Thermodynamic Description of a Gas Mixture

- To describe the properties of a mixture, it is necessary to specify the temperature, pressure, total volume, and the composition.
- Any unit may be used, but mole fraction is often convenient.

$$x_i = \frac{n_i}{n_1 + n_2 + \dots + n_r}$$

• Mole fraction is related to partial pressure:

$$\lim_{p \to 0} \frac{p_i}{p} = x_1$$

or:

$$\lim_{p \to 0} p = \frac{RT}{V} (n_1 + n_2 + \dots + n_r) = (p_1 + p_2 + \dots + p_r)$$

- The composition variables are not completely independent of each other.
 - Mole fractions must add up to unity.
 - Partial pressures must add up to the total pressure.
- Equilibria will impose additional constraints on composition.
 - Consider the reaction:

$$H_2 + I_2 \rightleftharpoons 2HI$$

- Only two of the three concentrations are independent.
- The third is determined by the equilibrium.
- Consider Figure 21.9 in which a container is separated into two compartments by a semipermeable membrane.



Figure 21.9 Schematic diagram of a box with semipermeable membrane separating pure component *i* from a mixture of gases containing component *i*. Only *i* can pass through the membrane.

- Compartment I contains pure *i* in equilibrium with with component *i* in the gas mixture in compartment II.
- The semipermeable membrane is also diathermal and rigid and heat but not work can be transferred from one compartment to the other.
- The system is in equilibrium, so:

$$\mu_i^I = \mu_i^{II} = \mu_i$$

$$T^I = T^{II} = T$$

• For gas mixtures at nonzero pressure:

$$\mu_i^I = \mu_i^*(T, \mathcal{P}) + RT \ln \frac{p^I}{\mathcal{P}} + \int_{0,T}^{p^I, T} \left[\overline{v}_i(p') - \frac{RT}{p'}\right] dp'$$

- For the system in Figure 21.9, $p_i^I = p_i^I I$.
- In the low pressure limit, $p_i^I = p^I = x_i^{II} p^I I$.
- Therefore the chemical potential of *i* in compartment II is:

$$\mu_i^{II} = \mu_i^*(T, \mathcal{P}) + RT \ln \frac{x_i^{II} p^{II}}{\mathcal{P}} + \int_{0,T}^{p^{II},T} \left[\overline{v}_i(p') - \frac{RT}{p'} \right] dp'$$

where:

$$\overline{v}_{i} = \left(\frac{\partial \mu_{i}}{\partial p}\right)_{T,n_{j}} = \frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_{i}}\right)_{T,n_{j\neq i}} = \frac{\partial}{\partial n_{i}} \left(\frac{\partial G}{\partial p}\right)_{T,n_{j\neq i}}$$
$$= \left(\frac{\partial V}{\partial n_{i}}\right)_{T,p,n_{i\neq j}}$$

- Chemical potential may be determined from the equation of state for the substance.
- The average molar volume for the mixture may be considered in terms of the virial equation of state:

$$v_m = \frac{V}{\sum_{i=1}^r n_i} = \frac{RT}{p} + B(x_1, x_2, \cdots, x_{r-1}, T)$$

where B is an extension of the virial equation to account for interaction of molecules and is proportional to the frequency of occurrence of all possible pairs.

• Thus:

$$B(x_1, x_2, \cdots, x_{r-1}, T) = \sum_{i=1}^r \sum_{j=1}^r x_i x_j B_{ij}(T)$$

- By symmetry, $B_{ij} = B_{ji}$.
- For a binary mixture:

$$\frac{V}{n_1 + n_2} = \frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2}$$

• But:

$$\overline{v}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T,p,n_2}$$

• Therefore:

$$\overline{v}_1 = \frac{RT}{p} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{11} + 2n_2^2 B_{12} - n_2^2 B_{22}}{(n_1 + n_2)^2}$$

• This may be rewritten as:

$$\overline{v}_1 = \frac{RT}{P} + x_1^2 (2B_{11} - B_{11}) + x_1 x_2 (2B_{11} - B_{12})$$

$$+x_2x_1(2B_{12}-B_{21})+x_2^2(2B_{12}-B_{22})$$

• Generally:

$$\overline{v}_i = \frac{RT}{P} + \sum_{j=1}^r \sum_{k=1}^r x_j x_k (2B_{ij} - B_{jk})$$

• Therefore:

$$\mu_i = \mu_i^*(T) + RT \ln \frac{px_i}{\mathcal{P}} + \sum_{j=1}^r \sum_{k=1}^r x_j x_k (2B_{ij} - B_{jk})p$$

• For a pure gas:

$$\mu_i = \mu_i^*(T) + RT \ln \frac{p}{\mathcal{P}} + B_{11}p$$

- In a mixture of real gases, interactions between molecules of 1 and 2 are not expected to be the same as interactions between molecules of 1 with 1 or molecules of 2 with 2.
- Yet it is desirable to make predictions about properties of gas mixtures and relate these properties to the properties of the pure components.
- Fugacity of component *i* in a mixture has been defined by Lewis and Randall as:

$$f_i = x_i p \exp\left[\int_0^p \left(\overline{v}_i - \frac{RT}{p'}\right) \frac{dp'}{RT}\right]$$

• This gives a partial fugacity:

$$f_i(T, p, x_i) = x_i f_i^0(T, p)$$

where f_i^0 is the fugacity of pure component *i*.

- If this is valid for a mixture, then that mixture is an ideal solution.
- The chemical potential in terms of fugacity is:

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

for a pure gas and

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

for a gas mixture.

• Substituting the pure gas expression into the expression for gas mixtures yields:

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{f_I^0}$$

• Thus for an ideal solution:

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

• For an equation of state that follows the virial form, it may be shown that:

$$f_i^0 = p \exp\left(\frac{Bp}{RT}\right)$$

 For a virial equation of state that has been extended to account for attractions between like and unlike molecules:

$$f_i^0 = x_i p_i \exp\left[\frac{\sum_{j=1}^r \sum_{k=1}^r x_j x_k (2B_{ij} - B_{jk})p}{RT}\right]$$

• As
$$p \to 0$$
, $f_i^0 \to p_i^0$ and $f_i \to p_i$.

- When considering a mixture of gases, entropy of mixing must be taken into account.
- The partial molar entropy of a gas is:

$$\overline{s}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,x_j}$$

• This gives:

$$\overline{s}_i = s_i^*(T, \mathcal{P}) - R \ln \frac{px_i}{\mathcal{P}} - \int_{0,T}^{p,T} \left[\left(\frac{\partial \overline{v}_i}{\partial T} \right)_{p',n_i} - \frac{R}{p'} \right] dp'$$

• For a system of pure gases that are separated:

$$S^0 = \sum_{i=1}^r n_i s_i^0$$

• For the same gases mixed:

$$S^m = \sum_{i=1}^r n_i \overline{s}_i$$

• The difference is due to the entropy of mixing.

• The entropy of mixing is:

$$\Delta S_{mix} = S^m - S^0 = \sum_{i=1}^r n_i (\overline{s}_i - s_i^0)$$

$$= -R\sum_{i=1}^{r} n_i \ln x_i + \sum_{i=1}^{r} n_i \int_{0,T}^{p,T} \left[\left(\frac{\partial v_i}{\partial T} \right)_{p'} - \left(\frac{\partial \overline{v}_i}{\partial T} \right)_{p',n_j} \right] dp'$$

• In the limit of low pressure for an ideal solution:

$$\left(\frac{\partial v_i}{\partial T}\right)_{p'} = \left(\frac{\partial \overline{v}_i}{\partial T}\right)_{p',n_j}$$

and for perfect gases:

$$\Delta S_{mix} = -R \sum_{i=1}^{r} n_i \ln x_i$$

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- Consider a container with two compartments in contact with a thermal reservoir (Figure 21.10).
- Pressure and temperature are the same on both sides:

$$n_a = \frac{pV^I}{RT}; \quad n_b = \frac{pV^{II}}{RT}$$

- When the partition is removed, the gases mix.
 - After mixing:

$$p = \frac{RT}{V^I + V^{II}}(n_a + n_b)$$

 Since molecules of a perfect gas in an ideal gas solution behave as if individually present, the gas in each compartment may be considered as expanding into the other.



Figure 21.10 Schematic representation of a box separated into two compartments I and II, both at the same temperature and pressure, but containing n_a mol of a and n_b mol of b, respectively.

• The entropy change for a perfect gas undergoing isothermal expansion is:

$$\Delta S = nR\ln\frac{V_2}{V_1}$$

• For each gas expanding into the other compartment:

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_a R \ln \frac{V^I + V^{II}}{V^I} + n_b R \ln \frac{V^I + V^{II}}{V^{II}}$$

$$= -n_a R \ln \frac{n_a}{n_a + n_b} - n_b R \ln \frac{n_b}{n_a + n_b}$$
$$= -n_a R \ln x_a - n_b R \ln x_b$$

and the spontaneous process has maximized entropy.

- Consider now the inverse process.
- This requires the use of a semipermeable membrane, through which species *a* can pass, but not species *b*.
- This membrane is inserted at one end of the container holding the mixture.
- It is then moved and used to compress the gas to an arbitrarily small volume.
 - Species *a* moves through the barrier, while species *b* is compressed to the arbritrarily small volume.
 - Recall that for compression:

$$s = -nRT\ln\frac{V_2}{V_1}$$

• The membrane does work only on species *b*, not species *a*.

- At the end of the compression a is in volume $V^{I} + V^{II}$, while b is in the arbitrarily small volume.
- Next the membrane is replaced with an impermeable piston, which is then moved to the original position of the barrier.
 - The system has been restored to its original state.
- The total work done is:

$$w = -n_b RT \ln \frac{0^+}{V^I + V^{II}} - n_a RT \ln \frac{V^I}{V^I + V^{II}} - n_b RT \ln \frac{V^{II}}{0^+}$$
$$= -(n_a RT \ln x_a + n_b RT \ln x_b)$$

• But for an isothermal expansion or compression in a perfect gas, $\Delta U = 0$.

• From the first law of thermodynamics, it follows:

$$T\int dS = \int pdV = -w_{sep'n}$$

and the entropy change due to separation is:

$$\Delta S_{sep'n} = n_a R \ln x_a + n_b R \ln x_b$$

$$\Delta S_{sep'n} = -\Delta S_{mix}$$

- Only molecules with some distinguishing feature may be separated.
 - If the molecules were all the same, they would stay on the same side of the semipermeable membrane and no separation would occur.
 - Dalton's law of partial pressures contains information on the distinguishability of molecules.

- Changes due to mixing are also associated with V, U, H, G, and A.
 - The value of the quantity in a mixture is different that that due to corresponding pure amounts.
 - The difference is the excess value.
- Consider volume:

$$v_E \equiv \frac{V^E}{\sum_{i=1}^r n_i} = v_m - \sum_{i=1}^r x_i v_i^0$$

• Similarly for enthalpy:

$$h_E \equiv \frac{H^E}{\sum_{i=1}^r n_i} = h_m - \sum_{i=1}^r x_i h_i^0$$

• We have already established that excess entropy is associated with mixing:

$$s_E \equiv \frac{\Delta S_{mix}}{\sum_{i=1}^r n_i}$$

- There are two factors that contribute to an excess function.
 - The first factor is the difference in intermolecular forces between molecules in the mixture and in the pure components.
 - This is what is addressed by the term:

$$\sum_{i=1}^{r} n_i \int_{0,T}^{p,T} \left[\left(\frac{\partial v_i}{\partial T} \right)_{p'} - \left(\frac{\partial \overline{v}_i}{\partial T} \right)_{p',n_j} \right] dp'$$

- This term is zero for a perfect gas and non-zero for gases with intermolecular forces.
- In a perfect gas mixture, the contribution of this term is zero.
- The second factor is due to the distinguishability of different molecular species.
- In entropy, this is addressed by the term:

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

• For any gas mixture, it may be shown:

$$H^{E} = \int_{0}^{p} \left[V^{E} - T \left(\frac{\partial V^{E}}{\partial T} \right)_{p', n_{j}} \right] dp'$$

• For a perfect gas mixture:

$$s_E \equiv \frac{\Delta S_{mix}}{\sum_{i=1}^r n_i} = -R \sum_{i=1}^r x_i \ln x_i$$
$$h^E = u^E = 0$$
$$v^E = 0$$
$$g_E \equiv \frac{\Delta G_{mix}}{\sum_{i=1}^r n_i} = RT \sum_{i=1}^r x_i \ln x_i$$
$$a_E \equiv \frac{\Delta A_{mix}}{\sum_{i=1}^r n_i} = RT \sum_{i=1}^r x_i \ln x_i$$

• For an ideal solution, it may be shown that:

$$\Delta S_{mix} = \sum_{1=i}^{r} n_i \left[\left(\frac{\partial \mu_i^0}{\partial T} \right)_P - \left(\frac{\partial \mu_i}{\partial T} \right)_{p,n_j} \right] = -R \sum_{i=1}^{r} n_i \ln x_i$$

Thermodynamic Description of Gaseous Reactions

• For mixture of gases that reaches equilibrium, it is necessary that:

$$\sum_{i=1}^{r} \nu_i \mu_i = 0$$

• Recall that:

$$\mu_i = \mu_i^*(T, \mathcal{P}) + RT \ln \frac{x_i p}{\mathcal{P}} + \int_{0,T}^{p,T} \left[\overline{v}_i(p') - \frac{RT}{p'} \right] dp'$$

• Therefore, at equilibrium:

$$\sum_{i=1}^{r} \nu_i \mu_i^*(T, \mathcal{P}) = -RT \sum_{i=1}^{r} \left[\ln \frac{x_i p}{\mathcal{P}} + \int_{0,T}^{p,T} \left(\overline{v}_i - \frac{RT}{p'} \right) \frac{dp'}{RT} \right] \nu_i$$

- Since the left-hand side of this equation is a function only of temperature, this means that specifying the temperature will fix the composition.
- The equilibrium coefficient K(T) is defined by:

$$-RT\ln K(T) \equiv \sum_{i=1}^{r} \nu_i \mu_i^*(T, \mathcal{P})$$

• This becomes:

$$K(T) = \prod_{i=1}^{r} \left(\frac{f_i}{\mathcal{P}}\right)^{\nu_i}$$

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• In the perfect gas limit, $f_i \rightarrow px_i$, therefore the equilibrium coefficient in terms of partial pressures is:

$$K_p \equiv \prod_{i=1}^r \left(\frac{x_i p}{\mathcal{P}}\right)^{\nu_i}$$

• In the limit of low pressure:

$$\lim_{p \to 0} K_p = K(T)$$

• It can be shown:

$$\sum_{i=1}^{r} \nu_i \mu_i^* = \Delta G^*(T, \mathcal{P})$$

• Therefore: $-RT \ln K(T) = \Delta G^*(T, \mathcal{P})$

- ΔG^* is the difference in molar free energy of reactants and products and depends only on temperature.
- This is in constrast to K_p which does depend on pressure.
- The temperature dependence of K(T) may be elucidated as follows:

$$-R\frac{d\ln K}{dT} = \frac{d}{dT}\left(\frac{\Delta G^*}{T}\right) = -\frac{\Delta G^*}{T^2} + \frac{1}{T}\frac{d\Delta G^*}{dT}$$

• Since G^* is a state function:

$$\frac{d\Delta G^*}{dT} = \Delta \left(\frac{dG^*}{dT}\right) = -\Delta S^*$$

• Therefore:

$$-R\frac{d\ln K}{dT} = -\frac{1}{T}\left(\frac{\Delta G^*}{T} + \Delta S\right) = -\frac{\Delta H^*}{T^2}$$

• It may also be shown that:

$$\Delta S^* = R \frac{d}{dT} (T \ln K) = \frac{\Delta H^* - \Delta G^*}{T}$$

- As K(T) increases, ΔS^* increases.
- The extent that a reaction proceeds when it reaches equilibrium is determined by thermodynamics through the balance of the enthalpy change required and T times the entropy change associated with the reaction.

- If ΔS^* is the same, an exothermic reaction will go more to completion than an endothermic reaction.
- If ΔH^* is the same, then the equilibrium position favours the side of the reaction that has the most molecules.
 - If a reaction has more molecules of products than molecules of reactants, production of products will be thermodynamically favoured.
 - If a reaction has more molecules of reactants than molecules of products, then the production of products is thermodynamically unfavoured.
- ΔH^* and ΔS^* are defined with respect to the reactants and products in their hypothetically perfect gas in a reference state.
 - The reference state what is most widely used is 1 atm pressure and a temperature of 25°C.

- This has been superseded by a standard pressure of 1 bar.
- In a nonideal mixture, the equilibrium coefficient K(T, p) has a slight dependence on pressure since there is a nonzero excess volume.
 - When the reference state is the hypothetical perfect gas, the equilibrium coefficient is independent of pressure.
 - This means that it is possible to calculate equilibrium coefficient and its temperature dependence from tabulated standard thermodynamic enthalpies, entropies, and Gibbs free energies.
 - If the reaction of interest is not tabulated, then Hess's law may be used to construct it from known reactions.

- In most cases, corrections for the fact that gases are not perfect are not necessary.
- There are a number of approximations that correct equilibrium coefficients for the effect of interactions among molecules.
 - For example, Lewis and Randall introduced an approximation based on:

$$B_{jk} = \frac{1}{2}(B_{jj} + B_{kk})$$

 Note that this contradicts molecular theory which shows that molecular interactions among different possible pairs of molecules are all different, ie. B_{jj}, B_{kk}, and B_{jk} are all different. • From this it may be shown that:

$$\ln \frac{K_p}{K(T)} = -p \frac{\Delta B}{RT}$$

where $\Delta B = \sum_{i=1}^{r} \nu_i B_{ii}(T)$.

- Although this does not have a solid physical basis, it does reasonably well at high pressures.
- It is convenient because it does not require knowledge of the thermodynamic properties of the mixture, but just properties of the pure components.
- If $\Delta B < 0$, this predicts that $K_p/K(T)$ is greater than unity and increases as p increases, resulting in a higher yield of products than is predicted by assuming perfect gases.

Thermodynamic Properties of Solids

- There are a number of important differences between gas and liquid phases.
 - In condensed phases N/V, the number density of molecules, is comparable to the closest packing density of the molecules.
 - This means that interactions between molecules are significant and that there are more than pairwise interactions involved.
 - The translational energy of the molecules is, on average, less than or approximately equal to the height of the potential energy barriers separating the equilibrium positions.
 - This potential energy of interaction has a significant effect on the structure of a condensed phase.

Thermodynamic Properties of Liquids

- Liquids exist over a limited range of temperatures and pressures.
- Consider pressure exerted by a liquid at temperature T.
 - If this liquid is in equilibrium with its vapour, then the pressure of the vapour and of the liquid must be equal.
 - The boundary separating a liquid and a gas may be considered a deformable boundary that permits the transfer of energy and matter.
 - When a liquid and vapour are in equilibrium, the pressure is denoted by p_{σ} , which is a function of temperature.
 - If an inert gas that is insoluble in the liquid is present, the vapour phase will have two components and p_{σ} is a function of temperature and the applied pressure.

• At equilibrium, the chemical potential of the vapour and liquid are equal:

$$\mu_L = \mu^*(T) + RT \ln \frac{p_\sigma}{\mathcal{P}}$$

• The derivative of chemical potential with pressure is:

$$\left(\frac{\partial \mu_L}{\partial p}\right)_T = v_L$$

• Therefore:

$$RT\left(\frac{\partial \ln p_{\sigma}}{\partial p}\right)_{T} = v_{L}$$

and the rate of change of vapour pressure with applied pressure may be determined.
- This equation is the Poynting equation.
- A typical molar volume is of the order of 100 cm^3 .
 - At room temperature, $(\partial \ln p_{\sigma}/\partial p)_T$ is about 4 $\times 10^{-3}$ atm⁻¹.
- The temperature dependence of vapour pressure is determined by differences in entropy and molar volume of vapour and liquid.
- Consider the pressure temperature curve for coexistence of liquid and vapour.
 - Since the chemical potentials of liquid and vapour are equal on this curve,

$$d\mu^G = d\mu^L$$

$$-s^G dT + v^G dp_\sigma = -s^L dT + v^L dp_\sigma$$

• This can be rearranged to:

$$\left(\frac{\partial p}{\partial T}\right)_{\sigma} = \frac{s^G - s^L}{v^G - v^L}$$

which is the Clausius-Clapeyron equation.

- If the system is far from the critical point, $s^G > s^L$ and $v^G > v^L$ and

$$\left(\frac{\partial p}{\partial T}\right)_{\sigma} \approx \frac{s^G}{v^G}$$

• Consider the thermal pressure coefficient for a liquid:

$$\gamma_V \equiv \left(\frac{\partial p}{\partial T}\right)_V$$

• This is related to the dependence of the internal energy on volume.

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

- The temperature dependence of γ_v is shown in Figure 23.2 (a).
 - For gas in equilibrium with liquid, $\gamma_{\sigma} = (\partial p / \partial T)_{\sigma}$ increases smoothly with temperature.
 - The dark solid lines are γ_v for liquid on the coexistence curve.
 - The lines on the right hand side are γ_v for various values of v and have slight temperature dependence.
 - The deviation from zero slope for temperature dependence indicates deviation of the fluid from ideality.



Figure 23.2 (a) The variation of the thermal pressure coefficient with temperature for the saturated gas and liquid, and for the homogeneous fluid at temperatures above saturation. (b) Thermal pressure coefficient of argon. From J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed. (Butterworths, London, 1969). (c) $(\partial u/\partial v)_T$ as a function of molar volume. From J. H. Hildebrand and R. L. Scott, *Regular Solutions* (Prentice-Hall, Englewood Cliffs, N.J., 1962).

- The sign of γ_v is determined by the sign of α , the coefficient of thermal expansion.
- It may be shown:

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial v/\partial T)_p}{(\partial v/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

- κ is always positive.
- α may be negative or positive.
- Therefore α and γ_V have the same sign.
- Determination of $(\partial p/\partial T)_V$ from p, v, T properties of liquids lead to some generalizations.
 - κ_T decreases with increasing pressure, with rate of decrease decreasing as pressure increases.
 - κ_T increases with temperature, with the effect most pronounced at low pressure.

- α increases as temperature increases.
- From this conclusions about μ may be reached.
 - If α is positive and since T is positive, γ_V is positive.
 - If p is low, then u will decrease as v decreases.
 - There will exist a pressure where $[T(\partial p/\partial T)_V p]$ becomes zero.
 - At pressures above this pressure, $(\partial u/\partial v)_T$ is negative and repulsive forces will dominate over attractive forces.
 - In this case, energy flows out of the liquid during compression.
- There are no simple equations of state for a liquid, but there are some empirical ones.
- The virial equation.

• The Tait equation is:

$$\frac{v_0 - v}{v_0 p} = \frac{A}{B + p}$$

• The Huddleston equation is:

$$\ln\left(\frac{pv^{2/3}}{v_0^{1/3} - v^{1/3}}\right) = A + B(v_0^{1/3} - v^{1/3})$$

- In the latter two, v_0 is the molar volume at zero pressure and A and B are positive empirical constants.
- If the virial equation is used, then several terms may be necessary, particularly in high density regions above the critical temperature.

- For the virial equation, the order of the term may be connected to the number of molecules interacting.
- There is no physical interpretation for either the Tait or Huddleston equation.
- For liquids, c_p has a much stronger temperature dependence than c_v .
- As in the case of gases, it is possible to calculate thermodynamic properties from the equation of state and the temperature dependent heat capacity.
- Also, as in the case of gases, the perfect gas will be used to define a reference state.
- A residual function f^E is defined:

$$f^{E}(T,v) = \int_{\infty}^{v} \left[\left(\frac{\partial f}{\partial v} \right)_{T} - \left(\frac{\partial f}{\partial v} \right)_{T}^{perfect \ gas} \right] dv$$

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- This will be considered in two steps.
 - The initial state is in the low pressure limit with infinite volume.
 - The vapour is compressed isothermally to a finite volume, v_G , which is the volume of the vapour phase at pressure p_σ and temperature T.
 - The second step is isothermal condensation to a liquid with volume v^L .
- Thus, when applied to enthalpy:

$$h^{E}(T,v) = \int_{\infty}^{v} \left[\left(\frac{\partial h}{\partial v} \right)_{T} - \left(\frac{\partial h}{\partial v} \right)_{T}^{perfect gas} \right] dv$$

$$= \int_{\infty}^{v} \left[T\left(\frac{\partial p}{\partial T}\right)_{v} + v\left(\frac{\partial p}{\partial v}\right)_{T} \right] dv + \Delta h_{vap}$$



Figure 23.4 Sketch of the variation with temperature of the residual enthalpy of gas and liquid along the liquid-vapor coexistence curve. The difference between the two curves is the latent heat of evaporation. From J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed. (Butterworths, London, 1969).

- h^E for liquid and vapour along the coexistence curve is shown in Figure 23.4.
- Note that the difference in h^E for the gas phase vanishes at the critical point.

Phase equilibria in One-Component systems

- When a phase transition occurs, there is a sudden change in physical and thermodynamic properties.
- The changes in enthalpy, entropy, and heat capacity are discontinuous.
- How and why do phase transitions occur?
 - Melting of solid.
 - Evaporation of liquid.
 - Sublimation of solid.

- 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 amorhphous 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:

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

• 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).



Figure 24.5 Phase diagrams for water. (a) Low-pressure ice-water vapor-liquid equilibrium. From J. Kestin, A Course in Thermodynamic (Blaisdell, Waltham, Mass., 1966). (b) High-pressure equilibria among various forms of ice. From B. Kamb, in E. Whalley, S. Jones, and 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 priniciple, 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 perovises skite structure with the B ion at the center: $\bigcirc A$, $\bigotimes B$, $\bigcirc O$. The general chemical formula is ABO₃.

• 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 (ABO₃)



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.

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_p dT + \left(\frac{\partial\mu}{\partial p}\right)_T dp$$

$$= -sdT + vdp$$

• 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:

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

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- 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

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

- 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 vapourization 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,

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

$$\mu^{(1)} = \mu^{(3)}$$
$$\mu^{(2)} = \mu^{(3)}$$

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• 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: dq = du dw.

• Therefore:

$$c_{\sigma} = \left(\frac{dq}{dT}\right)_{\text{phase equilibrium}}$$
$$\left[\left(\frac{du}{dT}\right) - \left(\frac{dw}{dT}\right)\right]_{\text{phase equilibrium}}$$

- 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 vapourization 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:

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

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• 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:
 - $\Delta h_{vap} = 40.67 \text{ J mol}^{-1}$.
 - $d\Delta h_{vap}/dT = -47.93 \text{ J K}^{-1} \text{ mol}^{-1}$

•
$$c_{pL} = 75.86 \text{ J K}^{-1} \text{ mol}^{-1}$$

- On this basis, $c_{\sigma G} = -80.91 \text{ J K}^{-1} \text{ mol}^{-1}$.
- 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 indistiguishable.
- 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,

$$c_V(T) \to \infty$$

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.