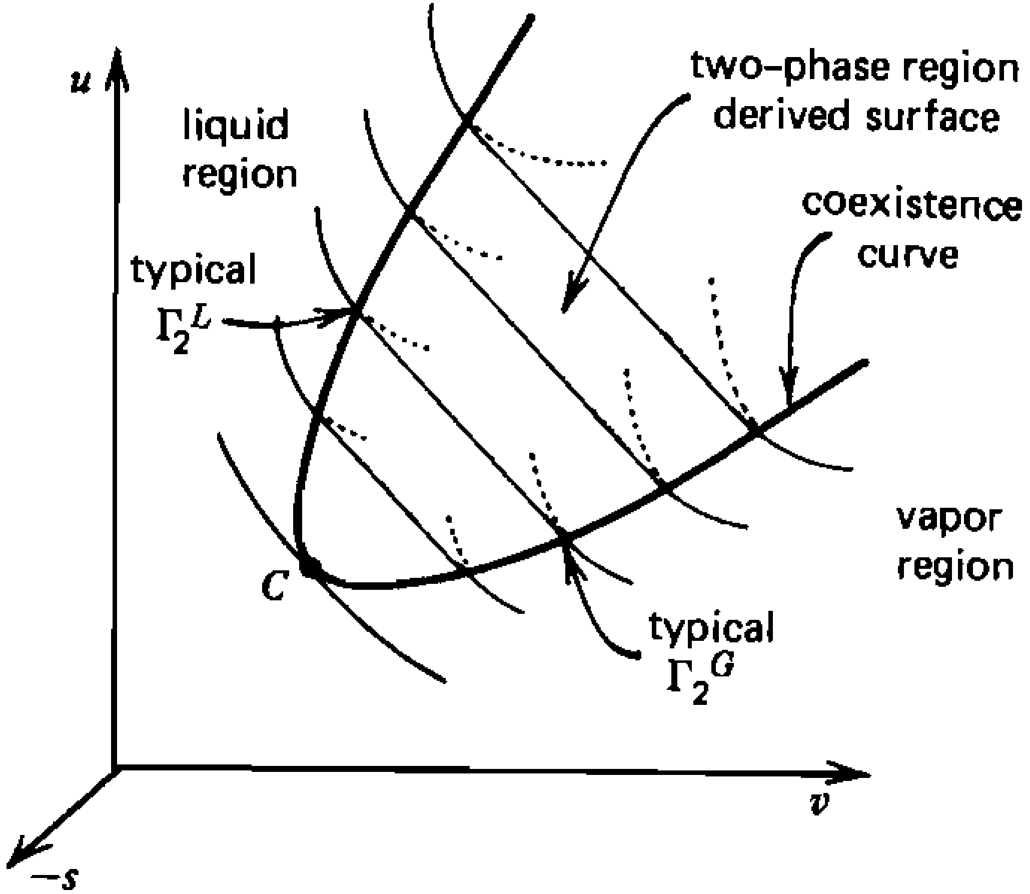


Figure 24.14 Schematic representation of the surface $u(s, v)$ in a region of vapor–liquid equilibrium. The derived surface lies below $u(s, v)$; each line shown in the two-phase region is an example of the common tangent to $u(s, v)$ at points Γ_2^L and Γ_2^G. The locus of the points of tangency defines the coexistence curve. C is the critical point. The dotted portions of $u(s, v)$ show regions of metastability.

- The necessary and sufficient conditions for stability are:

$$\left(\frac{\partial^2 u}{\partial s^2}\right)_v = \frac{T}{c_V} > 0$$

$$\left(\frac{\partial^2 u}{\partial s^2}\right)_v \left(\frac{\partial^2 u}{\partial v^2}\right)_s - \left(\frac{\partial^2 u}{\partial v \partial s}\right)_{s,v}^2 = \frac{T}{c_V}\left(\frac{c_p}{v\kappa_T c_V}\right) - \frac{\alpha^2 T^2}{\kappa_T^2 c_V^2} > 0$$

- This means:

$$\kappa_T > \alpha^2 T v / c_p > 0$$

- A one phase system is stable as long as the conditions for stability are satisfied for small displacements from equilbrium.
- But what about the other phase?
- The conditions for stability of the other phase must be considered.

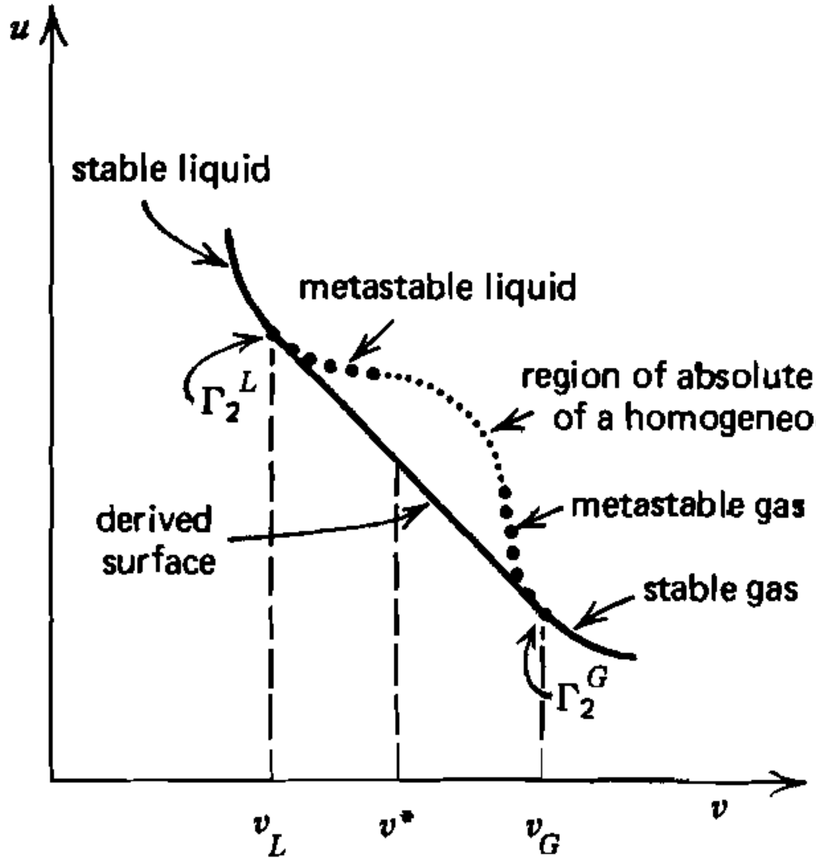


Figure 24.15 Schematic representation of the intersection of the two-phase region of $u(s, v)$ and a plane on which s is constant. The dotted lines are continuations of the homogeneous-phase energies; they represent metastable states of the system. If we attempt to prepare a homogeneous system with the volume v^* shown, it breaks up into liquid and gas, this being the region of absolute instability of a homogeneous phase.

- Consider a constant s cut of Figure 24.14 that includes the coexistence region.
    - This is illustrated in Figure 24.15.
- The straight line segment joining Γ_2^L and Γ_2^G is tangent to both points and lies on the derived surface.
- The slope of this line is:

$$\left(\frac{\partial u}{\partial v}\right)_s = -p$$

- In one phase of a pure substance p is a monotonic function of the volume since:

$$v\kappa_T = -\left(\frac{\partial v}{\partial p}\right)_T > 0$$

- This condition can continue to be satisfied even though u for that phase is above that of another phase.
  - This is represented by the dotted lines in Figures 24.14 and 24.15.
  - This metastable region continues until the inflection point is reached.
- At the inflection point:

  $$\left(\frac{\partial^2 u}{\partial s^2}\right)_v = 0$$

  and the conditions for stability cannot be satisfied.
- Therefore the homogeneous phase is absolutely unstable and a phase transition must occur.
- Metastable states may be observed.

- Consider a pure substance in the gas phase.
- Clusters of molecules that convert a gas to liquid may be formed very slowly so as to form a supersaturated vapour.
    - This means that the pressure of the system is in excess of the equilibrium vapour pressure of the liquid.
    - This system can exist long enough to be observed.
    - It must be prepared in the absence of any liquid because this system can only exist with slight perturbations that do not include the presence of the other phase.
    - Once the other phase occurs, the system has been perturbed such that it cannot maintain the metastable state.

- The region of $u(s.v)$ where $\left(\partial^2 u/\partial s^2\right)_v < 0$ consistutes a gap of absolute instability.
- This gap is spanned by the derived surface.
- Consider a hypothetical homogeneous system prepared with volume v^* with $v_L < v^* < v_G$.
    - This system can immediately decompose into liquid and vapour with the amounts of each determined by the lever rule.
- The energy of the system is lowest along the line:

$$v - x_L v_L + x_G v_G$$

- Consider Figure 24.16 which projects the $u(s, v)$ surface onto the (s, v) plane.

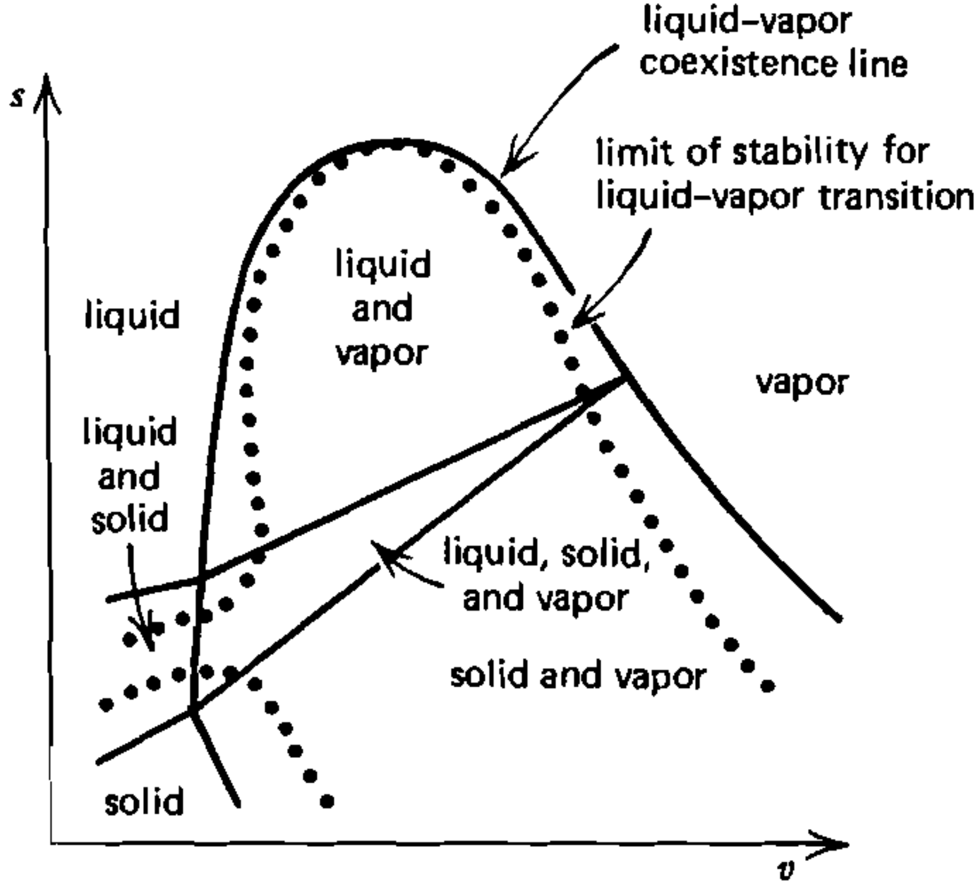


Figure 24.16 Projection of the surface $u(s,\ v)$ onto an $(s,\ v)$ plane, showing the several coexistence curves for equilibria involving pairs of phases and also the limit-of-stability curve (spinodal curve) for the liquid–gas transition. The area labels show projections of regions of $u(s,\ v)$ where the specified phases are stable, and of the derived surfaces where mixtures of phases are stable. Drawing courtesy of Prof. J. A. Beattie.

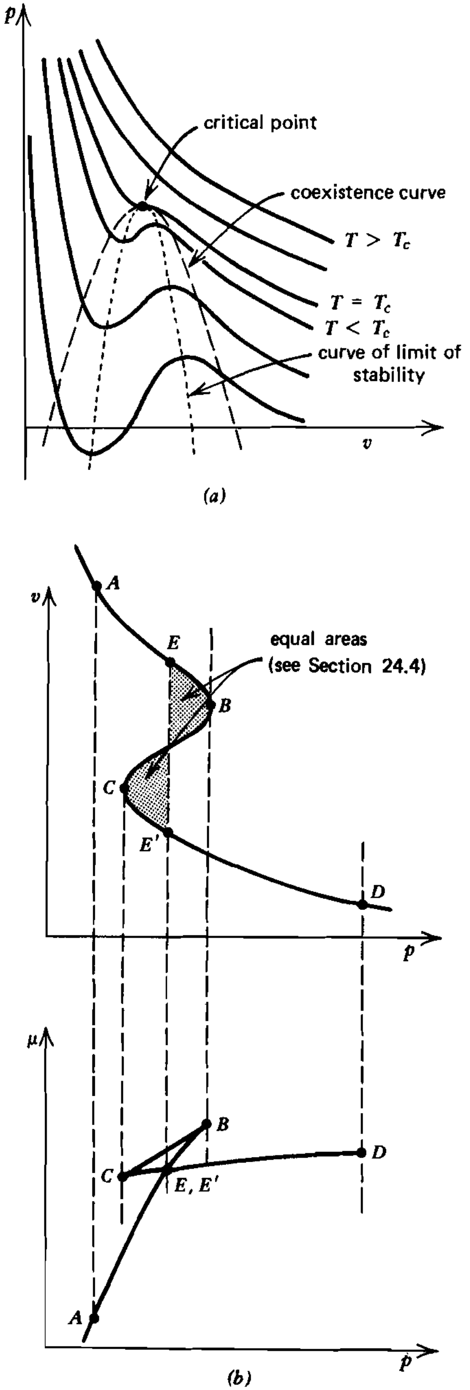


Figure 24.17 (*a*) Schematic representation of isotherms of the van der Waals equation of state. (*b*) Representation of the relation between v, p and μ, p plots for a van der Waals gas.

- Consider the van der Waals equation of state:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

- Isotherms are shown in Figure 24.17.
- One condition for stability is $(\partial p/\partial v)_T < 0$.
    - Therefore $(\partial p/\partial v)_T > 0$ represents an unstable region where a homogeneous phase is unstable.
- Consider an isotherm along which coexistence of liquid and gas is possible.
- The chemical potential is:

$$d\mu = -sdT + vdp$$

- Therefore:

$$\mu(p_2) - \mu(p_1) = \int_{p_1}^{p_2} v(p)dp$$

  on the isotherm.
- In the unstable region of the van der Waals isotherm $v(p)$ is triple valued.
  - Two values of p lie where $(\partial p/\partial v)_T < 0$.
  - The third value lies where $(\partial p/\partial v)_T > 0$.
  - There are two regions where a phase is metastable.
- In Figure 24.17, AE and $E'D$ are the stable regions.
- BE and CE' are the metastable regions.
- CD is the unstable region.
- EE' is the coexistence region.

- Consider stability conditions at the critical point.
- Recall that at the critical point:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

- Therefore the stability condition $(\partial p/\partial v)_T < 0$ cannot be satisfied.
- Instead the derivation of stability conditions (see Chapter 19) must be carried out to higher order.
- When $(\partial p/\partial v)_T = 0$, a stability condition becomes $\left(\partial^3 p/\partial v^3\right)_T < 0$.

- Consider isothermal compressibility at the critical point.
- κ_T become infinitely large.
- This means that the fluid can be compressed or expanded with negligible work being done on or by the system.
- Consider the volume at the critical point as divided into arbitrary subvolumes.
- These subvolumes can exchange energy and matter with their surroundings.
- The fluctuations in these subvolumes are large.
- Because the average density of the system is fixed, these fluctuations are not completely independent of each other.
- The fluctuations in density cause fluctuations in the refractive index of the fluid.

- This results in critical opalescence in light scattering.
- It is noted that $(\partial p/\partial v)_T = 0$ along the coexistence line in (p, v) space.
- However, critical opalescence is not observed, since although the system is not homogeneous, the liquid and vapour phases have distinct densities and refractive indices.
- In the coexistence region, the work done during a phase change is $-p_\sigma \Delta v$.
- As the critical point is approached:

$$\lim_{p_\sigma \to p_c} p_\sigma \Delta v \to 0$$

- In the coexistence region, the transition between liquid and vapour is a phase transition of the first kind.

- As the critical point is approached, the phase transition assumes characteristics of a transition of the second kind in that:

$$\Delta s = 0 \text{ and } \Delta v = 0$$

- Recall that the Claperyron equation defines $(\partial p/\partial T)_v$ for $T < T_c$.
- At $T = T_c$, $\Delta s/\Delta v$ is indeterminate.
- As T approaches T_c, L'Hospital's rule may be used to assess the behaviour of $\Delta s/\Delta v$:

$$\lim_{T\to T_c} \frac{\Delta s}{\Delta v} = \lim_{T\to T_c} \frac{(\partial \Delta s/\partial T)_p}{(\partial \Delta v/\partial T)_p} = \frac{1}{Tv}\left(\frac{c_{pG} - c_{pL}}{\alpha_G - \alpha_L}\right)$$

- Both the numerator and the denominator tend to ∞.

- Experimentally it has been shown that $(\partial p/\partial T)_v$ is finite.
- The critical point is a stable state of the system because it lies on both the coexistence curve and the spinodal curve.
    - The spinodal curve is the limit of stability for free energy.
- From this, relationships among the critical exponents $\alpha, \beta, \gamma, \delta$.
- Consider the pV diagram in Figure 25.18.
    - The critical isotherm is $A'CA$.
    - A coexistence isotherm is $B'DB$
    - Consider the cycle $CABDC$.
        - Since $\Delta v = 0$ along AB and CD no work is done.
        - For the cycle $\Delta U_{cycle} = 0$.

- For an arbitrary amount of substance:

$$q + w = 0 = T_c(S_A - S_C) - \int_C^A pdV + \int_{T_c}^{T_1} C_{VG} dT$$

$$+T_1(S_D - S_B) - \int_B^D pdV + \int_{T_1}^{T_c} (C_V)_{V=V_c} dT$$

- $(C_V)_{V=V_c}$ is the two phase heat capacity and is evaluated along DC where $V = V_c$
- Consider the identity:

$$S_A - S_C = S_A - S_B + S_B - S_D + S_D - S_C$$

and

$$S_B - S_D = (V_G - V_c)\left(\frac{\partial p}{\partial T}\right)_{T=T_1}$$

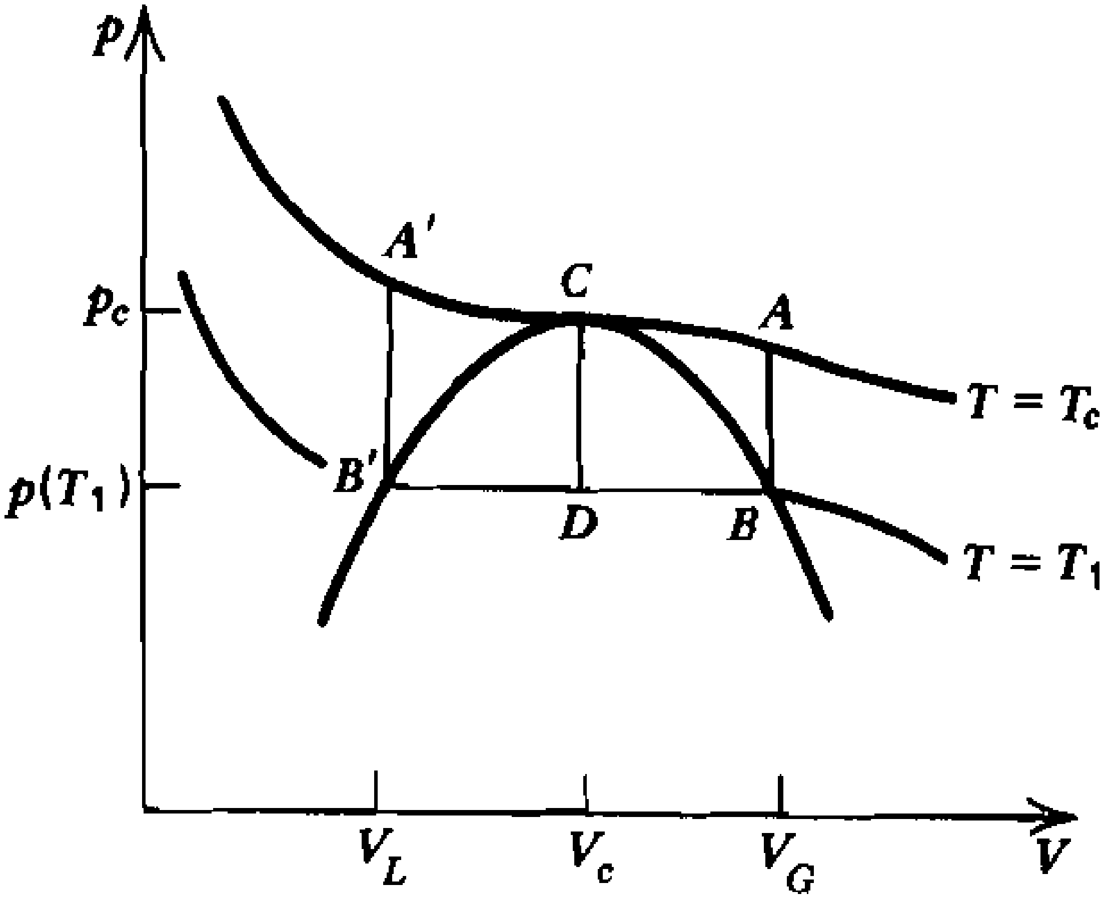


Figure 24.18 Schematic representation of the coexistence curv
and isotherms near the critical point.

- Therefore:

$$\int_{T_1}^{T_c} \frac{T_c - T}{T} (C_V)_{V=V_c} dT = \int_{T_1}^{T_c} \frac{T_c - T}{T} C_{VG} dT$$

$$+ \int_C^A (p_c - p) dV + (T_c - T_1)(V_G - V_c) \left[\left(\frac{\partial p}{\partial T} \right)_{T=T_1} - \frac{p_c - p(T_1)}{T_c - T_1} \right]$$

  for the cycle $CABDC$.

- Similarly for the cycle $A'CDB'A'$:

$$\int_{T_1}^{T_c} \frac{T_c - T}{T} (C_V)_{V=V_c} dT = \int_{T_1}^{T_c} \frac{T_c - T}{T} C_{VL} dT$$

$$+ \int_C^{A'} (p_c - p) dV + (T_c - T_1)(V_c - V_L) \left[\left(\frac{\partial p}{\partial T} \right)_{T=T_1} - \frac{p_c - p(T_1)}{T_c - T_1} \right]$$

- Multiplying the forgoing by $V_G - V_c$ and $V_c - V_L$ respectively and adding:

$$\left(\frac{1}{V_G - V_c} - \frac{1}{V_c - V_L}\right) \int_{T_1}^{T_c} \frac{T_c - T}{T} (C_V)_{V=V_c} dT$$

$$= \frac{1}{V_G - V_c} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_{VG} dT + \frac{1}{V_c - V_L} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_{VL} dT$$

$$+ \frac{1}{V_G - V_c} \int_{V_c}^{V_G} (p_c - p)_{T_c} dV + \frac{1}{V_c - V_L} \int_{V_L}^{V_c} (p - p_c)_{T_c} dV$$

- Note that the left-hand side of the equation follows the path DC along which:

$$x_L = \frac{V_G - V_c}{V_G - V_L}; \quad x_G = \frac{V_c - V_L}{V_G - V_L}$$

- This can be used to rewrite the equation:

$$\int_{T_1}^{T_c} \frac{T_c - T}{T} (C_V)_{V=V_c} dT = \int_{T_1}^{T_c} \left[x_L(T_1) C_{VL} + x_G(T_1) C_{VG} \right] dT$$

$$+ x_G(T_1) \int_{V_c}^{V_G} (p_c - p)_{T_c} dV + x_L(T_1) \int_{V_L}^{V_c} (p - p_c)_{T_c} dV$$

where

$$x_G(T_1) = \frac{V_c - V_L(T_1)}{V_G(T_1) - V_L(T_1}$$

$$x_L(T_1) = \frac{V_G(T_1) - V_c}{V_G(T_1) - V_L(T_1)}$$

are fixed values.

- This means that the phase equilibrium is suppressed.

- Note that:

$$T_c > T_1$$

$$V_G > V_c$$

$$V_c > V_L$$

$$C_{VG} > 0$$

$$C_{VL} > 0$$

- This means

$$\left(\frac{1}{V_G - V_c} - \frac{1}{V_c - V_L}\right) \int_{T_1}^{T_c} \frac{T_c - T}{T} (C_V)_{V=V_c} dT$$

$$> \frac{1}{V_G - V_c} \int_{V_c}^{V_G} (p_c - p)_{T_c} dV + \frac{1}{V_c - V_L} \int_{V_L}^{V_c} (p - p_c)_{T_c} dV$$

- For $T < T_c$, the critical relationships may be assumed to hold:

$$|V - V_c| = B(T_c - T)^{\beta}$$

$$p - p_c = -D|V - V_c|^{\delta - 1}(V - V_c$$

$$(C_V)_{V=V_c} = A(T_C - T)^{\alpha}$$

- When this is used with the previous inequality, the Griffith's inequality results: $\alpha + \beta(\delta - 1) \geq 2$
- It is also possible to show:

$$\alpha + 2\beta + \gamma \geq 2$$

$$\gamma(\delta + 1) \geq (2 - \alpha)(\delta - 1)$$

$$\gamma \geq \beta(\delta - 1)$$