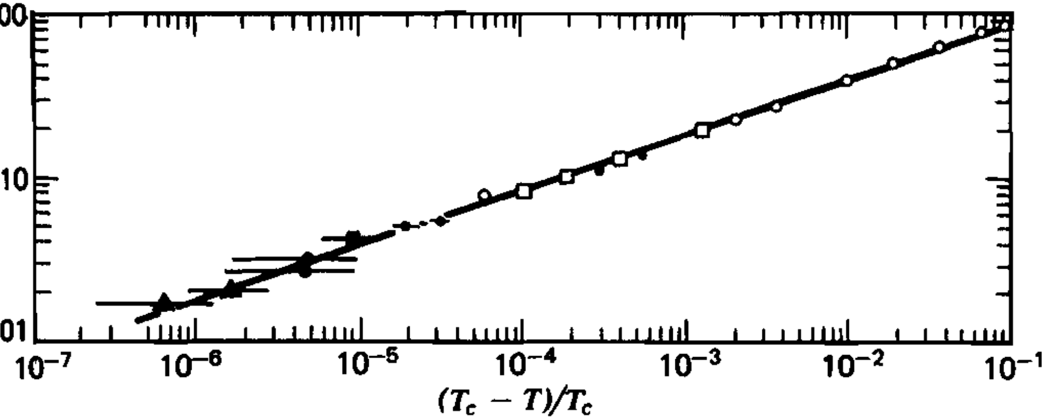


Figure 24.10 The dependence of $\rho_L - \rho_G$ on $T - T_c$ near T_c for CO_2. From P. Heller, *Rep. Prog. Phys.* **30** (II), 731 (1967).

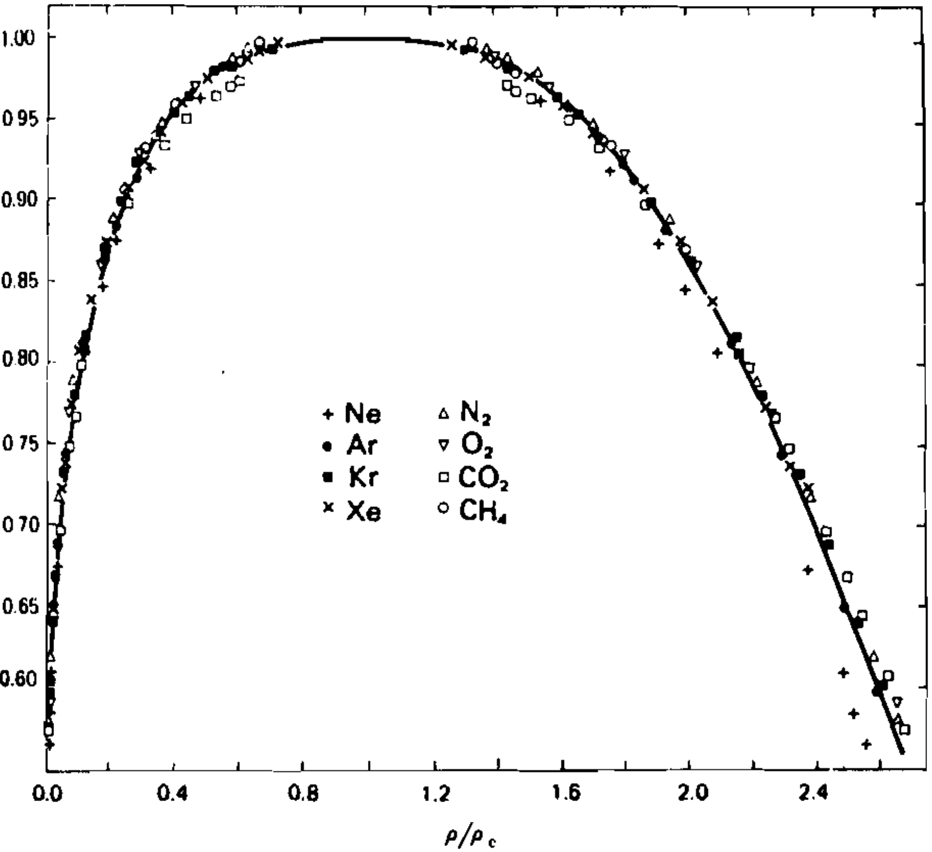


Figure 24.11 The liquid–gas coexistence curve for simple substances. The curve is a composite of data for Ne, Ar, Kr, Xe, N_2, O_2, CO_2, and CH_4. Note the use of the reduced variables T/T_c and ρ/ρ_c. From E. A. Guggenheim, *J. Chem. Phys.* **13,** 253 (1945).

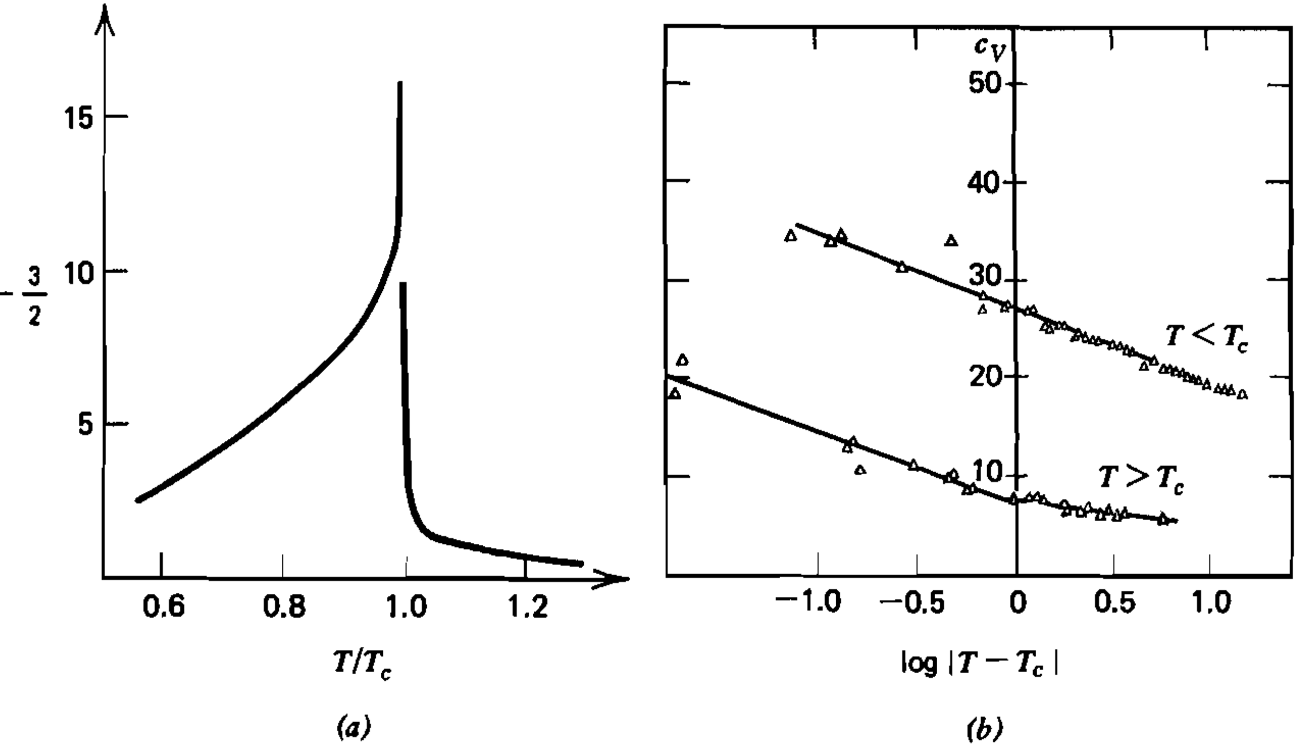


Figure 24.12 (*a*) Schematic diagram of the constant-volume heat capacity of argon near the critical point. (*b*) Variation of the constant-volume heat capacity of argon along the critical isochore. The data show that the variation of c_V near T_c is logarithmic. From P. A. Egelstaff and J. W. Ring [data 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.

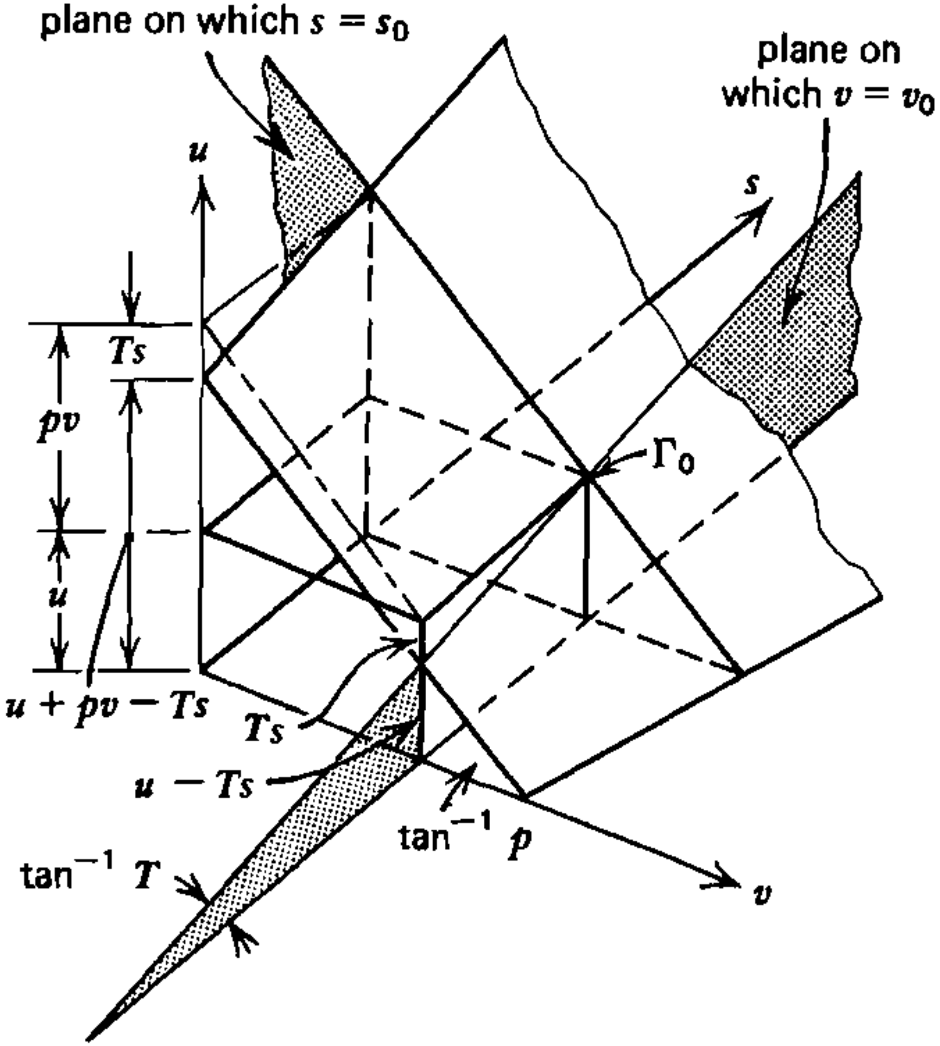


Figure 24.13 The tangent plane to the thermodynamic surface. Drawing courtesy of Prof. J. A. Beattie.

- 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.

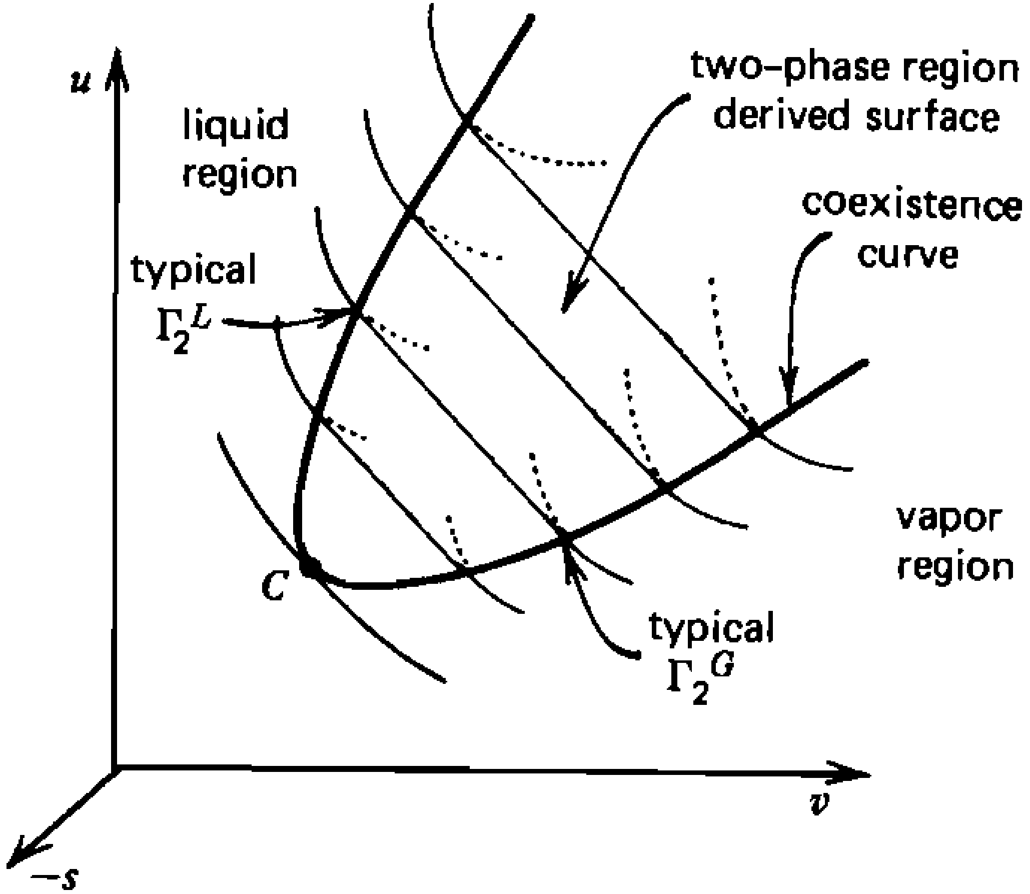


Figure 24.14 Schematic representation of the surface $u(s, v)$ in a region of vapor–liquid equilibrium. The derived surface lies below $u(s, v)$; each line shown in the two-phase region is an example of the common tangent to $u(s, v)$ at points Γ_2^L and Γ_2^G. The locus of the points of tangency defines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

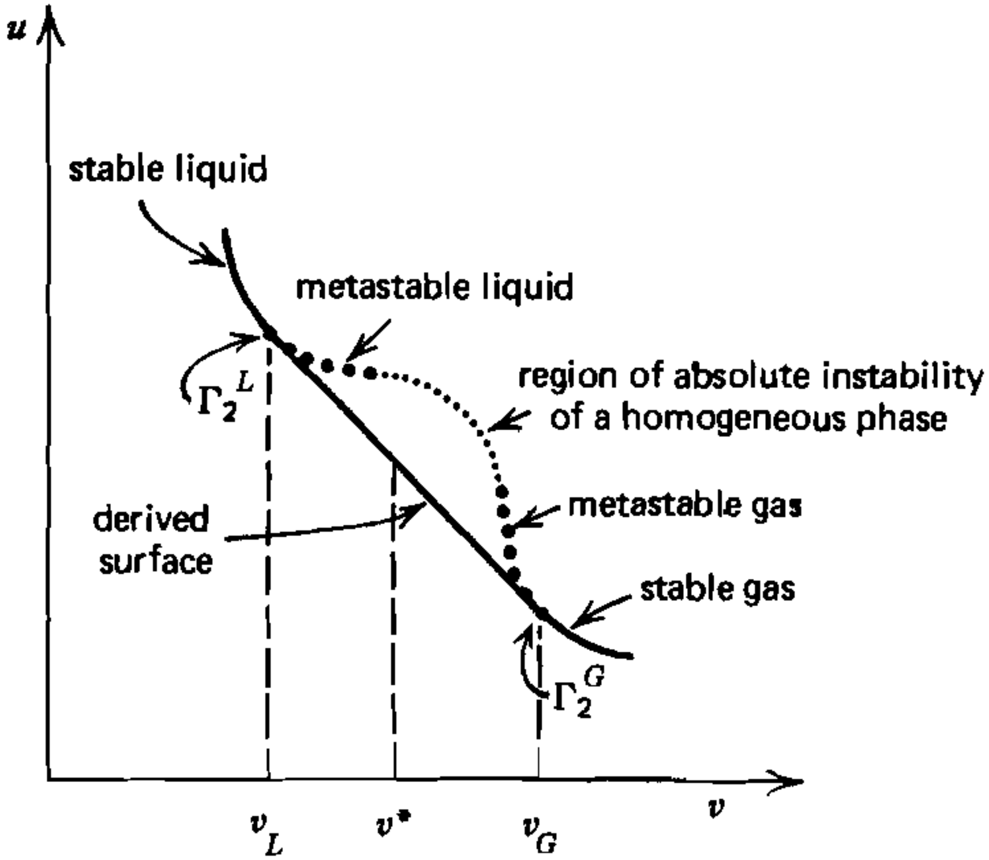


Figure 24.15 Schematic representation of the intersection of the two-phase region of $u(s, v)$ and a plane on which s is constant. The dotted lines are continuations of the homogeneous-phase energies; they represent metastable states of the system. If we attempt to prepare a homogeneous system with the 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.

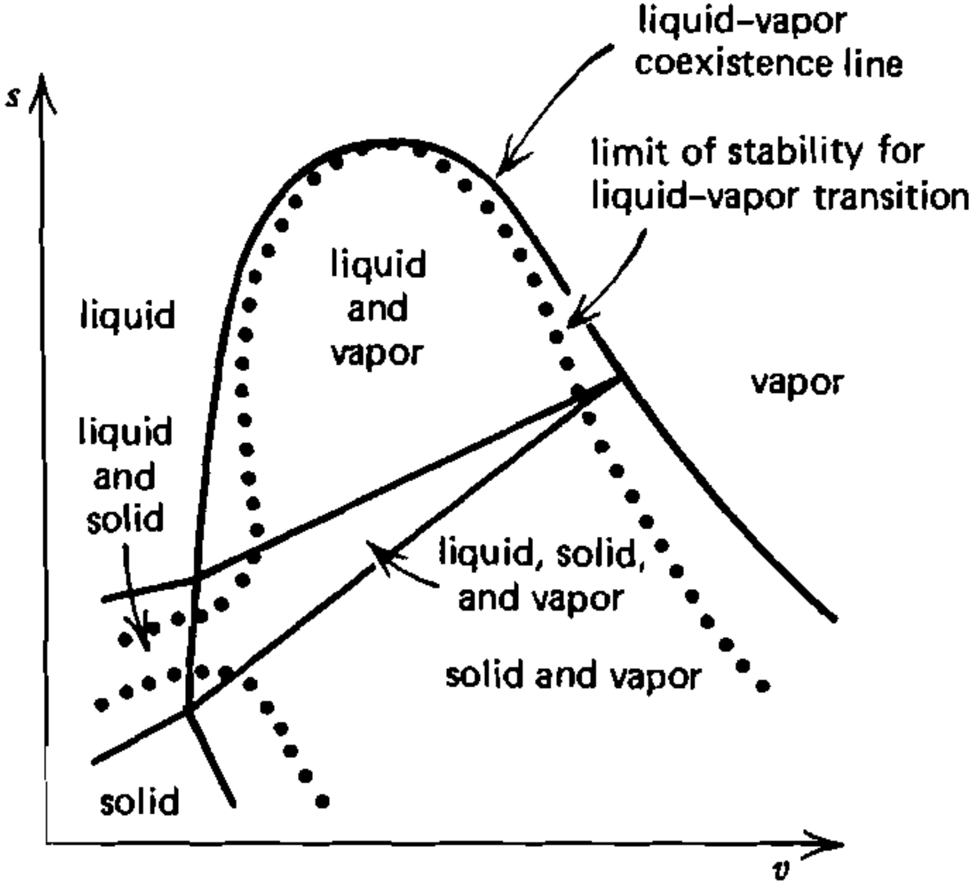


Figure 24.16 Projection of the surface $u(s, v)$ onto an (s, v) plane, showing the several coexistence curves for equilibria involving pairs of phases and also the limit-of-stability curve (spinodal curve) for the liquid–gas transition. The area labels show projections of regions of $u(s, v)$ where the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

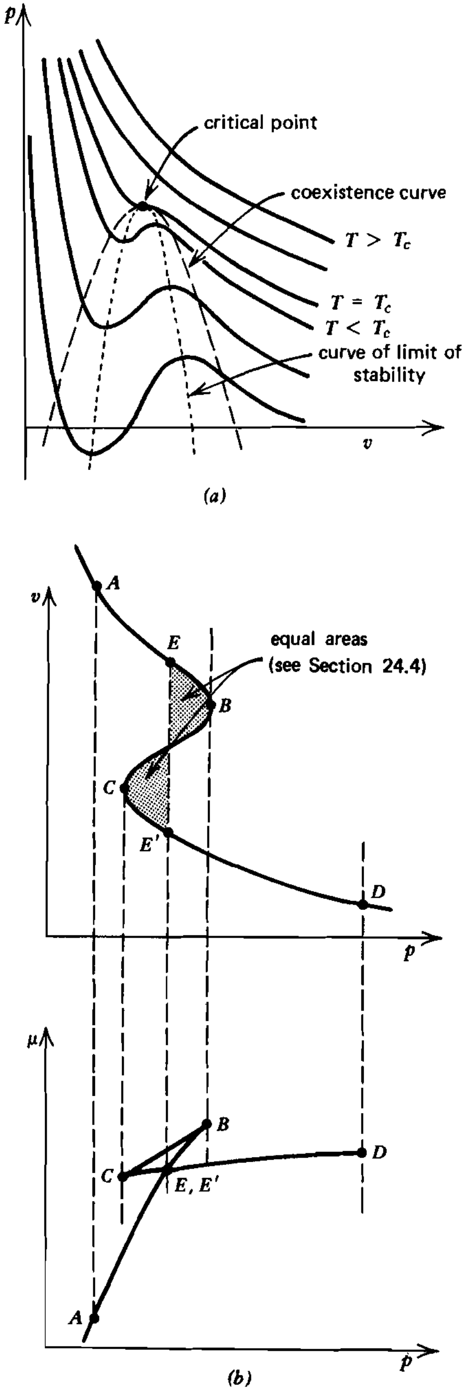


Figure 24.17 (*a*) Schematic representation of isotherms of the van der Waals equation of state. (*b*) Representation of the relation between v, p and μ, p plots for a van der Waals gas.

- 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:

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

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

- $(C_V)_{V=V_c}$ 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

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

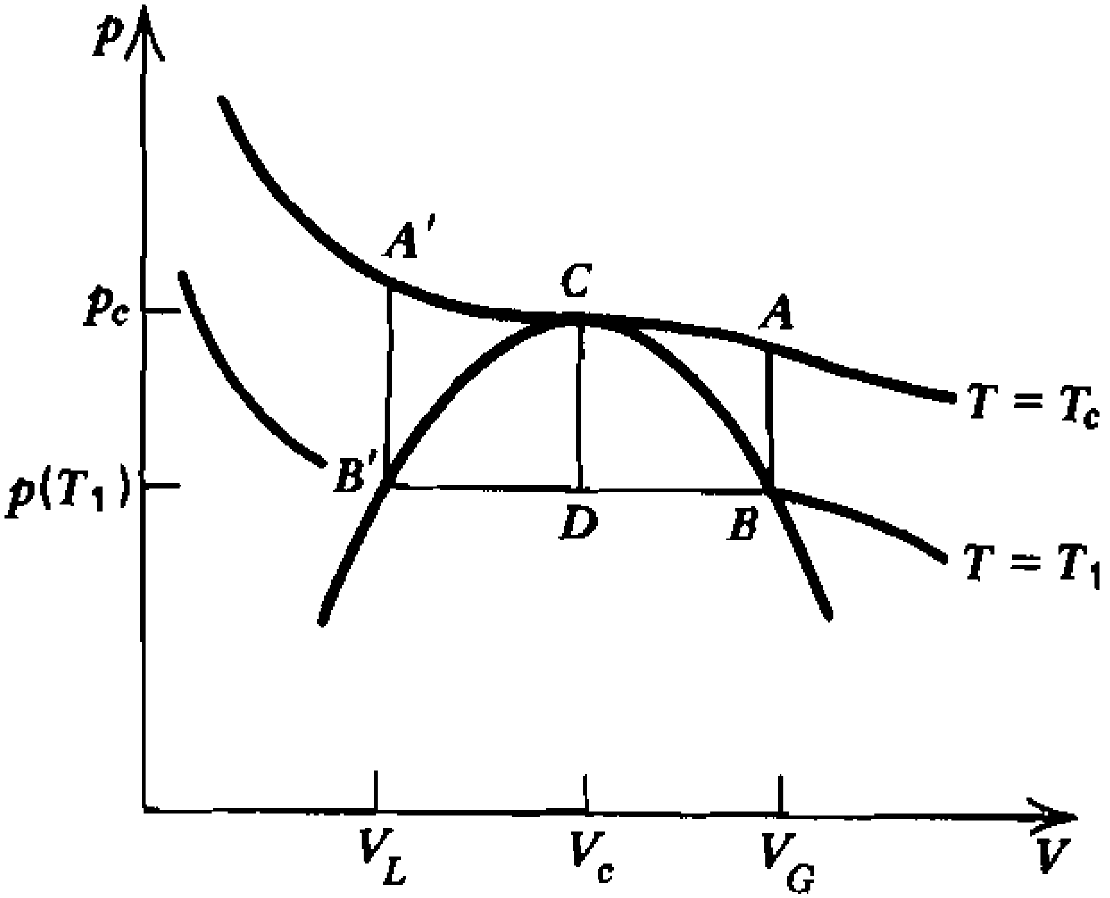


Figure 24.18 Schematic representation of the coexistence curv and isotherms near the critical point.

- 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:

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

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

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

Solutions of Nonelectrolytes

- Many chemical and physical phenomena are assoicated with properties of solutions.
- Vapour pressure varies with composition of solution.
- Solubility depends on the nature of the solvent.
- The position of equilibrium depends on the solvent system.
- Properties of solutions may be assessed on the basis of equilibrium with other phases.
- The characteristics of the equilibrium state may be determined by the dependence of the chemical potential of all phases and all components on temperature, pressure, and concentration.

- Measurements of composition in the liquid and vapour phase may be used to determine the chemical potentials of components.
- The deviation of a chemical potential from ideal behaviour can be considered in terms of molecular interactions.

The Chemical Potential of a Component in an Ideal Solution

- To study the thermodynamic properties of a solution, it is desirable to know the function dependence of the chemical potential of each species on composition, temperature, and pressure.
- In the gas phase, the equation of state is used, but this is not applicable to condensed phases.

- Specific knowledge of the equation of state cannot be required in a useful thermodynamic analysis of condensed phases.
- Consider a mixture in which no chemical reactions are occurring.
- When two liquids are mixed at constant temperature and pressure, there may be a change in volume and there may be heat evolved or absorbed.
- Occasionally, these changes in volume or enthalpy are too small to be measured.
- The changes in volume and enthalpy are related to how similar or dissimilar the molecules and their interactions are.

- In an ideal solutions, the interactions between molecules of different types are the same as interactions between molecules of the same type.
- An ideal solution is defined by the conditions:

$$(\Delta H_{mixing})_{T,p} = (H^E)_{T,p} = 0$$

$$(\Delta V_{mixing})_{T,p} = (V^E)_{T,p} = 0$$

- Consequently:

$$(\Delta U_{mixing})_{T,p} = (U^E)_{T,p} = 0$$

$$(\Delta G_{mixing})_{T,p} = -T(\Delta S_{mixing})_{T,p}$$

- This will permit the exploration of the dependence of chemical potential on composition.

- The superscript 0 refers to pure components.
- The chemical potential may be written by:

$$\Delta G_{mixing} \equiv G - G^0 = \sum_{i=1}^{r} n_i(\mu_i - \mu_i^0)$$

where n_i is the number moles of component i.

- The excess volume may be written as:

$$V^E \equiv V - V^0 = \left(\frac{\partial \Delta G_{mixing}}{\partial p}\right)_{T,n} = 0$$

The excess enthalpy may be written as:

$$H^E \equiv H - H^0 = -T^2 \left[\frac{\partial}{\partial T}\left(\frac{\Delta G_{mixing}}{T}\right)\right]_{p,n} = 0$$

- Assuming the the condition apply to each of the i terms, from the expression for V^E:

$$\left[\frac{\partial(\mu_i - \mu_i^0)}{\partial p}\right]_{T,n} = 0$$

- From the expression for H^E:

$$\left[\frac{\partial}{\partial T}\left(\frac{(\mu_i - \mu_i^0)}{T}\right)\right]_{p,n} = 0$$

- Together this means that the chemical potential of each component may depend on the composition and temperature:

$$\mu_i - \mu_i^0 = T w_i(n_1, \cdots, n_r)$$

- w_i is a function only of composition variables.
- μ_i^0 depends only on T and p.
- It has been shown previously for an ideal solution that:

$$w_i(n_1, \cdots, n_r) = R \ln x_i$$

- Therefore:

$$\mu_i = \mu_i^0 + RT \ln x_i$$

- This result depends on the assumption that the chemical potential has the same form for all species.
- Other choices of composition variables may be used instead of x_i, such as the volume fraction ψ_i may be more convenient for polymers.
- $\mu_i^0(T, p)$ is analogous to $\mu_i^*(T)$ for gases.

Chemical Potential of a Component in a Real Solution

- Real solutions have nonzero excess volumes and enthalpies.
- The nonideal behaviour needs to be addressed in terms of the chemical potential.
- For example the nonideal behaviour may be accounted for by an excess chemical potential:

$$\mu_i = \mu_i^0 + RT \ln x_i + \mu_i^E$$

- It may then be shown:

$$V^E = \left(\frac{\partial \Delta G_{mixing}}{\partial p}\right)_{T,n_1,\cdots,n_r} = \sum_{i=1}^{r} n_i \left(\frac{\partial \mu_i^E}{\partial p}\right)_{T,n_1,\cdots,n_r}$$

- Similarly:

$$H^E = -T^2 \left(\frac{\partial \left(\Delta G_{mixing}/T \right)}{\partial T} \right)_{p,n_1,\cdots,n_r}$$

$$= -T^2 \sum_{i=1}^{r} n_i \left(\frac{\partial \left(\mu_i^E/T \right)}{\partial T} \right)_{p,n_1,\cdots,n_r}$$

- Note that only the excess chemical potential makes a contribution to these.
- The entropy of mixing for a real solution has contributions from ideal mixing plus the contribution of the excess chemical potential:

$$\Delta S_{mixing} = - \left(\frac{\partial \Delta G_{mixing}}{\partial T} \right)_{p,n_1,\cdots,n_r}$$

- which gives:

$$\Delta S_{mixing} = -R\sum_{i=1}^{r} n_i \ln x_i - \sum_{i=1}^{r} n_i \left(\frac{\partial \mu_i^E}{\partial T}\right)_{p,n_1,\cdots,n_r}$$

- The excess entropy of mixing is:

$$-\sum_{i=1}^{r} n_i \left(\frac{\partial \mu_i^E}{\partial T}\right)_{p,n_1,\cdots,n_r}$$

.

- Instead of excess functions it is convenient to consider a mixture in terms of of deviations from mean molar properties.

- The mean molar volume is:

$$v_m \equiv \frac{V}{\sum_i n_i}$$

- Therefore the excess molar volume is:

$$v^E = \frac{V}{\sum_i n_i} - \frac{\sum_i n_i v_i^0}{\sum_i n_i} = \frac{V}{\sum_i n_i} - \sum_i x_i v_i^0$$

  where v_i^0 is the molar volume of pure component i at the temperature and pressure of the mixture.

- The mean and excess values of enthalpy, entropy, and free energy may be defined similarly.
- For components in solution, activity may be used in a similar way to fugacity.

- The chemical potential of i is:

$$\mu_i = \mu_i^0(T, p) + RT \ln \gamma_i x_i$$

  where $a_i = \gamma_i x_i$, a_i activity, and γ_i is the activity coefficient.
  - The activity may be thought of as an effective concentration.
  - The activity coefficient is dependent on temperature and pressure.
- It may be shown that:

$$\mu_i^E = RT \ln \gamma_i$$

  and that the activity coefficient contains all the information about deviations from ideal behaviour.

- These are only two ways of dealing with the nonideal behaviour for solutions.
  - Excess functions are convenient for solutions of nonelectrolytes.
  - Activity coefficients are useful for solutions of electrolytes.
- Changes in the chemical potential of i are measured with respect to the chemical potential of the standard state, $\mu_i^0(T,p)$.
  - $\mu_i^0(T,p)$ is independent of composition, therefore:

$$\mu_i^0(T,p) = \mu_i^L(T,p)$$

or

$$\mu_i^0(T,p) = \mu_i^L(T,p)$$

- The reference potential is the chemical potential of the pure substance (in solid or liquid phase) at the temperature and pressure of interest.
- This is one widely used convention.
- Another convention is to denote one component of the solution as the solvent and the remaining components as solutes.
    - Usually the component with the largest mole fraction is labelled “1” and is the solvent.
- The standard state for the solvent is the pure solvent:

$$\mu_1^0(T,p) = \mu_1^L(T,p)$$

while a hypothetical standard state is chosen for all other components (or solutes).

- The hypothetical state for solutes assumes that the properties are determined in the low concentration limit (and that the activity coefficient is unity).

$$\mu_i^0(T,p) = \mu_i^\theta(T,p) = \lim_{x_i \to 1} (\mu_i - RT \ln x_i)$$

- This standard state depends on the temperature, pressure, and the solvent.
    - Consider a solution of i in 1 that is sufficiently dilute so that each molecule of i is surrounded only by molecules of solvent.
    - The molecules of i are separated from each other so far that they cannot interact with each other.
    - If the solution is diluted further, the nature of the interaction of i with the solvent does not change.

- If the interaction of molecules of i with molecules of the solvent is different from the interaction of molecules of i with molecules of i then species i in the solvent will behave differently from species i as pure i.
- A hypothetical liquid of pure i where species i interacts with other molecules the same way that i interacts with the solvent will be different from pure i.
- In dilute solution,

$$\overline{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n'_j}$$

does not change with further dilution, but also is not equivalent to the partial molar volume of pure i.

- In the hypothetical reference state, the low concentration limit is v_i^{θ} not v_i^{0}.

- It is to be noted that this hypothetical reference state is not a state of infinite dilution, but rather a state where molecules of species i interacts with other molecules of i in the same manner i interacts with the solvent.
- Enthalpy changes and volume changes are among the more convenient properties to measure.
- Therefore it is desirable to consider these in terms of their excess values:

$$\left[\frac{\partial(\mu_i^E/T)}{\partial p}\right]_{T,n_1,\cdots,n_r} = R\left(\frac{\partial \ln \gamma_i}{\partial p}\right)_{T,n_1,\cdots,n_r} = \frac{\overline{v}_i - v_i^0}{T}$$

$$\left[\frac{\partial(\mu_i^E/T)}{\partial T}\right]_{p,n_1,\cdots,n_r} = R\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{p,n_1,\cdots,n_r} = \frac{\overline{h}_i - h_i^0}{T^2}$$

- These equations describe the behaviour of volume and enthalpy in terms of the excess chemical potential.
- Recall the Gibbs-Duhem equation:

$$\left(\sum_{i=1}^{r} n_i d\mu_i\right)_{T,p} = 0$$

- From this it follows:

$$\left(\sum_{i=1}^{r} n_i \; d\mu_i^E\right)_{T,p} = RT\left(\sum_{i=1}^{r} n_i \; d\ln\gamma_i\right)_{T,p} = 0$$

- This means that for a two-component system:

$$n_1(d\ln\gamma_1)_{T,p} + n_2(d\ln\gamma_2)_{T,p} = 0$$

- Therefore:

$$(1-x_2)\left(\frac{\partial \ln \gamma_1}{\partial x_2}\right)_{T,p} + x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T,p} = 0$$

- This means that μ_2^E can be determined from μ_1^E.

$$\mu_2^E = RT\ln\gamma_2 = RT\int_{x_2}^{1}\frac{1-x_2'}{x_2'}\frac{\partial \ln \gamma_1}{\partial x_2}dx_2'$$

$$= \int_{x_2}^{1}\frac{1-x_2'}{x_2'}\frac{\partial \mu_1^E}{\partial x_2}dx_2'$$

- To evaluate the excess chemical potential of component i, the dependence on the composition of the equation of state, the heat capacity of the solution, and the activity coefficient need to be known.

- A model equation of state would be convenient.
- Such a model equation of state may be defined by the following conditions:
  - The entropy of mixing has ideal form:

$$-R\sum_{i=1}^{r} n_i \ln x_I$$

  - The excess chemical potential for a binary mixture has the form:

$$\mu_1^E = RT\ln\gamma_1 = wx_2^2$$

$$\mu_2^E = RT\ln\gamma_2 = wx_1^2 = w(1-x_2)^2$$

  - It may be assumed that w is independent of temperature and pressure.

- This model mixture is a *regular mixture*.
- The heat of mixing takes the form:

$$\Delta H_{mixing} = -T^2 \left[n_1 \left(\frac{\partial}{\partial T} \frac{\mu_1^E}{T} \right)_{p,n_2} + n_2 \left(\frac{\partial}{\partial T} \frac{\mu_2^E}{T} \right)_{p,n_1} \right]$$

$$= n_1 w x_2^2 + n_2 w x_1^2$$

$$= n_1 w x_2 (1 - x_1) + n_2 w x_1 (1 - x_2)$$

$$= w(n_1 + n_2) x_2 (1 - x_2)$$

which is symmetric in x_1 and x_2.

- If w/RT is sufficiently large, the mixture will separate into two phases of distinct composition.
- It also allows the definition of a critical temperature above which the two phases are miscible.

- Instead of the regular solution, there are other models related to the virial expansion.
- For the mathematical description of activity in a two component system, the general solution is:

$$\ln \gamma_1 = \int x_2 \varphi(x_2) dx_2$$

$$\ln \gamma_2 = \int (1 - x_2) \varphi(x_2) dx_2$$

  where $\varphi(x_2)$ is some function of x_2.
- A virial-type form of $\varphi(x_2)$ is:

$$\varphi(x_2) = \sum_j \sum_k a_{jk}(T, p) x_2^j (1 - x_2)^k$$

  where $a_{jk}(T, p)$ do not depend on the composition.

- For the zeroth order approximation:

$$\ln \gamma_1 = \int x_2 a_{00}(T,p) dx_2 = \frac{1}{2} a_{00} x_2^2$$

$$\ln \gamma_2 = \int (1 - x_2) a_{00} dx_2 = \frac{1}{2} a_{00} (1 - x_2)^2$$

the result is equivalent to the regular mixture.

Partial Molar Quantities

- For Z, an extensive thermodynamic property, the corresponding partial molar quantity, $\overline{z}_i$, may be defined:

$$\overline{z}_i \equiv \left(\frac{\partial Z}{\partial n)i} \right)_{T,p,n_{j \neq i}}$$

- Because Z is extensive:

$$Z(\xi n_1, \xi n_2, \cdots, T, p) = \xi Z(n_1, n_2, \cdots, T, p)$$

- Upon differentiation with respect to ξ and setting $\xi = 1$ this gives:

$$Z = \sum_{i=1}^{r} n_i \overline{z}_i$$

- Thus partial molar quantities are intensive properties.
- Consider a binary solution with n_1 moles of 1 and n_2 moles of 2 in a total volume V.
  - Incremental additions of 1 and 2 are made to the solution such that:

$$\frac{\delta n_1}{\delta n_2} = \frac{n_1}{n_2}$$

- The partial molar volumes $\overline{v}_1$ and $\overline{v}_2$ depend only on the relative composition.
- Thus after the incremental additions:

$$V = n_1\overline{v}_1 + n_2\overline{v}_2$$

- A differential change in an extensive propery at constant T and p is:

$$(dZ)_{T,p} = \left(\sum_{i=1}^{r} n_i d\overline{z}_i\right)_{T,p} + \left(\sum_{i=1}^{r} \overline{z}_i dn_i\right)_{T,p}$$

- This leads to the constraint:

$$\left(\sum_{i=1}^{r} n_i d\overline{z}_i\right)_{T,p} = 0$$

- If $\overline{z}_i = \mu_i$, this is equivalent to the Gibbs-Duhem equation.
- Gibbs-Duhem type of constraints exists for changes to any partial molar quantity.
- Partial molar quantities may be determined experimentally.
- Define z_m, the mean molar value, by:

$$z_m \equiv \frac{Z}{\sum_{i=1}^{r} n_i} = \sum_{i=1}^{r} x_i \overline{z}_i$$

- Consider the case of a binary mixture:

$$\left(\frac{\partial z_m}{\partial x_1}\right)_{T,p} = \left(\frac{\partial}{\partial x_1}\left[x_1\overline{z}_1 + (1 - x_1)\overline{z}_2\right]\right)_{T,p}$$

- This may be rearranged to:

$$\left(\frac{\partial z_m}{\partial x_1}\right)_{T,p} = \overline{z}_1 - \overline{z}_2 + x_1 \left(\frac{\partial z_1}{\partial x_1}\right)_{T,p} + x_2 \left(\frac{\partial z_2}{\partial x_1}\right)_{T,p}$$

$$= \overline{z}_1 - \overline{z}_2$$

- This leads to:

$$\overline{z}_1 = z_m - x_2 \left(\frac{\partial z_m}{\partial x_2}\right)_{T,p}$$

$$\overline{z}_2 = z_m - x_1 \left(\frac{\partial z_m}{\partial x_1}\right)_{T,p}$$

- This is illustrated in Figure 25.1 where z_m is the tangent to the curve.

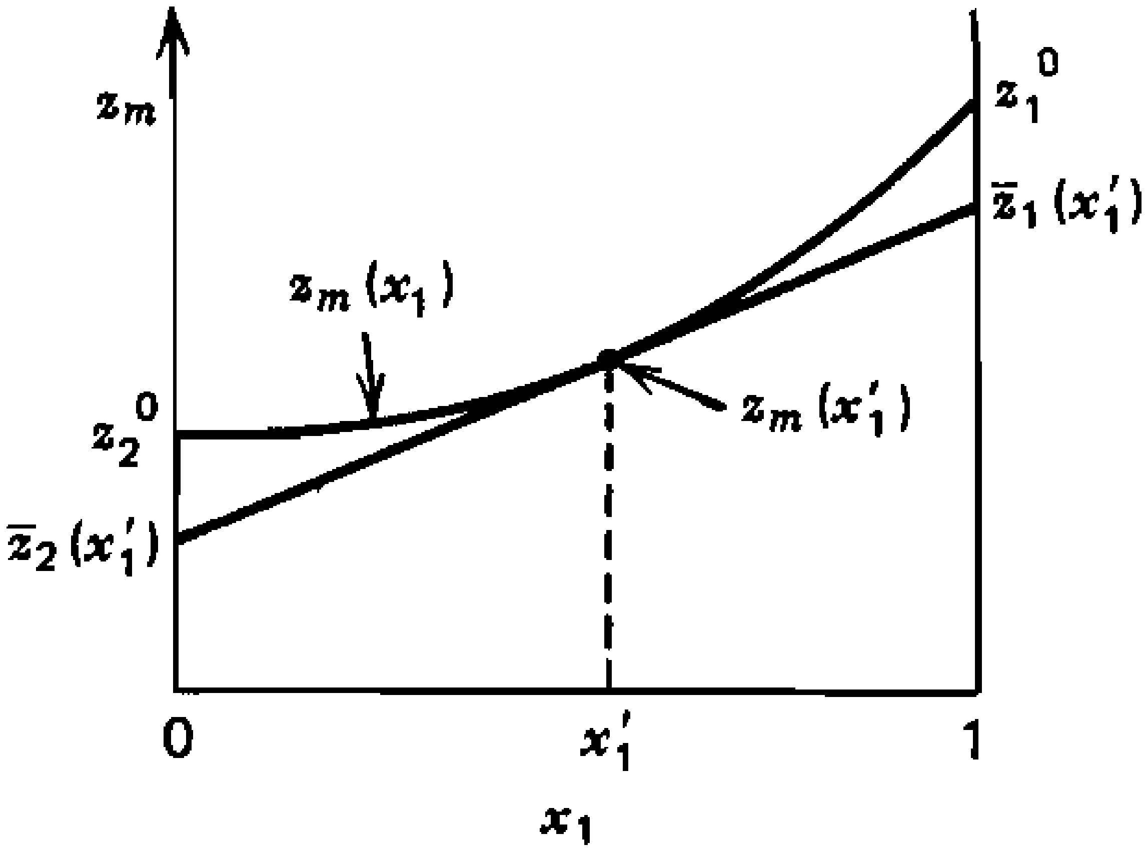


Figure 25.1 The mean molar function $z_m = Z/\Sigma n_i$ as a function of the mole fraction of component 1 in a binary mixture. The tangent to $z_m(x_1)$ at $x_1 = x_1'$ has intercepts $\bar{z}_2(x_1')$ at $x_1 = 0$ and $\bar{z}_1(x_1')$ at $x_1 = 1$.

Liquid-Vapour Equilibrium

- For each component of a mixture:

$$\mu_i(\mathrm{liquid}) = \mu_i(\mathrm{vapour})$$

- With pure i as the reference state:

$$\mu_i^0 + RT \ln \gamma_i x_i = \mu_i^*(T) + RT \ln \frac{f_i}{\mathcal{P}}$$

- This may be rearranged to give:

$$\gamma_i x_i = \frac{f_i}{\mathcal{P}} \exp\left[\frac{1}{RT}(\mu_i^* - \mu_i^0)\right]$$

- For pure i, $x_i = 1$, $\mu_i = \mu_i^0$ and $\gamma_i = 1$.

- This means:

$$1 = \frac{f_i^0}{\mathcal{P}} \exp\left[\frac{1}{RT}(\mu_i^* - \mu_i^0)\right]$$

  and

$$\gamma_i x_i = \frac{f_i}{f_i^0}$$

- For an ideal solution with an ideal vapour:

$$p_i = x_i p_i^0$$

  which is Raoult's Law.

- This means that the activity coefficient of i in solution may be obtained from measurement of fugacity of i in the gas phase.

- This also means that if γ_i is known the composition of the vapour phase may be predicted.
- Consider the equilibrium between an ideal gas mixture and an ideal condensed phase mixture.
- Dalton's law for the gas phase is:

$$p_i = y_i p$$

  where y_i is the mole fraction in the gas phase and p is the total pressure of the gas mixture
- Combining with Raoult's Law gives:

$$y_i p = x_i p_i^0$$

$$y_i = x_i \frac{p_i^0}{p}$$

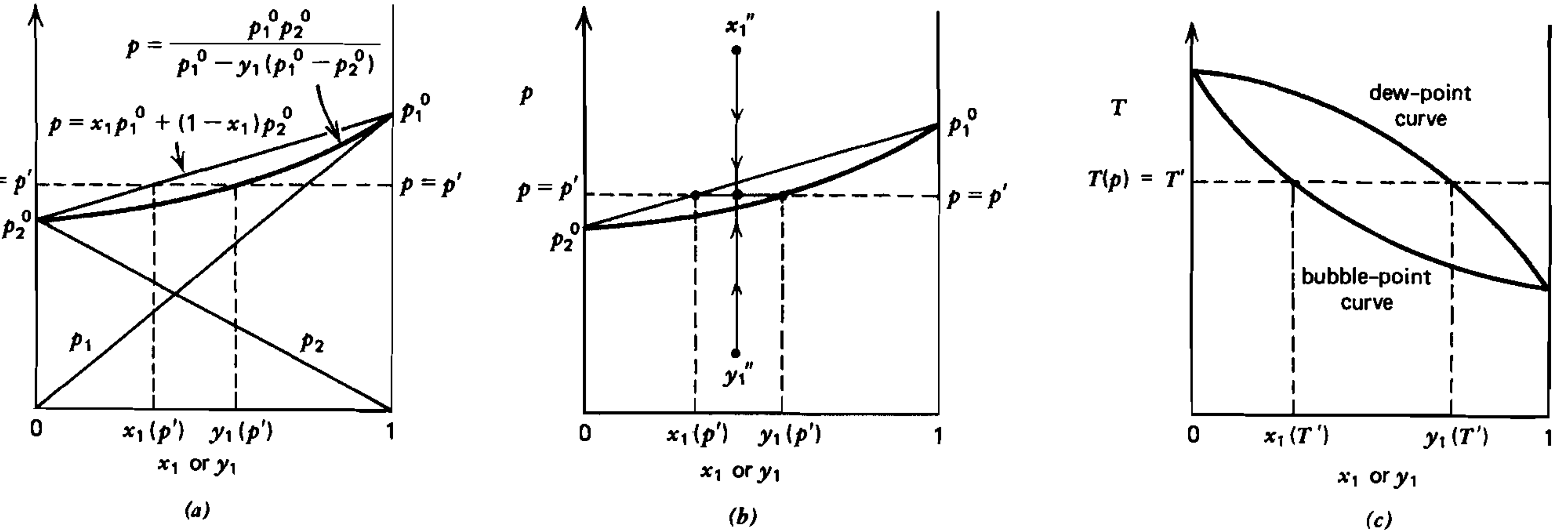
- This means that the compositions of the two phases can be very different.
- Consider the liquid vapour equilibrium of an ideal binary mixture (See Figure 25.2).
  - The total vapour pressure is:

    $$p = p_1 + p_2 = x_1 p_1^0 + x_2 p_2^0 = x_1(p_1^0 - p_2^0) + p_2^0$$

    which is the equation of a straight line.
  - But p is not a linear function of y_1.
  - It may be shown that:

    $$\frac{(y_1/y_2)}{(x_1/x_2)} = \alpha_{12} = \frac{y_1(1-x_1)}{x_1(1-y_1)} = \frac{p_1^0}{p_2^0}$$

    where α_{12} is independent of the composition.



re 25.2 (*a*) Schematic representation of the isothermal dependence of the total pressure of an ideal binary mixture on the mole frac-
of component 1 in the liquid, x_1, and on the mole fraction of component 1 in the vapor, y_1. (*b*) Schematic representation of the separa-
of a mixture into vapor and liquid phases when compressed to $p = p'$ isothermally from a state where p is less than the pressure along
dew-point curve, or when expanded isothermally from a state where p is greater than the pressure along the bubble-point curve.
chematic diagram of the bubble-point and dew-point curves on a temperature-composition diagram at constant pressure (ideal binary
ure).

- Total pressure may be expressed as a function of y_1, the composition variable for the gas phase:

$$p = \frac{p_1^0}{\alpha_{12} - y_1(\alpha_{12} - 1)} = \frac{p_1^0 p_2^0}{p_1^0 - y_1(p_1^0 - p_2^0)}$$

- This equation describes a rectangular hyperbola which is concave upward.
- At equilibrium vapour and liquid have the same pressure and the composition of each phase may be determined from the intersection of p' with each of the curves at $x_1(p')$ and $y_1(p')$
  - The line $p = x_1 p_1^0 + (1 - x_1)p_2^0$ is the bubble point curve.
  - The curve $p = p_1^0 p_2^0/(p_1^0 - y_1(p_1^0 - p_2^0))$ is the dew point curve.

- At pressures above the bubble point curve, the liquid phase is stable.
- At pressures below the dew point curve, the gas phase is stable.
- At pressures between the curves, liquid and vapour coexist with the composition of each determined by the total pressure.
- It is to be noted that p_1^0 and p_2^0 depend on temperature, usually in different ways.
  - This means that α_{12} is a function of temperature and the boiling point is not a linear function of composition.

$$y_1(T) = \frac{x_1 \alpha_{12}(T)}{1 + x_1 \left[\alpha_{12}(T) - 1\right]}$$

- A temperature composition diagram is shown in 25.2 (c).
    - If T is above the dew point curve, then the gas phase is stable.
    - If T is below the bubble point curve, then the liquid phase is stable.
    - The region between the two curves is the coexistence region, where the compositions of each phase is determined by the intersection of $T(p)$ with each of the bubble point and dew point curves.
    - As the composition of the liquid changes, its boiling point changes resulting in the enrichment of the vapour in one component.
        - This is the basis of distillation.
- Now consider an nonideal mixture where the gas is only slightly soluble in the liquid.

- The gas does not react with the solvent.
- It is generally observed that the solubility of a gas is proportional to its fugacity and increases as T decreases.
- Molecules of both solvent and solute may be transferred across the gas-liquid interface.
- Because both components are in both phases at equilibrium:

$$\mu_1(\text{gas phase}) = \mu_1(\text{liquid phase})$$

$$\mu_2(\text{gas phase}) = \mu_2(\text{liquid phase})$$

- The solvent is labelled 1 and the solute is labelled 2.
- Since the gas solute is only slightly soluble, x_1 is near unity.

- Therefore:

$$\mu_1(\text{liquid phase}) = \mu_1^0 + RT\ln x_1$$

$$\mu_2(\text{liquid phase}) = \mu_2^{\theta} + RT\ln x_2$$

- This assumes that the liquid phase is an ideal solution.
- The standard state for component 1, the solvent, is that of the pure liquid at the same temperature and pressure.
- The standard state for component 2, the solute, is the hypothetical state with the same properties per mole as an infinitely dilute solution.
- This gives:

$$\mu_2^*(T) + RT\ln\frac{f_2}{\mathcal{P}} = \mu_2^{\theta}(T, p, \text{solvent}) + RT\ln x_2$$

- Upon rearrangement this gives:

  $$\frac{f_2}{\mathcal{P}} = x_2 \exp\left(\frac{\mu_2^{\ominus} - \mu_2^*}{RT}\right) = x_2 k_2(T, p, \mathrm{solvent})$$

  which is Henry's Law with k_2 as the Henry's Law coefficient.
- In the low pressure limit, partial pressure may be used instead of partial fugacity and Henry's Law may be written as:

  $$p_2 = x_2 \mathcal{P} k_2(T, p, \mathrm{solvent})$$
- Thus the solubility of a gas is proportional to its partial pressure.
- Note that k_2 is specific to both the solute and solvent.

- For the solvent, it may be written:

$$\frac{f_1}{\mathcal{P}} = x_1 \exp\left(\frac{\mu_1^0 - \mu_1^*}{RT}\right)$$

- If the vapour is assumed to be ideal, then:

$$\frac{p_1}{\mathcal{P}} = x_1 \exp\left(\frac{\mu_1^0 - \mu_1^*}{RT}\right)$$

- It is to be noted that the choice of standard state is different for the solvent and the solute.
- Pure solvent liquid vapour equilibrium is described by:

$$\mu_1^*(T) + RT \ln \frac{f_1^0}{\mathcal{P}} = \mu_1^0(T)$$

- This can be rearranged to:

$$\frac{f_1^0}{\mathcal{P}} = \exp\left(\frac{\mu_1^0 - \mu_1^*}{RT}\right)$$

where the reference state for the solvent is that of the pure liquid.

- Therefore:

$$f_1 = x_1 f_1^0$$

- If the gas phase is ideal then:

$$p_1 = x_1 p_1^0$$

where p_1^0 is the vapour pressure of pure solvent.

- This is Raoult's Law.

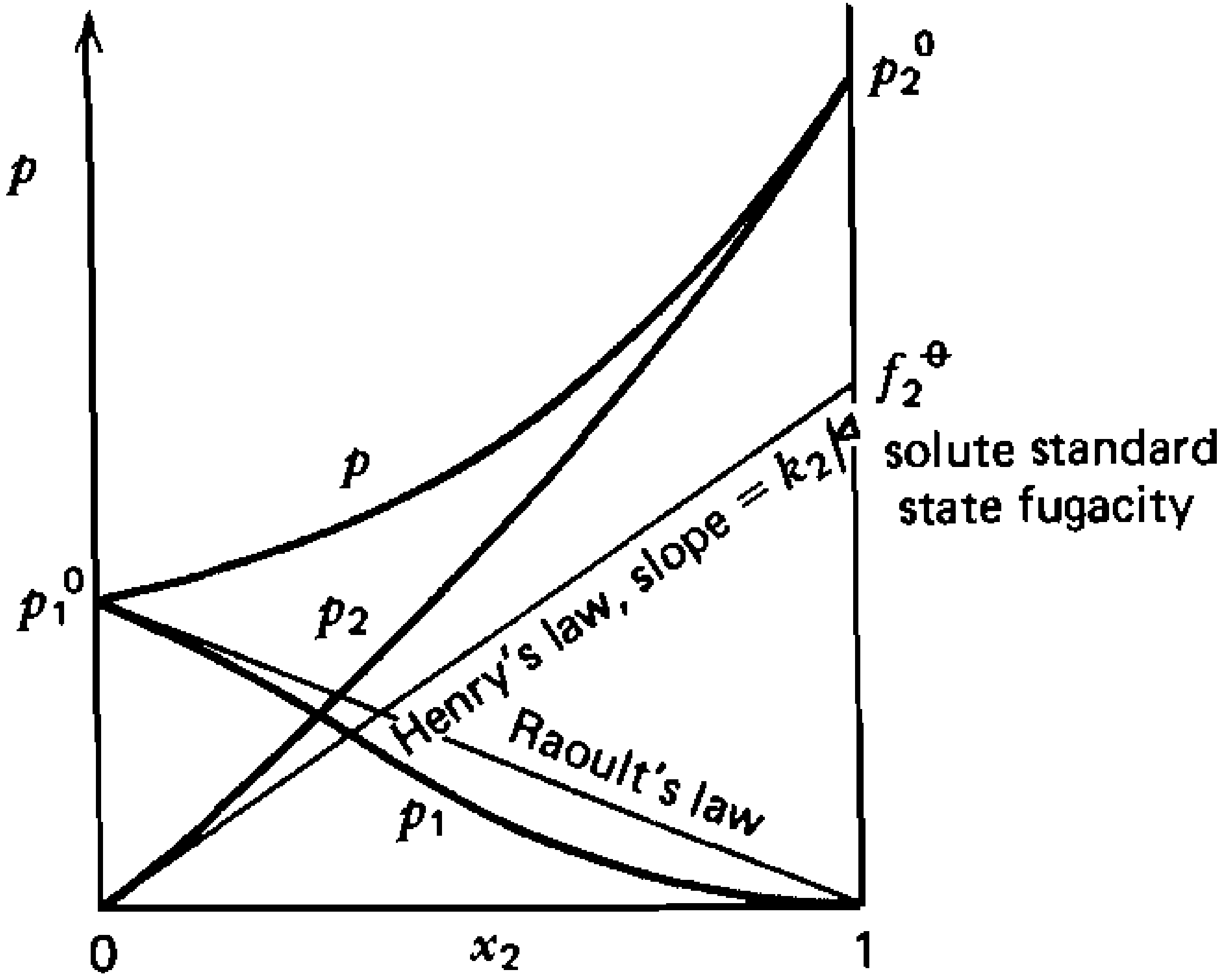


Figure 25.3 Schematic display of the Henry's law representation and the extrapolation to the standard state of the solute.

- When this is compared to Henry's Law, it is to be noted that k_2 is NOT the vapour pressure of the solute.
- Instead k_2 defines the fugacity of the solute in the hypothetical reference state.
- Raoult's Law and Henry's Law are compared in Figure 25.3,
- The fugacity of the solute, k_2 differs from the vapour pressure for the pure solute due to the difference in the hypothetical reference state.
  - The solute molecules are sufficiently far from each other that the solute-solute interactions can be assumed to be negligible.
  - In the solution, the solute molecules have less volume in which to move freely than is the case of the same molecules in the ideal gas phase.

- This means that they have lower entropy and that the entropy of solution is negative.
- The effective volume per molecule of solute in solution is usually different from the effective volume per molecule of pure solute.
- This is because the forces of interaction between solute molecules is different from the forces of interaction between molecules of solute and solvent.
- As a result the enthalpy of solution is usually nonzero and may be either positive or negative.
- The forces of interaction can lead to changes in local ordering of solvent molecules about the solute which also contributes to the entropy.
- All these factors contribute to the fugacity of the solute differing from the vapour pressure of pure solute.

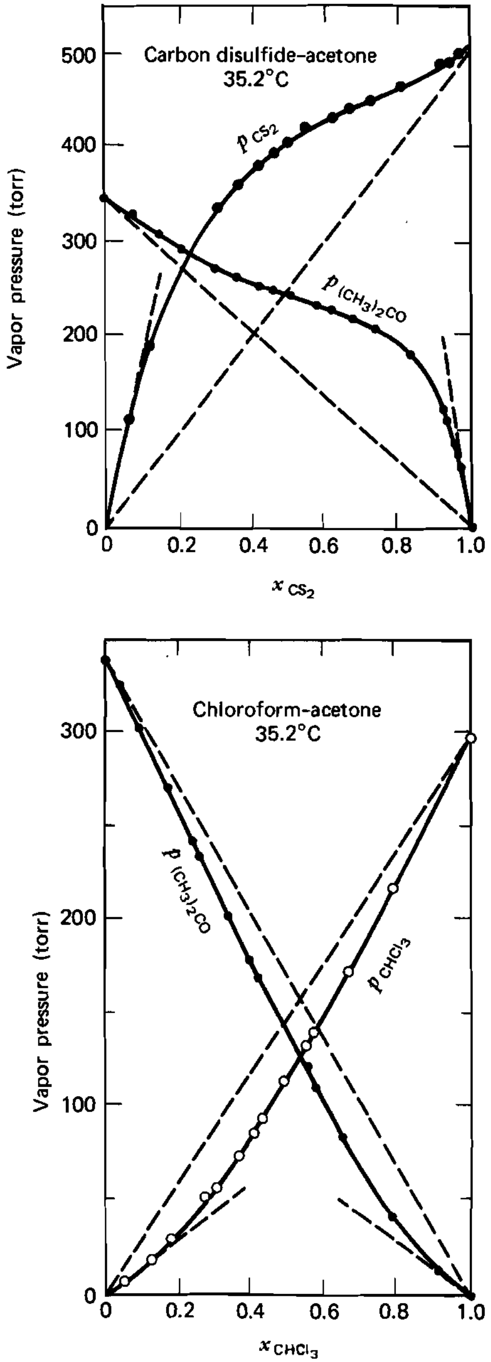


Figure 25.4 Partial pressure as a function of composition for carbon disulfide–acetone and chloroform–acetone solutions. From R. H. Cole and J. S. Coles, *Physical Principles of Chemistry* (Freeman, San Francisco, 1964).

- Consider a nonideal mixture of volative liquids that is not dilute.
- Deviations of vapour pressure from ideality may be positive or negative.
- This may be interpreted in terms of the interactions in the condensed phase.
  - If unlike molecules attract each other more than like molecules, then the vapour pressure will be lower than that predicted by Raoult's Law.
  - If unlike molecules repel each other more than like molecules, then the vapour pressure will be higher than that predicted by Raoult's Law.
- Enthalpy contributions tend to be the most significant but entropy contributions can be significant if the molecules are very different in size.

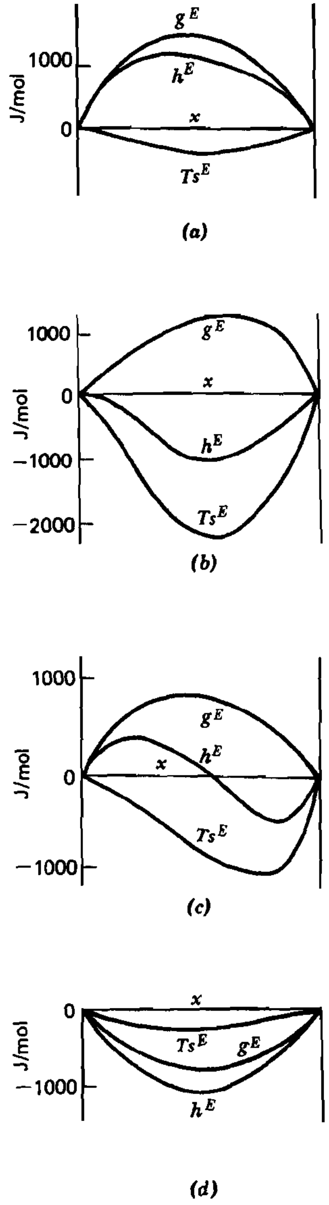


Figure 25.5 (*a*) The excess functions of the system acetonitrile + carbon tetrachloride at 45°C as a function of the mole fraction of acetonitrile. (*b*) The excess functions of water + pyridine at 80°C as a function of the mole fraction of water. (*c*) The excess functions of water + dioxane at 25°C as a function of the mole fraction of water. (*d*) The excess functions of water + hydrogen peroxide at 25°C as a function of the mole fraction of water. From J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed. (Butterworths, London, 1969).

- As shown in Figure 25.5, excess enthalpy and entropy are fucntions of concentrations.
- In principle, activity coefficients may be determined from measurement of vapour pressure as a function of concentration of solution, although in practice, such measurements may be difficult.
- Recall:

$$\gamma_i x_i = \frac{f_i}{f_i^0}$$

- If the total pressure and composition of the vapour can be determined and the composition of the liquid and the equation of state of the vapour are known, then γ_i may be determined.
- Usually the second virial coefficient is sufficient since the vapour pressure is low.

- For a binary solution:

  $$n_1(d\ln\gamma_1)_{T,p} + n_2(d\ln\gamma_2)_{T,p} = 0$$

  and

  $$(1-x_2)\left(\frac{\partial\ln\gamma_1}{\partial x_2}\right)_{T,p} + x_2\left(\frac{\partial\ln\gamma_2}{\partial x_2}\right)_{T,p} = 0$$

- If the vapour is ideal then:

  $$p_1 = \gamma_1 x_1 p_1^0$$

  $$p_2 = \gamma_2 x_2 p_2^0$$

- Therefore:

$$(1-x_2)\left(\frac{\partial \ln p_1}{\partial x_2}\right)_T + x_2\left(\frac{\partial \ln p_2}{\partial x_2}\right)_T = 0$$

  if it is assumed that p_1 and p_2 do not depend on the total pressure.

- This is the Duhem-Margules equation and is valid if the vapour behaves ideally and there is negligible dependence of p_1 and p_2 on the total pressure.
- This may be rearranged to:

$$\left(\frac{\partial p_1}{\partial x_2}\right)_T = \frac{(1-x_1)p_1}{(p_1-x_1p)}\left(\frac{\partial p}{\partial x_2}\right)_T$$

- Thus p_1, p_2, γ_1, and γ_2 may be determined from measurements of total pressure as a function of composition.
- The inverse problem is the calculation of bubble point and dew point curves as a function of composition from the dependence of the chemical potentials on composition.
- The condition for phase equilibrium at T and p is:

$$\mu_i^*(T) - \mu_i^0(T,p) + RT \ln \frac{f_i/\mathcal{P}}{\gamma_i x_i}$$

$$= \mu_i^* - \mu_i^0(T,p) + RT \ln \frac{p}{\mathcal{P}} + RT \ln \frac{f_i}{p} - RT \ln \gamma_i x_i = 0$$

- For coexistence of vapour and liquid at $T + dT$ and $p + dp$:

$$\mu_i^V(T + dT, p + dp) = \mu_i^L(T + dT, p + dp)$$

- Therefore:

$$-R \ln \frac{f_i/\mathcal{P}}{\gamma_i x_i} = \left[\frac{\partial}{\partial T} \frac{\mu_i^*(T) - \mu_i^0(T, p)}{T}\right]_p dT$$

$$+ \left[\frac{\partial}{\partial p}\left(\frac{\mu_i^*(T) - \mu_i^0(T, p)}{T}\right)_T + R \ln \frac{p}{\mathcal{P}}\right] dp$$

$$= \frac{h_i^0 - h_i^*}{T^2} dT - \frac{v_i^0(T, p) - RT/p}{T} dp$$

- This can be integrated to yield the bubble-point and dew-point curves.
- Consider the composition dependence ot isothermal liquid-vapour equilibrium:

$$\ln\left(\frac{\gamma_1^V y_1}{\gamma_1 x_1}\right) = -\frac{1}{RT}\int_{p_1^0}^{p} \Delta v_1^0 dp$$

$$\ln\left(\frac{\gamma_2^V y_2}{\gamma_2 x_2}\right) = -\frac{1}{RT}\int_{p_2^0}^{p} \Delta v_2^0 dp$$

  where $\gamma_i^V \equiv f_i/y_i p$ is the activity coefficient of i.
- Because the molar volume of liquid is negligible compared to the molar volume of the gas phase, Δv_1^0 and Δv_2^0 are the molar volumes of the respective gas phases.

- If the vapour phase is ideal, then

$$\gamma_i^V \equiv \frac{f_i}{y_i p} = \frac{y_i p}{y_i p} = 1$$

  and

$$\Delta v_1^0 = \Delta v_2^0 = \frac{RT}{p}$$

- Integration gives:

$$\ln\left(\frac{y_1}{\gamma_1 x_1}\right) = \ln\left(\frac{p_1^0}{p}\right)$$

$$\ln\left(\frac{y_2}{\gamma_2 x_2}\right) = \ln\left(\frac{p_2^0}{p}\right)$$

- These can be solved to give equations for the bubble-point curve:

$$x_2 = \frac{p_1^0\gamma_1 - p}{p_1^0\gamma_1 - p_2^0\gamma_2}$$

  and the dew-point curve:

$$y_2 = \frac{p_1^0 p_2^0\gamma_1\gamma_2 - pp_2^0\gamma_2}{pp_1^0\gamma_1 - pp_2^0\gamma_2}$$

- The activity coefficients are also related to the heat of vaporization:

$$\ln\left(\frac{\gamma_1^V y_1}{\gamma_1 x_1}\right) = \int_{T_{1b}}^{T} \frac{h_1^* - h_1^0}{RT'^2} dT'$$

$$\ln\left(\frac{\gamma_2^V y_2}{\gamma_2 x_2}\right) = \int_{T_{2b}}^{T} \frac{h_2^* - h_2^0}{RT'^2} dT'$$

- Upon integration these yield:

$$\Lambda_{1b} \equiv \int_{T_{1b}}^{T} \frac{h_1^* - h_1^0}{RT'^2} dT' = \frac{h_1^* - h_1^0}{R}\left(\frac{1}{T_{1b}} - \frac{1}{T}\right)$$

and

$$\Lambda_{2b} \equiv \int_{T_{2b}}^{T} \frac{h_2^* - h_2^0}{RT'^2} dT' = \frac{h_2^* - h_2^0}{R}\left(\frac{1}{T_{2b}} - \frac{1}{T}\right)$$

- If it is assumed that the vapour is ideal, then:

$$\gamma_1^V y_1 \rightarrow y_1 \text{ and } \gamma_2^V y_2 \rightarrow y_2$$

- Thus:

$$y_2 = \frac{\exp(\Lambda_{1b})\gamma_2 - \gamma_1\gamma_2}{\exp(\Lambda_{1b})\gamma_2 - \exp(-\Lambda_{2b})\gamma_2}$$

$$x_2 = \frac{\exp(\Lambda_{1b}) - \gamma_1}{\exp(\Lambda_{1b})\exp(\Lambda_{2b})\gamma_2 - \gamma_1}$$

Liquid-Solid Equilibrium

- Treatment parallels treatment of Gas-Condensed Phase equilibria, but neither phase can be assumed to be an ideal gas.
- It will not be covered in detail in class, but is included in material for the exam.

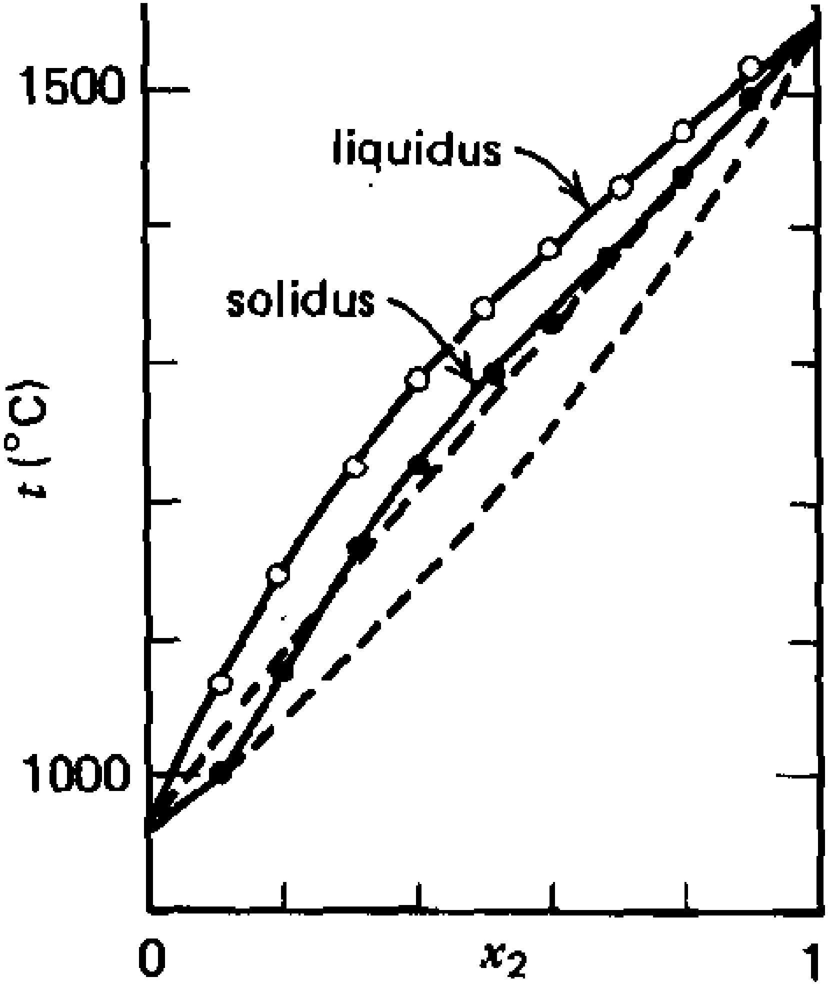


Figure 25.6 Phase diagram for liquid–solid equilibrium in the system Ag(1)–Pd(2). The dashed curves are the calculated liquidus and solidus lines for ideal solutions (Eqs. 25.98 and 25.99).

The Colligative Properties of Solutions: Boiling-Point Elevation, Freezing-Point Depression, and Osmotic Pressure

- Consider the case of a binary solution where the solute is not volatile.
  - This would be equivalent to assigning a vapour pressure of zero to the pure solute.
  - Our previous treatment would predict a lowering of the vapour pressure of the solution when compared to the vapour pressure of the pure solvent.
  - The vapour pressure of the solution is proportional to the mole fraction of the solvent.
  - This means that the boiling point of the solution will be elevated relative to the pure solvent.

- The measurement of boiling point elevation is the basis of some experimental techniques for determining molar mass of a solute or the activity coefficient of the solvent.
- When the solution is in equilibrium with the vapour, then:

$$\mu_1^V(T_{1b},p) = \mu_1^L(T_{1b},p)$$

- But

$$\mu_1^V(T,p) = \mu_1^L(T,p) + RT\ln\gamma_1 x_1$$

- Therefore:

$$\frac{\mu_1^V(T,p)}{T} - \frac{\mu_1^V(T_{1b},p)}{T_{1b}} = \frac{\mu_1^L(T,p)}{T} - \frac{\mu_1^L(T_{1b},p)}{T_{1b}} + RT\ln\gamma_1 x_1$$

- But

$$\ln \gamma_1 x_1 = -\int_{T_{1b}}^{T} \frac{h_1^V - h_1^L}{RT'^2} dT' = -\int_{T_{1b}}^{T} \frac{L_{1v}}{RT'^2} dT'$$

  where $L_{1V} \equiv h_1^V - h_1^L$, the latent heat of vapourization.
- L_{1v} will vary depending on the temperature due to the difference in the heat capacities of liquid and solid:

$$L_{1v} = \Delta h_{1v} + \left[c_p^V - c_p^L\right](T - T_{1b})$$

- Thus:

$$\ln \gamma_1 x_1 = -\int_{T_{1b}}^{T} \frac{\Delta h_{1v} + \Delta c_p (T' - T_{1b})}{RT'^2} dT'$$

- If $\theta = T - T_{1b}$ this may be rearranged to:

$$\ln \gamma_1 x_1 = -\int_0^\theta \frac{\Delta h_{1v} + \Delta c_p \theta'}{R(T_{1b} + \theta')^2} d\theta'$$

- If θ, the difference in the boiling point, is small compared to the boiling point, then:

$$\frac{1}{(T_{1b} + \theta)^2} = \frac{1}{T_{1b}^2} \left(1 - \frac{2\theta}{T_{1b}} + \cdots \right)$$

  which can be substituted into the integrand.

- Upon integration:

$$\ln \gamma_1 x_1 = -\frac{\Delta h_{1v} \theta}{R T_{1b}^2} + \left(\frac{\Delta c_p}{2R} + \frac{\Delta h_{1v}}{R T_{1b}} \right) \left(\frac{\theta}{T_{1b}} \right)^2 + \mathcal{O}(\theta^3)$$

- If θ is small, the second term can be ignored.
- It is also to be noted that everything on the right hand side of the equation depends only on the solvent.
  - This means that boiling point elevation depends only on the mole fraction of solute and not the nature of the non-volatile solute.
- If it can be assumed that solution is ideal and dilute then $\gamma_1 = 1$ and only the first order term needs to be retained:

$$\ln x_1 = -\frac{\Delta h_{1v}\theta}{RT_{1b}^2}$$

- When the solution is dilute, x_2 is small, and:

$$\ln x_1 = \ln(1 - x_2) = -x_2$$

- Therefore:

$$x_2 = \frac{\Delta h_{1v}\theta}{RT_{1b}^2}$$

- This can provide the basis for determination of molar mass.
- The mole fraction may be written as:

$$x_2 = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

- If $x_2 << 1$ then:

$$x_2 = \frac{w_2/M_2}{w_1/M_1}$$

- Therefore:

$$M_2 = \frac{w_2}{w_1/M_1}\frac{RT_{1b}^2}{\Delta h_{1v}\theta} = 1000\frac{w_2}{w_1}\frac{K_b}{\theta}$$

- K_b is the ebulliscopic constant and is defined as:

$$K_b \equiv \left(\frac{M_1}{1000}\right)\left(\frac{RT_{1b}^2}{\Delta h_{1v}}\right)$$

  and has units of K kg mol^{-1}.
  - Note that:

    $$\frac{M_2\ w_1}{1000\ w_2}$$

    is the molality, moles of solute per kg of solvent.

- This is applicable to solutes which no vapour pressure.
- Analoguous to this is freezing-point depression.
- Consider a solute that is insoluble in the crystalline phase of the solvent.
- It can be shown that:

  $$\ln \gamma_1 x_1 = -\frac{\Delta h_{1f}\theta}{RT_{1f}^2} - \left(\frac{\Delta c_p}{2R} + \frac{\Delta h_{1f}}{RT_{1f}}\right)\left(\frac{\theta}{T_{1f}}\right)^2 + \mathcal{O}(\theta^3)$$

  where the subscript f refers to freezing and $\theta = T_{1f} - T$.
- As before θ depends only on the solvent properties and not the solute.
- If the concentration of solute is low and (θ/T_{1f}) is small, then:

$$\ln \gamma_1 x_1 = -\frac{\Delta h_{1f}\theta}{RT_{1f}^2} = -\frac{\theta}{K_f}\frac{M_1}{1000}$$

where

$$K_f \equiv \left(\frac{M_1}{1000}\right)\left(\frac{RT_{1f}^2}{\Delta h_{1f}}\right)$$

- Then

  $$\theta = K_f m_2$$

  where m_2 is the molality of the solute.
- If the solution is ideal:

  $$x_2 = \frac{\Delta h_{1f}\theta}{RT_{1f}^2}$$