### Solutions of Nonelectrolytes

- Many chemical and physical phenomena are associated 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<sup>E</sup>:

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

• 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:

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

- $w_i$  is a function only of composition variables.
- $\mu_i^0$  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<sub>i</sub>, such as the volume fraction \u03c6<sub>i</sub> 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:

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

$$H^{E} = -T^{2} \left( \frac{\partial \left( \Delta G_{mixing}/T \right)}{\partial T} \right)_{p,n_{1},\cdots,n_{r}}$$
$$T^{2} \sum^{r} \left( \partial \left( \mu_{i}^{E}/T \right) \right)$$

$$= -T^2 \sum_{i=1}^r n_i \left( \frac{\partial \left( \mu_i^E / T' \right)}{\partial T} \right)_{p, n_1, \cdots, n_r}$$

- 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:

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

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• 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  $\gamma_i$  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,  $\mu^0_i(T,p).$ 
  - $\mu_i^0(T,p)$  is independent of composition, therefore:

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

or

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

- 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,

$$\overline{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n'_2}$$

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  $v_i^{\theta}$  not  $v_i^0$ .

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- 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:

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

- 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:

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

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

• This means that  $\mu_2^E$  can be determined from  $\mu_1^E$ .

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

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

 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. .- p.232/393

- 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. . – p.233/393

• 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  $\xi$  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 property 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:

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

• 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  $z_m = Z/\sum n_i$  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  $\overline{z}_2(x'_1)$  at  $x_1 = 0$  and  $\overline{z}_1(x'_1)$  at  $x_1 = 1$ .

### Liquid-Vapour Equilibrium

• For each component of a mixture:

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

• 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  $\gamma_i = 1$ .

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

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  $\gamma_i$  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  $\alpha_{12}$  is independent of the composition.



**ire 25.2** (a) Schematic representation of the isothermal dependence of the total pressure of an ideal binary mixture on the mole fracof 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 separaof 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. Schematic 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  $\alpha_{12}$  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:

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

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:

$$p_2 = x_2 \mathcal{P} k_2(T, p, \text{solvent})$$

- 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 volatile 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  $45^{\circ}$ C as a function of the mole fraction of acetonitrile. (b) The excess functions of water + pyridine at  $80^{\circ}$ C as a function of the mole fraction of water. (c) The excess functions of water + dioxane at  $25^{\circ}$ C as a function of the mole fraction of the mole fraction of water. (d) The excess functions of water + hydrogen peroxide at  $25^{\circ}$ 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 functions 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  $\gamma_i$  may be determined.
- Usually the second virial coefficient is sufficient since the vapour pressure is low.

• For a binary solution:

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

 $\mathsf{and}$ 

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

• If the vapour is ideal then:

$$p_1 = \gamma_1 x_1 p_1^0$$
$$p_2 = \gamma_2 x_2 p_2^0$$

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

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  $p_1$ ,  $p_2$ ,  $\gamma_1$ , and  $\gamma_2$  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 of 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,  $\Delta v_1^0$  and  $\Delta v_2^0$  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:

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

• 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:

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



$$y_2 = \frac{\exp(\Lambda_{1b})\gamma_2 - \gamma_1\gamma_2}{\exp(\Lambda_{1b})\gamma_2 - \exp(-\Lambda_{2b})\gamma_2}$$
$$x_2 = \frac{\exp(\Lambda_{1b}) - \gamma_1}{\exp(\Lambda_{1b})\exp(\Lambda_{2b})\gamma_2 - \gamma_1}$$

## 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 vaporization.

• L<sub>1v</sub> will vary depending on the temperature due to the difference in the heat capacities of liquid and solid:

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

• Thus:

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

• 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  $\theta$ , 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:

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

- If  $\theta$  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:

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

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

•  $K_b$  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<sup>-1</sup>.

• 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.
- Analogous 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  $\theta$  depends only on the solvent properties and not the solute.
- If the concentration of solute is low and  $(\theta/T_{1f})$  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

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

$$\theta = K_f m_2$$

where  $m_2$  is the molality of the solute.

• If the solution is ideal:

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

- Consider two phases separated by a rigid membrane that is permeable to the solvent but not solute.
  - As in the case of boiling point elevation and freezing point depression, the solute is excluded from one phase.
  - Heat can cross the membrane, but not work.
- At equilibrium:

$$p^{I} \neq p^{II}$$
$$T^{I} = T^{II}$$
$$\mu_{1}^{I} = \mu_{1}^{II}$$

• Chemical potential is related to pressure:

$$\left(\frac{\partial\mu_i}{\partial p}\right)_{T,x_i} = \overline{v}_i$$

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Figure 25.7 Schematic representation of an osmotic pressure experiment.

- The pressure of the pure solvent is  $p_0$  and the pressure of the solution is  $p_0 + \pi$  where  $\pi$  is the osmotic pressure.
- This gives the limits of integration:

$$\mu_i(T, p_0 + \pi, x) - \mu_i(T, p_0, x) = \int_{p_0}^{p_0 + \pi} \overline{v}_i dp$$

• When applied to a particular solvent becomes:

$$RT\ln\gamma_1 x_1 = \mu_1^L(T, p_0) - \mu_1^L(T, p_0 + \pi) = \int_{p_0}^{p_0 + \pi} \overline{v}_1 dp$$

• The partial molar volume of a solvent varies smoothly with pressure:

$$\overline{v}_1(p) = \overline{v}_1(p_0) + (p - p_0) \left(\frac{\partial \overline{v}_1}{\partial p}\right)_{T, x_0, p_0} + \cdots$$

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• Because  $(\partial \overline{v}_1 / \partial p)_{T,x_0,p_0}$  is small and the osmotic pressure of a dilute solutions is small,

$$\overline{v}_1(p_0) >> (p - p_0) \left(\frac{\partial \overline{v}_1}{\partial p}\right)_{T, x_0, p_0}$$

and in this limit:

$$RT\ln\gamma_1 x_1 = -\pi\overline{v}_1(p_0)$$

• If the solution is dilute and ideal then:

$$RT\ln x_1 = -RTx_2 = -\pi\overline{v}_1(p_0)$$

• Recall that in a dilute solution:

$$x_2 = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2} \approx \frac{w_2/M_2}{w_1/M_1} = \frac{n_1}{n_2}$$

• The total volume of the system is:

$$\frac{w_1}{M_1}\overline{v}_1 = n_1\overline{v}_1 = V$$

• Therefore, for an ideal dilute solution:

 $\pi V = n_2 R T$ 

• If the solution is not ideal or dilute:

$$-\pi\overline{v}_1(p_0) = RT\ln\gamma_1 x_1 \equiv g_1RT\ln x_1$$

where  $g_1$  is the osmotic coefficient and is usually expressed as a power series in  $c_2 = n_2/V$ .

$$g_1 = 1 + Bc_2 + Cc_2^2 + \cdots$$
• In the limit of a dilute solution:

$$\pi = RTc_2(1 + Bc_2 + Cc_2^2 + \cdots)$$

- Note the resemblance to the virial equation of state.
- The coefficients depend on the effective interaction potential of the solution.
- Osmotic pressure measurements can be used to determine the activity of the solvent.
- These three properties of solutions:
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure

are known as the colligative properties of a solution.

## **Chemical Reaction in Nonelectrolyte Solutions**

• At equilibrium,

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

- where  $\nu_i$  are the stoichiometric coefficients of the reaction.
- Recall

$$\Delta G^0 = -RT \ln K(T, p, \text{solvent})$$

where

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

 $\quad \text{and} \quad$ 

$$K(T, p, \text{solvent}) = \prod_{i=1}^{r} (\gamma_i x_i)^{\nu_i}$$

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- If the standard state is pure solid or liquid then the equilibrium coefficient is a function of temperature and pressure.
- If the standard state is the hypothetical state (same properties per unit mass as an infinitely dilute solution) then the equilibrium coefficient is a function of temperature, pressure, and the solvent.
- As in the case of a gas phase reaction, the temperature and pressure derivatives of the equilibrium coefficient depend on, respectively, the entropy and volume changes of the reaction.
- For an ideal solution:

$$K(T, p, \text{solvent}) = \prod_{i=1}^{r} x_i^{\nu_i}$$

- Equilibrium coefficients do not have units.
- When units other than mole fractions are used for composition, then the standard state is the hypothetical state for the substance.
- Molality units assume one component is the solvent.
- The relationship between mole fraction and molality is:

$$x_i = \frac{n_i}{n_1 + \sum_{j=2}^r n_j} = \frac{w_i/M_i}{w_1/M_1 + \sum_{j=2}^r w_j/M_j}$$

- Molality is defined as the number of moles of the substance in a 1000 g of solvent.
  - Therefore  $m_j = w_j/M_j$  if the amount of solvent is fixed at 1000 g.

• Therefore the mole fraction may be written:

$$x_i = \frac{m_j}{1000/M_1 + \sum_{j=2}^r m_j}$$

• Thus the activity coefficients may be written in terms of molality:

$$\mu_{i} = \mu_{i}^{0}(T, p) + RT \ln \left\{ \frac{\gamma_{i}m_{i}}{(1000/M_{1}) \left[ 1 + (M_{1}/1000) \sum_{j=2}^{r} m_{j} \right]} \right\}$$
$$= \mu_{i}^{0}(T, p) + RT \ln \left\{ \left[ \frac{\gamma_{i}}{1 + (M_{1}/1000) \sum_{j=2}^{r} m_{j}} \right] \left( \frac{m_{i}}{1000/M_{1}} \right) \right\}$$
$$= \mu_{i}^{0}(T, p) - RT \ln \mathcal{M}_{1} + RT \ln \gamma_{i}' m_{i}$$

• 
$$\gamma'_i$$
 and  $\mathcal{M}_1$  are defined as:

$$\gamma_i' \equiv \frac{\gamma_i}{1 + (M_1/1000) \sum_{j=2}^r m_j} = \frac{\gamma_i}{1 + \sum_{j=2}^r (m_j/\mathcal{M}_1)}$$
$$\mathcal{M}_1 \equiv \frac{1000}{M_1}$$

• Thus the activity is defined with a standard mass of solvent and the term  $RT \ln M_1$  is included in the definition of a new standard state for the potential:

$$\mu_i^{0m}(T, p, \text{solvent}) = \mu_i^0(T, p) + RT \ln \mathcal{M}_1$$

• The equilibrium coefficient may then be described by:

$$K_m(T, p, \text{solvent}) = \prod_{i=1}^r (\gamma'_i x_i)^{\nu_i}$$

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• Similarly, it is possible to define activity for a standard state of molarity:

$$\mu_i^{0c}(T, p, \text{solvent}) = \mu_i^0(T, p) + RT \ln \frac{v_i^0}{1000}$$

• A new activity coefficient  $\gamma''_i$  may be defined such that:

$$K_c(T, p, \text{solvent}) = \prod_{i=1}^r (\gamma_i'' c_i)^{\nu_i}$$

- In all cases the equilibrium coefficient is dimensionless.
  - When an equilibrium coefficient is written as if it had units, those units indicate the reference state and concentration scale.

## More about Phase Equilibrium in Mixtures

- Consider the stability of a mixture against phase separation.
- At constant temperature and pressure:

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

• Expressed in terms of mole fractions this becomes:

$$dG = (n_1 + n_2)\mu_1 dx_1 + (n_1 + n_2)\mu_2 d(1 - x_1)$$

$$= (n_1 + n_2)(\mu_1 - \mu_2)dx_1 = (n_1 + n_2)(\mu_2 - \mu_1)dx_2$$

- Therefore the slope of a plot of G against  $x_2$  has a slope that is proportional to  $\mu_2 \mu_1$  at each point of the curve.
- If there is no phase separation then G versus  $x_2$  is a continuous curve.



Figure 25.8 Schematic representation of the Gibbs free energy as a function of composition for a binary mixture. (a) One-phase region. (b) Two-phase region.

• If phase separation occurs into phases I and II and the phases have different composition then at equilibrium:

$$\mu_1^I = \mu_1^{II}$$
$$\mu_2^I = \mu_2^{II}$$

and

$$\mu_1^I - \mu_2^I = \mu_1^{II} - \mu_2^{II}$$

- In a plot of G against composition, each phase has a separate curve.
- The above condition for equilibrium means that when the slopes of the two curves are equal, the two phases are in equilibrium.
  - This is shown as points A and B in Figure 25.8.

- Because G depends on temperature, there exists a critical temperature above which the system is miscible and below which the system separates into two phases.
- This may be considered in terms of the dependence of G on composition.
- When the two phases are miscible (Figure 25.8 a), then everywhere G is concave upward:

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,p} > 0$$

• When the two phases are immiscible, (Figure 25.8 b), there is a region where

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,p} < 0$$

• These join two regions where:

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,p} > 0$$

• Between these are two inflection points where:

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,p} = 0$$

• At  $T_c$  these inflection points merge such that:

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T_c,p} = 0 \text{ and } \left(\frac{\partial^3 G}{\partial x_3^2}\right)_{T_c,p} = 0$$

• At the critical temperature:

$$\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T_c,p} = \left(\frac{\partial\mu_2}{\partial x_2}\right)_{T_c,p}$$

and

$$\left(\frac{\partial^2 \mu_1}{\partial x_2^2}\right)_{T_c,p} = \left(\frac{\partial^2 \mu_2}{\partial x_2^2}\right)_{T_c,p}$$

• Recall the Gibbs-Duhem relation for two components at constant *T* and *p*:

$$(1-x_2)\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p} + x_2\left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,p} = 0$$

• This may be differentiated with respect to  $x_2$ :

$$(1-x_2)\left(\frac{\partial^2 \mu_1}{\partial x_2^2}\right)_{T,p} + x_2\left(\frac{\partial^2 \mu_2}{\partial x_2^2}\right)_{T,p} - \left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,p} + \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,p} = 0$$

• Therefore at  $T_c$ :

$$\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T_c,p} = \left(\frac{\partial\mu_2}{\partial x_2}\right)_{T_c,p} = 0$$

and

$$\left(\frac{\partial^2 \mu_1}{\partial x_2^2}\right)_{T_c,p} = \left(\frac{\partial^2 \mu_2}{\partial x_2^2}\right)_{T_c,p} = 0$$

• This now may be put into terms of activity coefficients.

$$\left(\frac{\partial \ln \gamma_1}{\partial x_2}\right)_{T_c,p} - \frac{1}{1 - x_2} = 0$$
$$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T_c,p} + \frac{1}{x_2} = 0$$
$$\left(\frac{\partial^2 \ln \gamma_1}{\partial x_2^2}\right)_{T_c,p} - \frac{1}{(1 - x_2)^2} = 0$$
$$\left(\frac{\partial^2 \ln \gamma_2}{\partial x_2^2}\right)_{T_c,p} - \frac{1}{x_2^2} = 0$$

• Consider  $T_c$  for a regular mixture where:

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

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• Using the expressions for the activity coefficient at the critical point gives:

$$\frac{w}{RT_c}(2x_2)_c = \frac{1}{(1-x_2)_c}$$

$$\frac{w}{RT_c}2 = \frac{1}{(1-x_2)_c^2}$$

• When this pair of simultaneous equations is solved:

$$(x_2)_c = \frac{1}{2}$$
 and  $\frac{w}{RT_c} = 2$ 

• If w/RT > 2 then  $T < T_c$  and there is separation of the phases.

- Consider some T and p where a binary mixture separates into two phases with compositions  $x_1^I$ ,  $x_2^I$  and  $x_1^{II}$ ,  $x_2^{II}$ .
- How does the composition of each phase change if T and p are altered.
- This can be determined by the fact that  $\mu_1^I = \mu_1^{II}$  and  $\mu_2^I = \mu_2^{II}$  along the coexistence curves.
- Therefore:  $d\mu_1^I = d\mu_1^{II}$  and  $d\mu_2^I = d\mu_2^{II}$ .
- Upon expansion:

$$\left(\frac{\partial\mu_1}{\partial p}\right)_{T,x}^{I} dp + \left(\frac{\partial\mu_1}{\partial T}\right)_{p,x}^{I} dT + \left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p}^{I} dx_2$$

$$= \left(\frac{\partial\mu_1}{\partial p}\right)_{T,x}^{II} dp + \left(\frac{\partial\mu_1}{\partial T}\right)_{p,x}^{II} dT + \left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p}^{II} dx_2$$

$$= \left(\frac{\partial\mu_1}{\partial p}\right)_{T,x}^{II} dp + \left(\frac{\partial\mu_1}{\partial T}\right)_{p,x}^{II} dT + \left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p}^{II} dx_2$$

- A similar equation for component 2 can be written.
- Consider the free energy of mixing  $g_m$  where:

$$g_m = x_1 \mu_1 + x_2 \mu_2$$

• It can be shown that:

$$(\overline{v}_1^I - \overline{v}_1^{II})dp - (\overline{s}_1^I - \overline{s}_1^{II})dT - x_2^I \left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p}^I + x_2^{II} \left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p}^{II} = 0$$

and

$$(\overline{v}_2^I - \overline{v}_2^{II})dp - (\overline{s}_2^I - \overline{s}_2^{II})dT + x_1^I \left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p}^I - x_1^{II} \left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p}^{II} = 0$$

• For equilibrium states along the constant pressure coexistence line:

$$\left(\frac{\partial x_2}{\partial T}\right)_p^I = -\frac{(\overline{h}_1^I - \overline{h}_1^{II})x_1^{II} + (\overline{h}_2^I - \overline{h}_2^{II})x_2^{II}}{T(\partial^2 g_m/\partial x_2^2)_{T,p}^I(x_2^I - x_2^{II})}$$

$$\left(\frac{\partial x_2}{\partial T}\right)_p^{II} = -\frac{(\overline{h}_1^I - \overline{h}_1^{II})x_1^I + (\overline{h}_2^I - \overline{h}_2^{II})x_2^I}{T(\partial^2 g_m/\partial x_2^2)_{T,p}^{II}(x_2^I - x_2^{II})}$$

- Recall that for a stable phase  $(\partial^2 g_m / \partial x_2^2)_{T,p}^I > 0.$
- Therefore the sign of  $(\partial x_2/\partial T)_p$  is determined by the sign of the numerator and the sign of  $(x_2^I x_2^{II})$ .
- The numerator is the heat of solution of an infinitesimal amount of one phase in the other phase at constant T and p.

• Consider the constant temperature coexistence line:

$$\left(\frac{\partial x_2}{\partial p}\right)_T^I = \frac{x_2^{II}(\overline{v}_2^{II} - \overline{v}_2^I) + x_1^{II}(\overline{v}_1^{II} - \overline{v}_1^I)}{(x_2^{II} - x_2^I)(\partial^2 g_m / \partial x_2^2)_{T,p}^I}$$
$$\left(\frac{\partial x_2}{\partial p}\right)_T^{II} = \frac{x_2^I(\overline{v}_2^{II} - \overline{v}_2^I) + x_1^I(\overline{v}_1^{II} - \overline{v}_1^I)}{(x_2^{II} - x_2^I)(\partial^2 g_m / \partial x_2^2)_{T,p}^{II}}$$

- As in the case of the constant pressure coexistence line, the sign of  $(\partial x_2/\partial p)_T$  depends on the signs of the numerator and of  $(x_2^{II} x_2^I)$ .
- The numerators may be interpreted as the volume change when an infinitesimal amount of one phase is added to the other phase.

• Also to be considered are constant composition coexistence curves:

$$\left(\frac{\partial p}{\partial T}\right)_{x_2^I}^I = \frac{x_2^{II}(\overline{h}_2^{II} - \overline{h}_2^I) + x_1^{II}(\overline{h}_1^{II} - \overline{h}_1^I)}{T\left[x_2^{II}(\overline{v}_2^{II} - \overline{v}_2^I) + x_1^{II}(\overline{v}_1^{II} - \overline{v}_1^I)\right]}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_{x_2^{II}}^{II} = \frac{(\overline{v}_1^{II} - \overline{v}_1^I)(\overline{h}_2^{II} - \overline{h}_2^I) - (\overline{v}_2^{II} - \overline{v}_2^I)(\overline{h}_1^{II} - \overline{h}_1^I)}{T(\partial^2 g_m/\partial x_2^2)_{T,p}^{II} \left[x_2^{II}(\overline{v}_2^{II} - \overline{v}_2^I) + x_1^{II}(\overline{v}_1^{II} - \overline{v}_1^I)\right]}$$

 This is analogous to the Clausius-Clapeyron equation in that it describes the variation of total pressure with temperature for a phase of fixed composition in equilibrium with another phase. • If the composition is the same in both phases, i.e.  $x_1^I = x_1^{II}$  and  $x_2^I = x_2^{II}$ , then

$$\left(\frac{\partial T}{\partial x_2}\right)_p^I = 0$$
 and  $\left(\frac{\partial T}{\partial x_2}\right)_p^{II} = 0$ 

- Thus, if at constant *p*, the temperature along the coexistence line at a point of horizontal slope (i.e. a minimum, a maximum, or an inflection point), the two phase will have the same composition and the solution will form an azeotrope.
- If in a series of isothermal equilibrium states of a two phase binary system, the composition of the phases becomes the same, then the pressure of the system will have an extremum.
- These are the Gibbs-Konovalov theorems.





(b)

Figure 25.9 (a) Minimum- and maximum-boiling-point binary system phase diagrams. The bubble-point curve, labeled bpc, represents the liquid composition; the dew-point curve, labeled dpc, represents the vapor composition. (b) Phase diagrams for the binary systems acetone-carbon disulfide and acetone-chloroform. The partial pressures of components in these two systems are shown, at  $35.2^{\circ}$ C, in Fig. 25.4. From J. Hildebrand and R. Scott, *Regular Solutions* (Van Nostrand Reinhold, New York, 1950).

- Consider Figure 25.9, in which coexistence curves are shown for typical azeotropic systems.
- Systems with a maximum in the total vapour pressure curve have positive excess Gibbs free energy, while those with a minimum have negative excess Gibbs free energy.
- Stability of a system may be considered in terms of Figure 25.10.
- A g(T, p) surface is represented.
- A point on the surface Γ<sub>0</sub>, represents the Gibbs free energy of one mole of substance at pressure p<sub>0</sub> and temperature T<sub>0</sub>.
- The tangent plane to this surface is defined by  $(\partial g/\partial T)_{p=p_0} = -s_0$  and  $(\partial g/\partial p)_{T=T_0} = v_0$

$$g - g_0 = -s_0(T - T_0) + v_0(p - p_0)$$

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Figure 25.10 Free energy-temperature-pressure surface for a substance. The surfaces labeled V, L, and S refer to the vapor, liquid, and solid, respectively. (Courtesy of Prof. J. A. Beattie.) • The tangent plane cuts the g axis at:

$$g = g_0 + T_0 x_0 - p_0 v_0 = u_0$$

- Note that the surfaces u(s, v) and g(t, p) have a reciprocal relationship that arises from the Legendre transforms.
- Quantities represented by the tangent planes of g are on the u surface.
- Gaps on the *u* surface are bridged by derived surfaces.
- On the g surface it is convenient to consider each phase as having its own surface.
- If the lowest surface is considered at each T and p, then a composite surface can be constructed from portions of each of the surfaces for each phase.
- The seams represent coexistence regions.

- Consider Figure 25.10.
- The surfaces labelled V, L and S are for vapour, liquid, and solid.
- The intersections *EM*, *MA*, and *MD* projected onto the *T*, *P* plane. are respectively solid-vapour, solid-liquid and liquid-vapour coexistence lines.
- The continuations of each of these curves, M'F', M'B', and M'C' are the projections of the intersections of the metastable parts of the surface.
- Each of these extensions describes the metastable coexistence of two phases which are both unstable with respect to the third phase.
- The coexistence lines and the metastable extensions can be considered to divide the *g*, *T*, *p* space into six regions.

- Above E'M'B',  $g^V < g^S < g^L$
- Above  $B^\prime M^\prime D^\prime$  ,  $g^V < g^L < g^S$
- Above  $D^\prime M^\prime F^\prime$  ,  $g^L < g^V < g^S$
- Above F'M'A',  $g^L < g^S < g^V$
- Above A'M'C',  $g^S < g^L < g^V$
- Above  $C^\prime M^\prime E^\prime$ ,  $g^S < g^V < g^L$
- Since every point on the g(T,p) surface represents a stable state of the system, the surface is concave downward.
- Examination of the second derivatives verifies this.

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_p = -\left(\frac{\partial s}{\partial T}\right)_p = -\frac{c_p}{T} < 0$$

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

- Recall that for a stable system,  $c_p > 0$ , T > 0, v > 0, and  $\kappa_T > 0$ .
- Each point on the surface g(T, p) must be a minimum with respect to virtual variations.
  - Virtual variations would generate different surfaces that are everywhere above g(T,p) and its tangent plane.
- Consider the surface  $G(T, p, n_1, n_2, \cdots, n_r)$  for an *r*-component fluid.
- The system is completely defined by the temperature and pressure, the total mass, and the masses of r-1 components.

• The total free energy is:

$$G = \sum_{i=1}^{r} n_i \mu_i$$

and can be rewritten as:

$$g_m = \frac{G}{\sum_{i=1}^r n_i} = \sum_{i=1}^r x_i \mu_i = \left(1 - \sum_{i=2}^r x_i\right) \mu_1 + \sum_{i=2}^r x_i \mu_i$$

- If the variables  $T, p, x_2, \dots, x_r$  define orthogonal axes, then  $g_m$  is a surface in r+2 dimensional space.
- The constraints of stability will now be considered.
- The system will be stable at T and p if  $g_m(T, p, x_2, \dots, x_r)$  is a minimum.

- Let  $\Gamma_0 = (T_0, p_0, x_2^0, \dots, x_r^0)$  which is a point on  $g_m(T, p, x_2, \dots, x_r)$ .
- Virtual variations generate new states in the vicinity of  $\Gamma_0$  that lie on  $g'_m$ ,  $g''_m$ , each of which lies above  $g_m$  and the tangent plane through  $\Gamma_0$ .
- Therefore for small displacements  $\Delta x_2, \dots, \Delta x_r$  at T, p:

$$\Delta g_m - (\Delta g_m)_{\text{tangent plane}} > 0$$

- $\Delta g_m$  can be expanded in a Taylor series about  $\Gamma_0$
- $(\Delta g_m)_{\text{tangent plane}}$  is described by the first order terms.
- $\Delta g_m (\Delta g_m)_{\text{tangent plane}}$  is described by the second order terms:

$$\left(\frac{\partial^2 g_m}{dx_2^2}\right)_{T,p,n} (\Delta x_2)^2 + \left(\frac{\partial^2 g_m}{dx_2 dx_3}\right)_{T,p,n} \Delta x_2 \Delta x_3 + \cdots + \left(\frac{\partial^2 g_m}{dx_2 dx_r}\right)_{T,p,n} \Delta x_2 \Delta x_r + \left(\frac{\partial^2 g_m}{dx_3 dx_2}\right)_{T,p,n} \Delta x_3 \Delta x_2 + \cdots + \left(\frac{\partial^2 g_m}{dx_3 dx_r}\right)_{T,p,n} \Delta x_3 \Delta x_r + \cdots + \left(\frac{\partial^2 g_m}{dx_r dx_2}\right)_{T,p,n} \Delta x_r \Delta x_2 + \cdots + \left(\frac{\partial^2 g_m}{dx_r^2}\right)_{T,p,n} (\Delta x_r)^2 > 0$$

• This condition for stability is equivalent to requiring that the determinate of the corresponding matrix is positive.

- Any system that satisfies these conditions is stable with respect to adjacent states.
- Consider  $g_m(T, p, x_2)$  which represents the equilibrium states of a binary mixture in four dimensions.
- Consider a fixed pressure situation, which reduces it to three dimensions,  $g_m$ , T, and  $x_2$ .
- This can then be projected onto the (T, x<sub>2</sub>) plane to give a temperature composition diagram (see Figure 25.11 (a).
- Intersections of  $g_m$  with different constant T planes gives the subsequent diagrams in  $(g_m, x_2)$  space, which are all for the same pressure.
- In the case of binary mixture, the second order term has only one contribution.

• The binary mixture will be state if:

$$\left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p,n} > 0$$

and unstable if:

$$\left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p,n} < 0$$

• The limit of stability is:

$$\left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p,n} = 0$$

 The stability condition may be expressed in terms of chemical potential using the Gibbs-Duhem equation. • The Gibbs-Duhem equation may be written as:

$$x_1 \left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,p,} + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,p,} = 0$$

• The condition for spontaneity becomes:

$$\left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,p,} > 0$$

which implies:

$$\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p,} < 0$$

$$\left(\frac{\partial\mu_2}{\partial x_1}\right)_{T,p,} < 0$$

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• The constant temperature and pressure slope of the free energy-composition curve is:

$$\left(\frac{\partial g_m}{\partial x_1}\right)_{T,p} = \mu_1 - \mu_2 = -\left(\frac{\partial g_m}{\partial x_2}\right)_{T,p}$$

- This means that when  $x_1 \to 0$ ,  $g_m \to \mu_1^0$ , and  $(\partial g_m / \partial x_1)_{T,p,n} \to -\infty$  and when  $x_1 \to 1$ ,  $g_m \to \mu_1^0$ , and  $(\partial g_m / \partial x_1)_{T,p,n} \to \infty$
- From this the properties of a free energy versus composition diagram may be inferred.
  - For a homogeneous system,  $g_m$  is concave upward and is tangent to the axis at  $x_2 = 0$  and  $x_2 = 1$ .
  - For a system where vapour, liquid, or solid can exist, there will be three curves, one for each phase.


**Figure 25.11** (a) Temperature-composition diagram for a binary mixture in which neither compounds nor solid solutions are formed, there is no miscibility gap, and there are no minimum- or maximum-boiling mixtures. (b)  $T_1$  is greater than the boiling points of both components, hence the vapor is the stable state for all compositions. (c) The temperature is, in this case, equal to the boiling temperature of component 2, hence  $g_m^L = g_m^V$  at  $x_2 = 1$ . Everywhere else the vapor is the most stable state. (d)  $T_3$  intersects the region where vapor and liquid coexist. For large  $x_2$  the liquid phase is most stable, for small  $x_2$  the vapor phase is most stable. The common tangent is the line along which  $g_m$  is least, hence describes the equilibrium situation of coexisting liquid and vapor between domains where either only liquid ( $x_2 \ge b$ ) or only vapor ( $x_2 \le a$ ) is stable. The phase coexistence domain is  $a < x_2 < b$ . (e)  $T_4$  coincides with the boiling point of component 1, so this case is the analog of that in Fig. 25.11c and  $g_m^L = g_m^V$  at  $x_2 = 0$ . (f, g) The analogs of Figs. 25.11b and 25.11c with liquid and solid replacing vapor and liquid in the descriptions. (h)  $T_7$  intersects the coexistence lines for liquid-solid 1 and liquid-solid 2, hence two common tangents need to be drawn in the  $g_m$ ,  $x_2$  diagram. (i)  $T_8$  touches the liquid-solid coexistence curve at only one point, where solids 1 and 2 and liquid are in equilibrium. This is called the eutectic temperature. (j)  $T_9$  lies below the melting points of both solids, hence the two solids are coexisting phases. All of the preceding also apply to solid solutions; only the free energy-composition diagram needs relabeling for the appropriate phases. (Courtesy of Prof. J. A. Beattie.)



Figure 25.12 Temperature-composition diagram at constant pressure and the corresponding molar free energy-composition diagrams at constant pressure and temperature. (Courtesy of Prof. J. A. Beattie.)



Figure 25.13 The components form a compound C that melts congruently. (Courtesy of Prof. J. A. Beattie.)



Figure 25.14 The components form a compound C that melts incongruently. (Courtesy of Prof. J. A. Beattie.)



Figure 25.15 The components form a maximum-boiling liquid. (Courtesy of Prof. J. A. Beattie.)



Figure 25.16 The liquid components are not miscible in all proportions. (Courtesy of Prof. J. A. Beattie.)

- The lowest curve represents the most stable phase.
- If phases can coexist, then the curves for each of the phases will have common tangents.
- Consider now the properties of three component mixtures.
  - In this case,  $\Delta_{r-1} = \Delta_2$
- In this case:

$$\left(\frac{\partial^2 g_m}{\partial x_1^2}\right)_{T,p,n} \left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p,n} - \left[\left(\frac{\partial^2 g_m}{\partial x_1 x_2}\right)_{T,p,n}\right]^2 > 0$$
$$\left(\frac{\partial^2 g_m}{\partial x_1^2}\right)_{T,p,n} > 0 \quad \text{and} \quad \left(\frac{\partial^2 g_m}{\partial x_2^2}\right)_{T,p,n} > 0$$

0



$$g_m = x_1\mu_1 + x_2\mu_2 + x_3\mu_3$$
$$g_m = x_1\mu_1 + x_2\mu_2 + (1 - x_1 - x_2)\mu_3$$

it can be shown at constant T and p:

$$\left(\frac{\partial g_m}{\partial x_1}\right)_{T,p,x_2} = \mu_1 - \mu_2$$

$$\left(\frac{\partial g_m}{\partial x_2}\right)_{T,p,x_1} = \mu_2 - \mu_3$$

- The limiting cases may now be considered:
  - When  $x_1 \to 1$ ,  $g_m \to \mu_1^0$ ,  $(\partial g_m / \partial x_2)_{T,p,x_3} \to -\infty$ and  $(\partial g_m / \partial x_1)_{T,p,x_2} \to -\infty$

- When  $x_2 \to 1$ ,  $g_m \to \mu_2^0$ ,  $(\partial g_m / \partial x_3)_{T,p,x_1} \to -\infty$  and  $(\partial g_m / \partial x_1)_{T,p,x_3} \to -\infty$
- When  $x_3 \to 1$ ,  $g_m \to \mu_3^0$ ,  $(\partial g_m / \partial x_1)_{T,p,x_2} \to -\infty$  and  $(\partial g_m / \partial x_2)_{T,p,x_1} \to -\infty$
- The other type of limiting case is when one component becomes negligible:
  - When  $x_1 \rightarrow 0$ :

$$g_m = x_2 \mu_2 + (1 - x_2) \mu_3$$
$$\left(\frac{\partial g_m}{\partial x_2}\right)_{T,p,x_3} \to \infty \text{ and } \left(\frac{\partial g_m}{\partial x_3}\right)_{T,p,x_2} \to \infty$$

• When 
$$x_2 \rightarrow 0$$
:

$$g_m = x_1 \mu_1 + (1 - x_1) \mu_3$$

$$\left(\frac{\partial g_m}{\partial x_3}\right)_{T,p,x_1} \to \infty \text{ and } \left(\frac{\partial g_m}{\partial x_1}\right)_{T,p,x_3} \to \infty$$

• When 
$$x_3 \rightarrow 0$$
:

$$g_m = x_1 \mu_1 + x_2 \mu_2$$
$$\left(\frac{\partial g_m}{\partial x_1}\right)_{T,p,x_2} \to \infty \text{ and } \left(\frac{\partial g_m}{\partial x_2}\right)_{T,p,x_1} \to \infty$$

 A triangular prism may be used to represent the equilibrium states of a ternary system (see Figure 25.17) where each side of the triangular base represents the axes in one component.





- The limit of one pure component corresponds to a vertex of the triangle while the limit of one component absent corresponds to a side of the the triangle.
- $g_m$  or T is the vertical axis of the prism.
- Some limiting cases are considered in Figure 25.18.
- The ternary system in 25.18 (a) which shows T as function of composition does not form solid solutions, so it is possible for liquid to be in equilibrium with pure solids of one or more of the components.
- The three components are miscible in the liquid phase.
- *T*<sub>1</sub>, *T*<sub>2</sub> and *T*<sub>3</sub> are the melting points of each of the pure components.
- Figure 25.18 (b) shows  $g_m$  as a function of composition, while (c-f) are projections of  $g_m$  at various temperatures.



**Figure 25.18** (a) The temperature-composition surface at p = 1 atm for the condensed phases of a ternary system with no compound formation, no solid solutions, and no miscibility gap in the liquid phase. Points in the surfaces (1, 4, 7, 6), (2, 5, 7, 4), (3, 6, 7, 5) give the compositions of the liquid phase in equilibrium at various temperatures with the solid components 1, 2, 3, respectively. Points on the curves (4, 7), (5, 7), (6, 7) give the composition of the liquid in equilibrium at various temperatures with the two solids 1 and 2, 2 and 3, 1 and 3, respectively. The point 7 gives the temperature and composition of the liquid in equilibrium with the three solids 1, 2, 3. Points 4, 5, and 6 are binary eutectic points, 7 is a ternary eutectic point. When the curves (4, 7), (5, 7), and (6, 7) are projected onto the composition triangle, an arrow is appended to show the direction of decreasing temperature. (b) Molar free energy-composition surface corresponding to (a). (c), (d), (e), (f) Projections of (b) on the composition triangle for different temperatures. The labels on the temperatures correspond to the numbers in part (a). (Courtesy of Prof. J. A. Beattie.)

## **Spectroscopy and Diatomic Molecules**

- In a molecule nuclei are not fixed:
  - They can vibrate about an equilibrium position.
  - They can revolve around a molecule's centre of mass.
- Energy levels are associated with these motions.
- These may be accessed through quantum mechanics or through spectroscopy.
- Insights from quantum mechanics will be used to interpret molecular spectra.
- Consider a molecule of H<sub>2</sub> in the ground electronic state.
  - The E(R) may be obtained from quantum mechanics and represents the electronic energy of the molecule as a function of R, the separation of the two nuclei.
  - The Born-Oppenheimer approximation is used, which is based on the fact that nuclei are much heavier than electrons.

- This allows the Schrödinger equation to be separated into nuclear and electronic parts which are then solved separately, with the final wavefunction being the product of the nuclear and electronic wavefunctions.
- The Heisenberg uncertainty principle means that nuclei cannot be in fixed positions.
- The quantum mechanical description of the molecule gives the probability of the atoms in a molecule being is a particular position relative to each other.

## **Vibrations of Diatomic Molecules**

- When the Born-Oppenheimer approximation is used, E(R) may be obtained from the electronic portion of the Schrödinger equation.
- E(R) becomes the effective potential energy for the nuclear portion of the equation.

• Thus the nuclear portion of the Schrödinger equation is:

$$\left(\frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B}\right)\Psi_{nucl}(R_n) = \left[E - E(R)\right]\Psi_{nucl}(R_n)$$

where  $R_n$  represents all the nuclear coordinates, E the total energy of the molecule.

- It is now assumed that the translational, rotational, and vibrational motions may be separated from one another.
  - Corrections for this inaccuracy will be applied later.
- This approximation gives:

$$\mathbf{H}_{nucl} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \mathbf{H}_{trans} + \mathbf{H}_{vib} + \mathbf{H}_{rot}$$
$$E - E(R) = E_{trans} + E_{vib} + E_{rot}$$

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• This means that the wavefunction is:

$$\Psi_{nucl}(R_n) = \Psi_{trans} \Psi_{vib} \Psi_{rot}$$

- Thus  $\mathbf{H}_{trans}$  and  $\Psi_{trans}$  depend only on the motion of the centre of mass.
- $\mathbf{H}_{vib}$  and  $\Psi_{vib}$  depend only on the intermolecular separation.
- $\mathbf{H}_{rot}$  and  $\Psi_{rot}$  depend only on the angular coordinates describing the orientation of the molecules in space.
- Each type of motion give an equation:

$$\mathbf{H}_{j}\Psi_{j}=E_{j}\Psi_{j}$$

- For translational motion, this is the equation for a particle in free space.
- Quantum and classical solutions give the same result.
- The operator for total energy may be rewritten in centre of mass coordinates:

$$[E - E(R)] = \left[\frac{p_X^2 + p_Y^2 + p_Z^2}{2M}\right] + \left[\frac{p_R^2}{2\mu} + V(R)\right]$$
$$+ \left[\frac{1}{2\mu R^2} \left(p_\theta^2 + \frac{p_\phi^2}{R^2 \sin^2 \theta}\right)\right]$$

where X, Y, Z are the coordinates of the centre of mass, M is the total mass,  $\mu$  is the reduced mass,  $p_R$  is the radial momentum, and  $p_{\theta}$  and  $p_{\phi}$  are the components of the angular momentum.

- Consider now the vibrational motion of a diatomic.
- Since E(R) depends only on R, it may be identified as V(R).
- Thus the Schrödinger equation for vibrational motion is:

$$\mathbf{H}_{vib}\Psi_{vib} = \left[\frac{p_R^2}{2\mu} + E(R)\right]\Psi_{vib} = E_{vib}\Psi_{vib}$$

where  $p_R = i\hbar(\partial/\partial R)$ , the radial relative momentum operator.

- This equation can be solved to give the vibrational eigenfunctions  $\Psi_{vib}$  and the vibrational eigenvalues (energy levels)  $E_{vib}$ .
- The form of the solution depends on the functional form of E(R).

- For most functional forms of E(R) only numerical solutions are feasible.
- As an approximation, E(R) will be replaced by a function of R for which exact solutions are possible.
- To determine what a suitable "replacement" function would be, the properties of the actual E(R) must be considered.
  - E(R) has a stable minimum where dE(R)/dR = 0at  $R = R_e$ .
  - Since dE(R)/dR gives the binding force, the force on either side of  $R_e$  will restore the separation to  $R_e$ .
  - There exist values of *E* such that the molecule is bound.
  - The resulting wave functions are oscillatory functions of *R*, decaying exponentially in the forbidden regions.

- The number of bound states that a diatomic may have depends on E(R) for the particular electronic state under consideration.
  - From spectroscopy, it is known that the H<sub>2</sub> molecule has 15 bound vibrational states (from v = 0 to v = 14) in the ground electronic state.
- For a model form for E(R), it will be assumed that the restoring force, dE(R)/dR, is proportional to the displacement from equilibrium:

$$F(R) \propto |R - R_e|$$

• This is consistent with the harmonic oscillator described by:

$$F(R) = -k(R - R_e)$$
 and  $V(R) = \frac{1}{2}k(R - R_e)^2$ 

• If x is defined as  $R - R_e$ , then:

$$F(x) = -kx$$
 and  $V(x) = \frac{1}{2}kx^2$ 

- This is the equation of a parabola.
- However, this does not behave like the potential for a real molecule since it predicts an infinite number of vibrational levels and does not asymptotically approach the dissociation limit.
- In spite of this, it does a reasonably good job of predicting the energy levels in the region near the equilibrium separation.
- The harmonic oscillator model predicts uniformly spaced energy levels.
- But how well does this model do?



**Figure 7.1** Vibrational energy levels of the H<sub>2</sub> molecule. Solid lines (——) represent the experimental E(R) curve and energy levels; dashed lines (- - -) give the parabolic approximation described in the text and the first few of the corresponding harmonic oscillator levels; and the dotted line ( $\cdot \cdot \cdot \cdot \cdot$ ) is a Morse potential fit. The inset shows an enlargement of the region near the minimum. The two "dissociation energies" are indicated:  $D_e = 4.748 \text{ eV}, D_0 = 4.477 \text{ eV}.$ 

- Consider a "typical" diatomic:
  - The well depth is about 5 eV or  $8 \times 10^{-19}$  J.
  - The amplitude of the vibration is about 1  $Å(|R R_e| \le 0.5 Å).$
  - If it is assumed that at  $|R R_e|$ , V(R) is the well depth, then k may be determined.

$$k = \frac{2V(R)}{(R - R_e)^2} = \frac{2 \times 8 \times 10^{-19} \text{ J}}{(0.5 \times 10^{-1} \text{ m})^2} = 640 \text{ N m}^{-1}$$

- Once k has been determined, then it may be combined with the reduced mass of the diatomic under consideration to determine the oscillator frequency.
  - For the H $_2$  molecule, the reduced mass is about  $8 \times 10^{-28}$  kg.

• Therefore the oscillator frequency is:

$$\nu(H_2) = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2\pi} \left(\frac{640 \text{ N m}^{-1}}{8 \times 10^{-28} \text{ kg}}\right)^{1/2}$$
$$= \frac{(80 \times 10^{28} \text{ s}^{-2})^{1/2}}{2\pi} = 1.5 \times 10^{14} \text{ s}^{-1}$$

• When this frequency is converted into wavenumbers:

$$\frac{\nu}{c} \equiv \overline{\nu} = 5000 \text{ cm}^{-1}$$

• Since the spacing of vibrational levels is  $h\nu$ , this can now be calculated:

$$\Delta E(H_2) = h\nu(H_2) = (6.6 \times 10^{-34} \text{ Js})(1.5 \times 10^{14} \text{ s}^{-1}) \approx 10^{-19} \text{ Js}$$

- For the harmonic oscillator, the lowest energy level is  $\frac{1}{2}h\nu$  above the minimum.
- When the harmonic oscillator energy levels are compared with the actual levels as determined by spectroscopy, it is observed that while the first two levels agree well, the higher levels do not.
  - Because at room temperature, only the lowest two or three vibrational levels have non-negligible populations, the harmonic oscillator approximation has proved to be quite useful.
- This approximation does break down for molecules with very shallow or non-parabolic wells.
- The vibrational energy levels of a real molecule may be fitted to a power series in  $(v + \frac{1}{2})$ .

- The first order term may be identified with a harmonic oscillator, (v + <sup>1</sup>/<sub>2</sub>)hv<sub>e</sub>.
- For H<sub>2</sub>,  $\nu_e = 1.3192 \times 10^{14} \text{ s}^{-1}$ .
- This indicates that the harmonic oscillator model can predict within 10% the ground state energy of the molecule.
- The suitability of the harmonic oscillator model may also be assessed by isotope effects.
- E(R) is the same for all isotopic combinations of the same atoms, since the electronic structure of a diatomic is determined by the nuclear charge.
- For a given E(R), the harmonic oscillator model predicts that  $\nu_e \propto \mu^{-1/2}$  or that  $\mu^{-1/2}\nu_e$  is a constant.
- For isotopic analogues of H<sub>2</sub>, this works well.

## **Table 7.1** Test of Harmonic Oscillator Model with VibrationalConstants of H2 Isotopes

(Atomic masses: <sup>1</sup> H, 1.00782 amu; D, 2.01410 amu)			
Molecule	Reduced Mass, <u> µ</u> (amu)	Vibrational Frequency, $v_e \times 10^{-14}(s^{-1})$	$\frac{\mu^{1/2} V_e}{10^{14} \text{amu}^{1/2} \text{s}^{-1}}$
<sup>1</sup> HD	0.67171	1.1429	0.9367
D <sub>2</sub>	1.00705	0.9345	0.9378

- The deviations may be accounted for by the fact that E(R) is not perfectly parabolic.
- The harmonic oscillator vibrational energy levels are:

$$E_{vib}(v) = (v + \frac{1}{2})h\nu_0$$

where  $\nu_0$  is the oscillator frequency and v is the vibrational quantum number of the diatomic molecule.

• The vibrational wavefunctions are  $\Psi_v(z)$  (see Table 4.1), where z is a dimensionless displacement variable:

$$z \equiv \left(\frac{4\pi^2 \mu \nu_0}{h}\right)^{1/2} \left(R - R_e\right)$$

• v gives the number of nodes in the wavefunction and v+1 gives the number of maxima in the wavefunction.<sup>348/393</sup>

- 2)
- 12z)
$6z^4 - 48z^2 + 12)$
-

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## Table 4.1 Harmonic Oscillator Wave Functions



(a)



**Figure 4.4** The quantum mechanical harmonic oscillator. (a) Potential energy curve, energy levels  $E_n$  and superimposed wave functions  $\psi_n(z)$ , where  $z \equiv (m\omega/\hbar)^{1/2}x$ . (b) Probability densities for n = 0, 1, 4, 10, with the dashed lines (- - ) giving the probabilities for classical oscillators of the same energies.

- As v increases the harmonic oscillator model becomes less accurate and the oscillator behaves more like a classical oscillator.
- In connection with E(R) there are two representations of dissociation energy that are widely used.
  - $D_e$  is the depth of the well. This is of interest to theoreticians.
  - D<sub>0</sub> is the difference between the zero point energy and the dissociation limit. This is of interest to experimentalists and represents bond energy.
  - For the harmonic oscillator:

$$D_e = D_0 + (v + \frac{1}{2})h\nu_0$$

- For a more accurate representation of the energy levels of the diatomic molecule, anharmonic corrections may be applied to the harmonic oscillator model.
- The harmonic oscillator models assumes that E(R) is parabolic, while it actually rises more steeply at small R and becomes less steep at large R.
- Therefore, the correction should be positive for  $R < R_e$ and negative for  $R > R_e$ .
- The term  $(R R_e)^n$  where n is odd will change sign in the appropriate direction at  $R_e$ .
- Since a parabola involves  $(R R_e)^2$ , n = 3 will give the next lowest power term.
- The higher power corrections to the harmonic oscillator model are referred to as the anharmonicity.

• Defining  $x = R - R_e$ , an anharmonic oscillator may be described by:

$$V(R) = \frac{1}{2}kx^2 - \frac{1}{3}k'x^3$$

$$F(R) = -kx + k'x^2$$

- For most molecules, the anharmonic correction shifts the position of the energy levels that would be populated at room temperature by about 1%.
- It still does not do a good job at describing the higher vibrational energies, because even with anharmonic corrections, the model V(R) does not level off to the dissociation limit.
- This can be addressed to some extent by adding higher order terms.

The vibrational energy may also be expressed as a power series in v + <sup>1</sup>/<sub>2</sub>:

$$E_{vib}(v) = h\nu_e \left[ (v + \frac{1}{2}) - x_e (v + \frac{1}{2})^2 + y_e (v + \frac{1}{2})^3 + \cdots \right]$$

where v = 0, 1, 2, ... and  $\nu_e, x_e, y_e, ...$  are determined from spectroscopic data.

- $\nu_e, x_e, y_e, \ldots$  may be related to E(R).
- This is not trivial.
- A functional form that is closed for E(R) needs to be assumed.
- One particularly convenient one is the Morse potential:

$$V(R) = D_e \left[ 1 - e^{-a(R-R_e)} \right]^2$$

- $D_e$  is the well depth.
- a may be shown to be  $a = \pi \nu_e (r \mu / D_e)^{1/2}$ .
- The Morse potential has the property of rising more steeply at small R and levels off to the dissociation limit at large R such that  $V(0) = \infty$  and  $V(\infty) = D_e$ .
- When the Schrödinger equation is solved using the Morse potential, the eigenvalues match the sum of the first two terms in the power series expansion of E(vib) in terms of  $(v + \frac{1}{2})$ .
- The Morse potential is shown in Figure 7.1 and matches the true potential poorly at large R.
- Information about energy levels may be obtained experimentally by observing transitions between them with spectroscopy.
- Transitions can be induced by radiation and observed as discrete spectral lines in an absorption spectra.
- For most heteronuclear molecules, the vibrational absorption spectra lie in the near infrared in the region corresponding to (0.6-12)  $\times 10^{13}$  s<sup>-1</sup> or 200 4000 cm<sup>-1</sup> or 2.5 50  $\mu$ m.
- Isolated homonuclear molecules do not exhibit vibrational spectra.
- Consider the interaction of radiation with a diatomic.
- A photon may be considered as a oscillating electric field that interacts with the electrons of the molecule (see Figure 7.2).
- A heteronuclear diatomic molecule has a dipole moment which oscillates as the molecule oscillates.



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**Figure 7.2** Interaction between an electric field and an oscillating (molecular) dipole. (a) The forces exerted on the dipole by the field, which alternately tend to compress or stretch the dipole as the field direction changes. (b) Field varies much faster than the molecular vibration ( $\nu >> \nu_e$ ); here and in the subsequent diagrams, the instantaneous forces on the dipole are indicated by arrows. (c) Field varies much slower than the molecular vibration ( $\nu << \nu_e$ ). (d) Field and dipole oscillate at the same frequency ( $\nu = \nu_e$ ), but 90° out of phase. As shown here, the dipole absorbs energy from the field; for a field phase 180° different, the forces are reversed and the dipole gives up energy to the field.

- Consider a photon with a wavelength greater than any dimension of the molecule.
- The electric field is uniform in space but oscillates with time.
- The component of this field that is parallel to the axis of a bond exerts an instantaneous force on the dipole that will either compress or stretch the bond.
- Whether or not this will affect the vibration will depend on whether the frequency of the photon matches the frequency of the molecular vibration.
- If the frequency of the photon is higher than that of the molecular vibration, then the field of the photon reverses in less than one period of the molecular vibration.

- If the frequency of the photon is lower than that of the molecular vibration, then the field varies slowly over many vibrational periods and would eventually effect the average value of *R* over the period of the photon, but will not change the state of the molecule.
- If the frequency of the photon closely matches the frequency of the vibration and is in the right phase with respect to the vibration then there will be energy exchange between the molecule and the field.
  - If the field is stretching the molecule while it is expanding and compresses it while the molecule is contracting, then the molecule will be excited.
  - If the field is stretching the molecule while it is contracting and compresses it while the molecule is expanding, then the molecule will be deexcited.
  - This is typical of electric dipole transitions.

- If a molecule is homonuclear, then there is no dipole and an oscillating electric field can exert no net force on the vibrating molecule.
- This why homonuclear diatomics do not have vibrational spectra.
- Classical mechanics cannot account for the quantization of molecules or spectra.
- A quantum mechanical approach is needed.
- The quantum mechanical treatment gives as the transition probability:

$$\mu_{v,v'} = \int_0^\infty \Psi_{v'}^*(R)\mu(R)\Psi_v(R)dR$$

describing the transition between v and v'.

- $\mu(R)$  is the instantaneous dipole moment of the molecule.
- $\Psi_v$  and  $\Psi_{v'}$  are the vibrational wavefunctions for states v and v'.
- In the case of a molecule with no dipole,  $\mu(R)$  is always zero, and thus the transition probability is rigourously zero.
- In order to probe experimentally the vibrational levels of a homonuclear diatomic, the vibrational transitions accompanying electronic transitions need to be probed.
- Quantum mechanics also give rise to selection rules.
- Consider a heteronuclear diatomic.
- For the integral to be nonzero, in addition to  $\mu(R) \neq 0$ , the properties of the wavefunctions must be considered.

- The integral will be nonzero only when v and v' differ by 1.
- This gives the selection rule  $\Delta v = \pm 1$ .
- A heteronuclear diatomic that is described as a harmonic oscillator changes energy one vibrational quantum at a time.
- But real molecules are not harmonic.
- The vibrational wavefunctions of a real molecule may be described as a linear combination of the harmonic oscillator wavefunctions.
- This means that the transition probabilities for transitions that are not  $\Delta v = \pm 1$  can be nonzero.
- However the probabilities of these other transitions are much smaller.



**Figure 7.3** Schematic representation of molecular vibrational absorption spectra (neglecting rotational effects). (a) Harmonic oscillator model:  $\Delta v = \pm 1$  only, all transitions at the same frequency  $v_0$ . (b) Real diatomic molecule: The energy levels are not evenly spaced, so one can observe a band of lines beginning near  $v_e$ ; since the selection rule is not rigorous, there is a weaker band  $(\Delta v = \pm 2)$  near  $2v_e$ , and still weaker bands at  $3v_e$ ,  $4v_e$ , . . . Within each band, the intensity of a given line is proportional to the population of the initial state; the intensities as drawn here correspond to a gas with  $hv_e/k_BT \approx 1.8$  (cf. Chapter 21).

- In Figure 7.3 are shown the spectrum predicted by a harmonic oscillator and the spectrum predicted by an anharmonic oscillator.
- Since the spectrum is determined by the spacing of the energy levels, the harmonic oscillator spectrum has only one line.
- The spectrum that arises from the anharmonic oscillator has a series of lines with different values of  $\Delta v$ .
  - The transition between v = 0 and v = 1 requires more energy than the transition between v = 1 and v = 2, therefore the line arising from the latter will be at a lower frequency than the line arising from the former.
  - Transitions for which  $\Delta v = 2$  will be at a higher frequency than those for  $\Delta v = 1$ .

- The relative intensity of the lines contains information about the relative populations of the initial states.
- For real molecules, vibrational transitions are accompanied by changes in rotational states.
  - This means that vibrational spectra contain bands of closely spaced rotational-vibrational lines.
- As shown in Table 7.2, vibrational constants vary among molecules.
- Part of this variation is due the electronic structure of the molecule.
- Part of this variation is due to the reduced mass.
- The values shown may be corrected for differences in the reduced mass for the isotopic analogues.

			$\tilde{V}_e(\text{cm}^{-1})$	$\bar{V}_e x_e$	$\tilde{v}_e Y_e$		Be	α
Molecule	μ (amu)	$R_e$ (Å)	$(\tilde{V}_e \equiv V_e/c)$	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(eV)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
<sup>1</sup> H <sub>2</sub>	0.50391	1.7412	4400.39	120.815	0.7242	4.4773	60.864	3.0764
HD ( <sup>1</sup> H <sup>2</sup> H)	0.67171	0.7412	3812.29	90.908	0.504	4.5128	45.663	2.0034
$D_2(^2H_2)$	1.00705	0.7412	311.70	61.82	0.562	4.5553	30.457	1.0786
First-row hom	onuclear molecul	25						
$^{7}Li_{2}$	3.50800	2.6725	351.44	2.592	-0.0058	1.12	0.6727	0.00704
<sup>11</sup> B <sub>2</sub>	5.50465	1.590	1051.3	9.4		2.9	1.212	0.014
<sup>12</sup> C <sub>2</sub>	6.00000	1.2425	1854.71	13.340	-1.172	6.24	1.8198	0.01765
$^{14}N_{2}$	7.00154	1.094	2358.07	14.188	0.0124	9.7598	1.9987	0.01781
<sup>16</sup> O <sub>2</sub>	7.99745	1.2075	580.19	11.98	0.0475	5.1156	1.4456	0.01593
<sup>19</sup> F <sub>2</sub>	9.49910	1.409	919.0	13.6		1.604	0.8901	0.0146
Other homonu	clear molecules							
<sup>23</sup> Na <sub>2</sub>	11.4949	3.0786	159.23	0.726	-0.0027	0.75	0.1547	· 0.00079
<sup>39</sup> K <sub>2</sub>	19.48185	3.923	92.64	0.354		0.51	0.0562	0.00022
<sup>85</sup> Rb <sub>2</sub>	42.4558	4.20	57.28	0.96	-0.0008	0.47	0.0127	0.0000264
<sup>133</sup> Cs <sub>2</sub>	66.9525	4.58	41.99	0.080	0.0002	0.45		
<sup>35</sup> Cl <sub>2</sub>	17.48222	1.9878	559.71	2.70		2.484	0.2441	0.00153
<sup>79</sup> Br <sup>81</sup> Br	39.9524	2.2809	323.33	1.081		1.9708	0.0811	0.00032
$^{127}I_{2}$	63.4502	2.6666	214.52	0.607	-0.0013	1.5437	0.0374	0.00012
Hydrides								
<sup>7</sup> Li <sup>1</sup> H	0.88123	1.5954	1405.65	23.200	0.1633	2.429	7.5131	0.2132
$^{12}C^{1}H$	0.92974	1.124	2859.1	63.3		3.47	14.448	0.530
<sup>16</sup> O <sup>1</sup> H	0.94808	0.9706	3735.21	82.81		4.392	18.871	0.714
<sup>I</sup> H <sup>19</sup> F	0.95705	0.9168	4139.04	90.05	0.932	5.86	20.9560	0.7958
<sup>1</sup> H <sup>35</sup> CI	0.97959	1.2746	2991.09	52.82	0.2244	4.4361	10.5936	0.3072
<sup>1</sup> H <sup>81</sup> Br	0.99511	1.4145	2649.21	45.22	0.0029	3.755	8.4651	0.2333
${}^{1}H^{127}I$	0.99988	1.6090	2308.09	38.981	-0.1980	3.053	6.5108	0.1686
Other heteron	uclear molecules							
<sup>7</sup> Li <sup>19</sup> F	5.12381	1.5638	910.34	7.929		5.94	1.3454	0.02030
<sup>9</sup> Be <sup>16</sup> O	5.76432	1.3310	1487.32	11.830	0.0224	4.60	1.6510	0.0190
<sup>11</sup> B <sup>14</sup> N	6.16351	1.281	1514.6	12.3		3.99	1.666	0.025
<sup>12</sup> C <sup>14</sup> N	6.46219	1.1720	2068.70	13.144		7.567	1.8991	0.01735
<sup>12</sup> C <sup>16</sup> O	6.85621	1.1283	2169.82	13.294	0.0115	11.09	1.9313	0.01751
<sup>14</sup> N <sup>16</sup> O	7.46676	1.1508	1904.03	13.97	-0.0012	6.50	1.7046	0.0178
<sup>23</sup> Na <sup>35</sup> Cl	13.8707	2.3606	366	2.05		4.25	0.2181	0.00161
<sup>39</sup> K <sup>79</sup> Br	26.0850	2.8207	213	0.80	0.0011	3.925	0.0812	0.00040

Table 7.2 Vibrational and Rotational Constants of Some Diatomic Molecules

## **Rotations of Diatomic Molecules**

- Consider the rotational behaviour of diatomic molecules.
- It will be assumed that the rotational motion can be separated from the translational and vibrational motions.
- The rigid rotator model will be used.
- The diatomic molecule will be treated a a rigid symmetric top which has two equal moments of inertia:

$$I_0 \equiv I_x = I_y \neq I_z$$

where the z axis is the bond axis.

• The Hamiltonian of the rigid symmetric top is:

$$\left| \mathbf{H}_{rot} = \frac{1}{2I_0} \mathbf{L}^2 + \frac{1}{2} \left( \frac{1}{I_z} - \frac{1}{I_0} \right) L_z^2 \right|$$

- $\mathbf{L}^2$  and  $L_z^2$  are the angular momentum operators.
- The eigenvalues of  $\mathbf{H}_{rot}$  are:

$$E_{rot} = \frac{\hbar^2}{2} \left[ \frac{J(J+1)}{I_0} + l_z^2 \left( \frac{1}{I_z} - \frac{1}{I_0} \right) \right]$$

• For a diatomic molecule:

$$I_z \equiv \sum_i m_e(x_i^2 + y_i^2)$$

and is very small since it is due to the electrons and the fact that the atoms have nonzero radii.

• Also:

$$I_0 = \mu R^2$$

- Therefore  $I_z << I_0$ .
- The energy associated with the L<sub>z</sub> term may be either vary large or very small depending on the electronic state and is constant for that electronic state.
  - Therefore it can be included with the electronic part of the Hamiltonian.
- Thus the rotational energy of the molecule may be written as:

$$E_{rot} = \frac{J(J+1)\hbar^2}{2I_0} = \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

where J = 0, 1, 2, ... and J is the rotational quantum number.

• This equation has the form of the rigid rotator equation.

- Each energy level has a degeneracy of 2J + 1.
- The angular momentum about an axis through the center of mass is  $M_J\hbar$ .
- $M_J$  has 2J + 1 allowed values,  $J, J 1, \ldots, -J + 1, -J$ .
- The rotational wavefunctions are the spherical harmonics  $Y_{J,M_J}(\theta,\phi)$ .
- The limitations on the validity of this model are due to the fact that real molecules vibrate.
- A further understanding of this may be gained by examining the rotational and vibrational periods.
- The angular momentum of diatomic molecule with fixed R is  $\mu R_e^2 \omega$  and the rotational energy is  $E_{rot} = \frac{1}{2} \mu R_e^2 \omega^2$ .
- The eigenvalue for angular momentum is  $L^2 = J(J+1)\hbar^2$ .

• Combining these gives:

$$\omega = \frac{\left[J(J+1)\right]^{1/2} \hbar}{\mu R_e^2} = \left(\frac{E_{rot}}{\mu R_e^2}\right)^{1/2}$$

- Equipartion predicts an average value of kT as the rotational energy of a diatomic molecule.
  - For a hydrogen molecule at room temperature the average period is:

$$\tau_{rot} = \frac{2\pi}{\omega} = 2\pi \left(\frac{\mu R_e^2}{2k_B T}\right)^{1/2}$$

$$= 2\pi \left[ \frac{(8.3676 \times 10^{-28} \text{ kg})(0.7412 \times 10^{-10} \text{ m})}{2(1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \right]^{1/2}$$

$$= 2\pi (5.55 \times 10^{-28} \text{ s}^2)^{1/2} = 1.48 \times 10^{-13} \text{ s}$$

- The vibrational period is the reciprocal of the frequency.
  - For a harmonic oscillator model of the hydrogen molecule, this is:

$$\tau_{vib} = \nu_e^{-1} = (1.3192 \times 10^{14} \text{ s}^{-1})^{-1} = 7.58 \times 10^{-15} \text{ s}$$

- This means that a hydrogen molecule will vibrate about 20 times in the course of one vibrational period.
- Thus it may be assumed that the effects of vibration will average out over the course of one rotation and an average (rigid) bond length may be assumed.
- However the rigid rotator model is inadequate for spectroscopy.

- The average R value should increase with the vibrational quantum number v.
- Rigorously,  $R_e^{-2}$  should be replaced by the value of  $R^{-2}$  averaged over a vibrational period and

$$\langle R^{-2} \rangle_v < R_e^{-2}$$

• The rotational energy levels can be approximated by:

$$E_{rot} = J(J+1)hcB_v = J(J+1)hc\left[B_e - \alpha_e\left(v + \frac{1}{2}\right) + \ldots\right]$$

where

$$B_e = \frac{h}{4c\mu R_e^2},$$

 $\alpha_e$  is a constant,  $B_v$  is the rotational state v, and  $B_e$  is the rigid rotator value.

• For H<sub>2</sub>:

 $1.0546 \times 10^{-34} \text{ J s}$ 

 $8\pi (2.9979 \times 10^{-8} \text{ m/s})(8.368 \times 10^{-28} \text{ kg})(0.7412 \times 10^{-10} \text{ m})^2$ 

$$= B_e = 60.9 \text{ cm}^{-1}$$

which agrees well with experiment.

- $\alpha_e$  is determined experimentally to be  $\approx$  3.0 cm<sup>-1</sup>.
- Measurements of  $B_e$  are used to determine  $R_e$ .
- Molecules with large  $R_e$  have small  $B_e$ .
- The rigid rotator model assumes that the nuclei are point masses.
- This assumption breaks down if the electronic state of the molecule does not have zero angular momentum relative to the nuclei.

• Consider the eigenvalue equation for the symmetric top:

$$E_{rot} = J(J+1)hcB_v + M_J^2hc(A-B_v)$$

where  $A \equiv \hbar/4\pi c I_z$ .

• The quantum numbers J and  $M_J$  are defined by:

$$\left|\mathbf{J}\right|^2 = J(J+1)\hbar^2 \text{ and } J_z = M_J\hbar$$

which are the square and z component of the total angular momentum of the molecule.

- Electronic and nuclear motions contribute to J.
- J<sub>z</sub> is almost entirely due to the angular momentum of electrons about the bond axis.

- L, the orbital electronic angular momentum, and S can couple with each other and the nuclear angular momentum in many ways.
- Consider the simplest case.
  - For most electronic states, the orbital electronic angular momentum is strongly coupled to the bond axis.
  - Only the *z* component is quantized.
  - Therefore:

$$\left|L_z\right| = \Lambda \hbar$$

 If the electronic state is a singlet state with S = 0 (i.e. all the electrons are paired), L<sub>z</sub> is the only contribution to J<sub>z</sub>.

$$\left|J_{z}\right| = \Lambda \hbar \text{ and } \left|M_{J}\right| = \Lambda$$

• The eigenvalue equation becomes:

$$E_{rot} = J(J+1)hcB_v + \Lambda^2 hc(A - B_v)$$

where

$$\Lambda = 0, 1, 2, \dots$$
 and  $J = \Lambda, \Lambda + 1, \Lambda + 2, \dots$ 

- Although the second term is part of the electronic hamiltonian, it is important to consider the restrictions that it places on allowed quantum numbers.
- Rotational transitions occur if the molecule has a dipole.
- A homonuclear diatomic does not have a pure rotational spectrum.

• For heteronuclear diatomics, the rotational spectrum has a selection rule for electric dipole transitions of

$$\Delta J = \pm 1$$

• Therefore, the only allowed pure rotational transitions have:

$$\Delta E = 2J'hcB_v$$
 or  $\overline{\nu} = 2J'B_v$ 

where J' is the quantum number of the upper state.

- The rigid rotator model predicts a pure rotational spectrum consisting of a series of evenly spaced lines, beginning with  $\overline{\nu} = 2B_v$  and continuing in intervals of  $2B_v$  (see Figure 7.4).
- The series is usually found in the far infrared or in the microwave region.



Figure 7.4 Pure rotational absorption spectrum of a diatomic molecule. Given the selection rule  $\Delta J = \pm 1$ , there is a series of lines with the constant wavenumber spacing  $2B_{\nu}$ . The intensities of the lines are proportional to the populations of the initial states, and as drawn here correspond to a gas with  $B_{\nu}hc/k_BT \approx 0.1$  (cf. Chapter 21).

- The spacing of rotational lines is one of the best methods of determining bond lengths.
- Generally the spectrum is best resolved if the gas is at low pressure.
- Usually the frequency of radiation is varied and absorbance determined from the power loss from the source to the detector.
- The first spectra were obtained by using a prism between the source and the sample to vary the wavelength and a photographic plate to detect the photons transmitted.
- With current technology, it is possible to obtain spectra very accurately and in great detail.
- To a first approximation, lines in a rotational spectra are equally spaced. and B<sub>v</sub> may be estimated as half the spacing in wavenumbers.

## **Spectra of Diatomic Molecules**

- When  $h\nu$  equals the energy difference between two energy levels a transition may be induced.
- In the microwave and far infrared regions, pure rotational spectra may be observed.
- In the near and middle infrared regions, vibrational spectra may be observed.
  - Vibrational transitions are accompanied by rotational transitions.
- Radiation in the visible and ultraviolet region may cause electronic transitions.
  - These are usually accompanied by vibrational and rotational transitions.
- Higher energies such as those in the X-ray region may cause excitation of inner core electrons.



re 7.5 Energy levels of the N<sub>2</sub> molecule. (a) Electronic states, with vibrational levels (v = 0, 1, 2, ...) shown in the lowest three. [Not n is the  $W^3\Delta_u$  state; this state has about the same minimum energy as the  $B^3 \prod_g$  (see Table 7.6), but its  $R_e$  is not known.] The energy zero ground electronic-vibrational state ( $X^1\Sigma_g^+$ , v = 0). After W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 1227 (1965). (b) Rotational structure of the two lowest vibrational levels of the ground state; the energy zero is the same as in (a).

- There are two main classes of spectroscopy:
  - In emission spectroscopy, the sample is excited (thermally, electrically, or in some other way), then the emitted radiation is observed as it relaxes to an equilibrium state.
  - If the sample is excited by radiation, then it is fluorescence spectroscopy.
  - In absorption spectroscopy, the sample is placed between the light source and the detector.
    - As the sample absorbs radiation, the molecules are excited to higher levels.
    - The absorbance is determined from the measurement at the detector of the attenuation of the original light source.
- Consider now the basic components of a spectrometer.

- The sample:
  - May be liquid or gas.
  - Must be in a holder that is transparent to the radiation being used.
  - For UV below 2000 Å, air is opaque and the spectrum must be taken in a vacuum.
- Radiation source:
  - There are number of light sources, depending on the wavelength of interest.
  - For UV and visible ranges, light sources include tungsten filament lamps and electrical discharges.
  - For IR, heat rods of a refractory material are used.
  - In the microwave region, Klystron tubes are used.
  - Radiowave generators are used at longer wavelengths.

- Optical system:
  - The purpose of the optical system is to select the wavelength of the radiation.
  - This may be done by using either a prism or a diffraction grating as a dispersing element.
  - It is also possible to use a tunable laser as the light source.
  - Radio and microwaves are also tunable.
  - If the light source is tunable, a dispersing element is not needed.
- Detector:
  - The first spectrophotometers used photographic emulsions on plates with the intensity of a line determined by the extent of darkening.

## • (Continued:)

- More recent spectrophotometers use electronic means of detection with photosensitive semiconductors, photoelectric cells, thermocouples and bolometers, and crystal diodes.
- Computerized postprocessing is used to give the relationship between intensity and wavelength or wavenumber.
- A transition between bound states of a molecule has a definite energy and frequency (  $\Delta E = h\nu$ ).
- There are a number of factors that lead to the observation of non-zero line widths.
  - The natural line width is the consequence of the uncertainty priniciple.

- Doppler broadening is due to the fact that molecules are moving randomly with some moving toward or away from the detector.
- Pressure broadening is due to the perturbation of energy levels do to interactions with other molecules.
  - Pressure broadening can be controlled by controlling the density and pressure of the sample.

Simultaneous vibration-rotation spectra

- For most diatomic molecules in the ground electronic state, pure vibrational transitions are forbidden.
- The selection rules are:

$$\Delta v = \pm 1$$
 and  $\Delta J = \pm 1$ 

 $(\Delta v = \pm 1 \text{ is only approximately true for real oscillators.})$ 



Figure 7.6 The infrared spectrum of HCl vapor associated with transitions (a)  $v=0 \rightarrow v=1$  and (b)  $v=0 \rightarrow v=2$ . The individual rotation vibration lines are all doublets because of the presence of the isotopic species H<sup>35</sup>Cl and H<sup>37</sup>Cl; the former is the more intense. Number above spectral lines specify  $\Delta J$ . From C. F. Meyer and A. A. Levin, *Phys* Rev. 34, 44 (1929).



Figure 7.7 Schematic representation of a vibration-rotation band in the infrared spectrum of a diatomic molecule in a  $\Sigma$  electronic state. Each line in the band corresponds to a transition between a lower level v'', J'' and an upper level v', J', with J' = J'' - 1 in the P branch and J' = J'' + 1 in the R branch. The lines are labeled with the running number m, defined in Eq. 7.29. The band origin  $\tilde{v}_0$  corresponds to the forbidden transition v';  $J' = 0 \leftrightarrow v''$ ; J'' = 0. The spectrum is drawn for  $B_{v'} < B_{v''}$  so that the band converges to a head (not shown) in the R branch.

- Some representative spectra are shown in Figures 7.6 and 7.7.
- For each vibrational transition, there is an entire family of vibration-rotation lines.
- The lines are nearly equally spaced with a gap in the middle.
  - This gap corresponds to the position of a hypothetical line with  $\Delta J = 0$ .
  - Such a transition is forbidden for a  $\Sigma$  state.
  - The position of this missing line is referred to a the null line or band origin with wavelength  $\overline{\nu}_0$ .
  - The group of lines with  $\overline{\nu} < \overline{\nu}_0$  is the *P* branch.
  - The group of lines with  $\overline{\nu} > \overline{\nu}_0$  is the R branch.
- By convention, a single prime denotes the upper state, while a double prime denotes the denotes the lower state

- The P branch corresponds to J' = J'' 1
- The R branch corresponds to J' = J'' + 1
- The wavenumbers associated with the transitions are:

$$\overline{\nu} = \frac{E' - E''}{hc} = \overline{\nu}_0 + B'_v J' (J' + 1) - B''_v J'' (J'' + 1)$$

where

$$\overline{\nu}_0 = \frac{E'_{vib} - E''_{vib}}{hc}$$

•  $\overline{\nu}$  may be rewritten as:

$$\overline{\nu} = \overline{\nu}_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$$

where m = -J'' for the P branch and m = J'' + 1 in the R branch.
- For a rigid rotator,  $B'_v = B''_v$ , and the lines are evenly spaced.
- For a real rotator,  $B_v$  increases with v, therefore  $B'_v < B''_v$  for any real infrared emission.
- This means that the quadratic term is negative and the spaces between successive lines decreases with increasing *m*.
- There can exist some value \$\overline\$ such that the spacing would decrease to zero.
- At values of m above this mean that  $\overline{\nu}$  would start to increase with m
- This gives rise to the band head in the R branch, usually at very high values of m which means that it is usually difficult to observe.

- If the ground state is not a Σ state, then ΔJ = 0 transitions (Q branch) are allowed in addition to ΔJ = ±1.
- For the *Q* branch:

$$\overline{\nu}_Q = \overline{\nu}_0 + (B'_v + B''_v)J + (B'_v - B''_v)J^2$$

- Since the spacing between the energy levels increase smoothly, the is no band head.
- The lines in the Q branch are very close together and, when not resolved, appear as a single intense line.
- Molecules may also scatter radiation.
- Radiation leaves the molecule in a different direction than before it interacted with the molecule.