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## THERMODYNAMICS

### 1. Free energy calculations.

- a. Engel and Reid, problem 6.2.

$$\Delta G = ?$$
$$dG = VdP - SdT$$

The system is at constant temperature, therefore:

$$dG = VdP$$
$$\Delta G = \int_{10.5\text{bar}}^{0.5\text{bar}} VdP = nRT \int_{10.5\text{bar}}^{0.5\text{bar}} \frac{dP}{P} = (2.5)(8.3144)(350\text{K}) \ln \frac{(0.5)}{(10.5)} = -22.1\text{kJ}$$

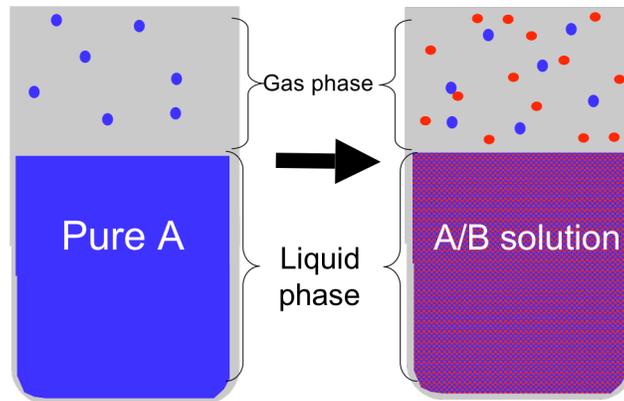
- b. Engel and Reid, problem 6.3.

$$\Delta A = ?$$
$$dA = -PdV - SdT$$

Again, the system is at constant temperature, thus:

$$\Delta A = \int_{35.0\text{L}}^{12.0\text{L}} -PdV = -nRT \int_{35.0\text{L}}^{12.0\text{L}} \frac{dV}{V} = -(2.0)(8.3144)(298\text{K}) \ln \frac{(12.0)}{(35.0)} = 5.30\text{kJ}$$

2. **Vapor-liquid equilibria.** Consider the experimental setup described in the cartoon below: We have a closed beaker containing either a quantity of pure liquid A or a solution of liquid A mixed with liquid B. The liquids are in equilibrium with the gas phase above them (pure gaseous A in the one case and a mixture of gaseous A and B in the other). The systems are equilibrated at constant temperature and pressure. Assuming the vapors can be modeled as ideal gases, answer the following questions:



- a. What is the equilibrium condition on the chemical potentials of A molecules in the case of pure A liquid in equilibrium with its gas? What is the condition on the chemical potential of A molecules for A molecules in the solution in equilibrium with the A/B gas mixture?

For any closed system at constant temperature and pressure, the chemical potentials of a given species must be the same in each phase. For the pure A liquid in equilibrium with its vapor:

$$\mu_A^{liquid} = \mu_A^{vapor}$$

For A in solution with B, we have:

$$\mu_A^{liquid\_solution} = \mu_A^{vapor\_mixture}$$

- b. Show that at equilibrium, the difference between the standard state chemical potentials of the pure liquid A and pure A gas is:

$$\mu_i^{o,liquid}(T) - \mu_i^{o,gas}(T) = RT \ln \frac{P^*}{P^o}$$

...where  $P^*$  is the vapor pressure of pure A (the pressure of pure A gas above pure A at the given temperature and pressure) and  $P^o$  is the reference pressure for the ideal gas.

We find this relationship by simply expanding the equilibrium condition above for the case of the pure A liquid in equilibrium with its vapor:

$$\begin{aligned} \mu_A^{liquid} &= \mu_A^{vapor} \\ \mu_A^{o,liquid} + RT \ln a_A^{liquid} &= \mu_A^{o,vapor} + RT \ln \left( \frac{P^*}{P^o} \right) \end{aligned}$$

The activity of A in the pure liquid state can be taken as approximately 1, therefore:

$$\mu_i^{o,liquid}(T) - \mu_i^{o,gas}(T) = RT \ln \frac{P^*}{P^o}$$

c. Show that for the solution, the activity of A molecules is:

$$a_A^{solution} = \frac{P_i}{P^*}$$

...where  $P^*$  is the vapor pressure of A above pure liquid A, as in part (b), and  $P_i$  is the partial pressure of A gas in the A/B gas mixture above the solution.

For the A/B solution, A molecules in the liquid phase are in equilibrium with the gas phase as given above:

$$\begin{aligned} \mu_A^{solution} &= \mu_A^{gas\_mixture} \\ \mu_A^{o,liquid} + RT \ln a_A^{solution} &= \mu_A^{o,vapor} + RT \ln \left( \frac{P_A}{P^o} \right) \end{aligned}$$

Note that the superscript for the standard state chemical potential of A in the liquid solution phase says 'liquid' rather than 'solution' - because the standard state chemical potential is the free energy of pure liquid A, which is the same reference state for both pure A and for a solution of A mixed with B molecules.. This fact allows us to use the result from part (b) to simplify the expression:

$$\mu_i^{o,liquid}(T) - \mu_i^{o,gas}(T) = RT \ln \frac{P^*}{P^o}$$

and:

$$\mu_A^{o,liquid} + RT \ln a_A^{solution} = \mu_A^{o,vapor} + RT \ln \left( \frac{P_A}{P^o} \right)$$

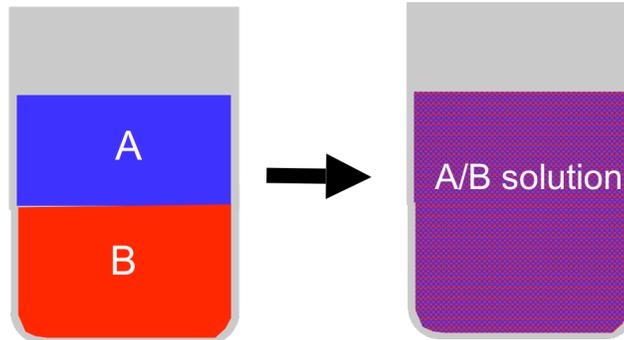
$$RT \ln a_A^{solution} = \mu_A^{o,vapor} - \mu_A^{o,liquid} + RT \ln \left( \frac{P_A}{P^o} \right)$$

$$RT \ln a_A^{solution} = -RT \ln \left( \frac{P^*}{P^o} \right) + RT \ln \left( \frac{P_A}{P^o} \right)$$

$$RT \ln a_A^{solution} = RT \ln \left( \frac{P_A P^o}{P^o P^*} \right)$$

$$\therefore a_A^{solution} = \frac{P_A}{P^*}$$

3. **Spontaneous formation of solutions.** Prove that if two pure liquids A and B are placed together in a container, formation of a solution from the two is always a spontaneous process if the pair form an ideal solution.



To prove the process of forming a solution is spontaneous, we must show that the free energy change on forming the solution is  $< 0$ :

$$\Delta G = G_{\text{solution}} - G_{\text{unmixed\_components}} = G_{\text{solution}} - (G_{\text{pureA}} + G_{\text{pureB}})$$

The initial state is pure A and pure B (unmixed), while the final state is the solution. The free energy change for this process is then expanded as:

$$\Delta G = [n_A \bar{G}_A + n_B \bar{G}_B] - (n_A \mu_A^o + n_B \mu_B^o)$$

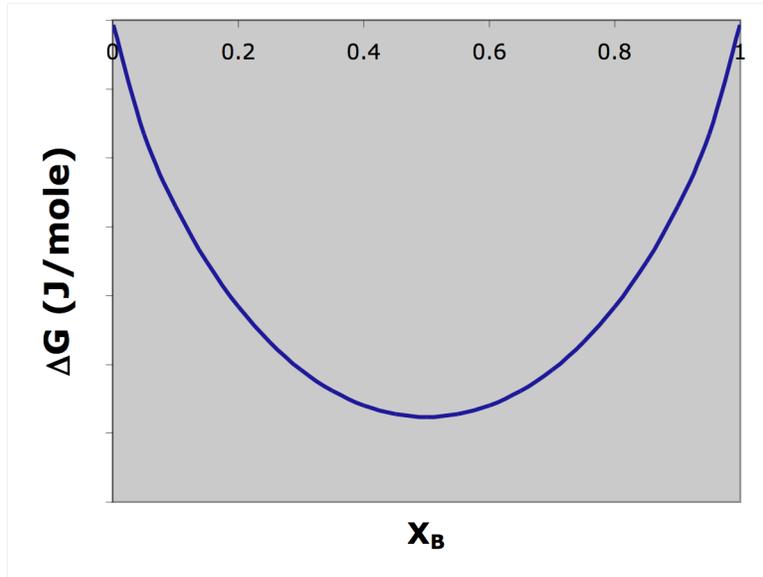
$$\Delta G = [n_A \mu_A + n_B \mu_B] - n_A \mu_A^o - n_B \mu_B^o$$

$$\Delta G = [n_A (\mu_A^o + RT \ln a_A) + n_B (\mu_B^o + RT \ln a_B)] - n_A \mu_A^o - n_B \mu_B^o$$

$$\Delta G = [n_A (\mu_A^o + RT \ln X_A) + n_B (\mu_B^o + RT \ln X_B)] - n_A \mu_A^o - n_B \mu_B^o$$

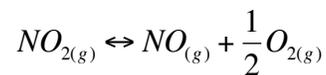
$$\Delta G = n_A RT \ln X_A + n_B RT \ln X_B$$

Now, because  $X_A$  and  $X_B$  are always  $\leq 1$ , the natural log terms are always negative- and thus  $\Delta G$  is less than zero for all values of  $X_A/X_B$ . This is illustrated by the plot below of  $\Delta G$  for the mixing process vs.  $X_B$ :



#### 4. Chemical reaction equilibria.

- a. Consider the gas phase reaction of  $\text{NO}_2$  shown below. At  $T = 700 \text{ K}$ , the equilibrium constant  $K_p = 0.379$ . At a total pressure of  $2 \text{ atm}$ , the partial pressure of oxygen in the reaction is  $0.378 \text{ atm}$  at equilibrium. Determine the molar standard state free energy of reaction and the equilibrium composition of the gas mixture (final partial pressure of each component) for these conditions.



At equilibrium, we have:

$$\Delta \bar{G}_{rxn} = 0$$

$$\Delta \bar{G}_{rxn}^o + RT \ln K_p = 0$$

$$\therefore \Delta \bar{G}_{rxn}^o = -(8.3144 \frac{\text{J}}{\text{mole} \cdot \text{K}})(700\text{K}) \ln(0.379) = 5,650 \frac{\text{J}}{\text{mole}}$$

$$K_p = \frac{\left(\frac{P_{NO}}{P^\circ}\right)\left(\frac{P_{O_2}}{P^\circ}\right)^{1/2}}{\left(\frac{P_{NO_2}}{P^\circ}\right)}$$

$$0.379 = K_p = \frac{\left(\frac{P_{NO}}{1}\right)(0.378)^{1/2}}{\left(\frac{P_{NO_2}}{1}\right)}$$

$$\therefore \left(\frac{P_{NO}}{P_{NO_2}}\right) = 0.616$$

$$P_{NO} + P_{NO_2} + 0.378 \text{ atm} = 2 \text{ atm}$$

Solving the last two equations for the two unknowns, we find  $P_{NO_2} = 1.003 \text{ atm}$  and  $P_{NO} = 0.619 \text{ atm}$ .

- b. We wish to mix an initial  $x$  moles  $SO_3(g)$  and 1 mole  $SO_2(g)$  to obtain a final partial pressure of oxygen equal to 0.05 atm in a reactor at 1100 K under a total pressure of 1.2 atm at equilibrium. Calculate  $x$  given:



(Modified from C.H.P. Lupis, *Chemical Thermodynamics of Materials*, problem V.6)

We know that at equilibrium:

$$\Delta \bar{G}_{rxn}^\circ (T = 1100K) = 3747 \frac{J}{mole} = -RT \ln K_p = -RT \ln \frac{\left(\frac{P_{SO_3}}{P^\circ}\right)}{\left(\frac{P_{O_2}}{P^\circ}\right)^{1/2} \left(\frac{P_{SO_2}}{P^\circ}\right)}$$

Taking  $P^\circ = 1 \text{ atm}$ , we have:

$$K_p = 0.664 = \frac{P_{SO_3}}{(P_{O_2})^{1/2} (P_{SO_2})}$$

$$0.664 (P_{O_2})^{1/2} = \left(\frac{P_{SO_3}}{P_{SO_2}}\right)$$

We also know that at any point during the reaction, we have the following numbers of moles of each species:

$$n_{O_2} = \frac{1}{2}\xi$$

$$n_{SO_2} = 1 + \xi$$

$$n_{SO_3} = x - \xi$$

$$n_{total} = \frac{1}{2}\xi + 1 + \xi + x - \xi = 1 + \frac{1}{2}\xi + x$$

The partial pressures must sum to give the total pressure in the system, and we are asked to solve for the case where the total pressure is 1.2 atm and the oxygen partial pressure is 0.05 atm:

$$P_{SO_2} + P_{SO_3} + P_{O_2} = P$$

$$X_{SO_2}P + X_{SO_3}P + 0.05atm = 1.2atm$$

$$\frac{n_{SO_2}}{n_{total}}P + \frac{n_{SO_3}}{n_{total}}P + 0.05atm = 1.2atm$$

$$\left(\frac{n_{SO_2} + n_{SO_3}}{n_{total}}\right)1.2atm + 0.05atm = 1.2atm$$

$$\left(\frac{1 + x}{1 + \frac{1}{2}\xi + x}\right)1.2atm + 0.05atm = 1.2atm$$

Equation (i):  $\frac{1 + x}{1 + \frac{1}{2}\xi + x} = 0.9583$

We can rewrite the equilibrium condition from above to get a second equation in terms of  $x$  and the extent of reaction  $\xi$ :

$$0.664(P_{O_2})^{1/2} = \left(\frac{P_{SO_3}}{P_{SO_2}}\right)$$

$$0.148 = \left(\frac{P_{SO_3}}{P_{SO_2}}\right) = \left(\frac{X_{SO_3}P}{X_{SO_2}P}\right) = \left(\frac{n_{SO_3}}{n_{SO_2}}\right) = \frac{x - \xi}{1 + \xi}$$

Equation (ii):  $0.148 = \frac{x - \xi}{1 + \xi}$

Using equations (i) and (ii) to solve for  $\xi$  and  $x$  (the quantity we are after), we find:

$$x = 0.275$$

$$\xi = 0.111$$

5. Gas-solid reactions.

a. Engel and Reid problem 6.13.

At equilibrium, the free energy change of reaction is zero:

$$\begin{aligned}\Delta\bar{G}_{rxn} &= 0 \\ \Delta\bar{G}_{rxn}^o + RT \ln K_p &= 0 \\ \Delta\bar{G}_{rxn}^o + RT \ln \frac{\left(\frac{P_{NH_3}}{P^o}\right) (a_{Fe}^s)^2}{(a_{Fe_2N}^s) \left(\frac{P_{H_2}}{P^o}\right)^{3/2}} &= 0 \\ \Delta\bar{G}_{rxn}^o + RT \ln \frac{\left(\frac{P_{NH_3}}{P^o}\right) (1)^2}{(1) \left(\frac{P_{H_2}}{P^o}\right)^{3/2}} &= 0\end{aligned}$$

Note that in the last line we have applied the standard approximation, taking the activities of the solids as  $\sim 1.0$ . We are given values for the ratio  $P_{NH_3}/P_{H_2}$  at each temperature. These can be used to calculate  $P_{NH_3}$  and  $P_{H_2}$  using the fact that the partial pressures must sum to give the total pressure of the system:

$$(i) \quad P_{NH_3} + P_{H_2} = P = 1 \text{ atm}$$

Knowing the partial pressures,  $K_p$  at each temperature is obtained directly from:

$$(ii) \quad K_p = \frac{\left(\frac{P_{NH_3}}{P^o}\right)}{\left(\frac{P_{H_2}}{P^o}\right)^{3/2}} = \frac{P_{NH_3}}{(P_{H_2})^{3/2}}$$

Using Equation (i) and (ii), we get  $K_p = 3.85$  and  $1.56$  at  $T = 700\text{K}$  and  $800\text{K}$ , respectively.

(b) Calculate  $\Delta\bar{H}_{rxn}^o$  and  $\Delta\bar{S}_{rxn}^o$ :

We know that the equilibrium constant is related to the free energy change per mole of reaction:

$$\Delta \bar{G}_{rxn}^o = -RT \ln K_p$$

$$\frac{-\Delta \bar{G}_{rxn}^o}{RT} = \ln K_p$$

Now, the enthalpy change is related to the free energy change:

$$\Delta \bar{G}_{rxn}^o = \Delta \bar{H}_{rxn}^o - T \Delta \bar{S}_{rxn}^o$$

$$\Delta \bar{H}_{rxn}^o = \Delta \bar{G}_{rxn}^o + T \Delta \bar{S}_{rxn}^o$$

We have shown before in class that the entropy change is a derivative of the free energy with respect to temperature, which we can prove by comparing the differential form of Gibbs free energy to the definition of  $dG(T,P)$ :

$$dG = VdP - SdT$$

$$dG(T,P) \equiv \left( \frac{\partial G}{\partial P} \right)_T dP + \left( \frac{\partial G}{\partial T} \right)_P dT$$

$$\therefore \left( \frac{\partial G}{\partial T} \right)_P = -S$$

Using this relationship, we can write:

$$\Delta \bar{H}_{rxn}^o = \Delta \bar{G}_{rxn}^o + T \Delta \bar{S}_{rxn}^o$$

$$\Delta \bar{H}_{rxn}^o = \Delta \bar{G}_{rxn}^o + T \left( - \frac{\partial \Delta \bar{G}_{rxn}^o}{\partial T} \right)$$

$$\Delta \bar{H}_{rxn}^o = \Delta \bar{G}_{rxn}^o - T \left( \frac{\partial \Delta \bar{G}_{rxn}^o}{\partial T} \right)$$

(Note that an alternative expression can be derived, as shown in section 6.10 of Engel and Reid). Now, with the given data, the best we can do is estimate the partial derivative by calculating the change in free energy at the two given temperatures:

$$\Delta \bar{G}_{rxn}^o = -RT \ln K_p$$

$$\Delta \bar{G}_{rxn}^o (T = 700K) = -7.85 \frac{kJ}{mole}$$

$$\Delta \bar{G}_{rxn}^o (T = 800K) = -2.96 \frac{kJ}{mole}$$

$$\left( \frac{\partial \Delta \bar{G}_{rxn}^o}{\partial T} \right) \cong \frac{(\Delta \bar{G}_{rxn}^o (T = 700K) - \Delta \bar{G}_{rxn}^o (T = 800K))}{700 - 800K} = 48.9 \frac{J}{mole \cdot K}$$

$$\therefore \Delta \bar{H}_{rxn}^o = -7.85 \frac{kJ}{mole} - (700K) \left( 48.9 \frac{J}{mole \cdot K} \right) = -42.1 \frac{kJ}{mole}$$

$$\Delta \bar{S}_{rxn}^o (T = 700K) = - \left( \frac{\Delta \bar{G}_{rxn}^o - \Delta \bar{H}_{rxn}^o}{T} \right) = - \left( \frac{-7,850 + 42,100}{700} \right) = -48.9 \frac{J}{mole \cdot K}$$

$$\Delta \bar{S}_{rxn}^o (T = 800K) = -48.9 \frac{J}{mole \cdot K}$$

- (c) Last, we are to estimate the standard state free energy change per mole of reaction at T = 298 K. We need an expression to relate the change in free energy with temperature to changes in the equilibrium constant:

$$\Delta \bar{G}_{rxn}^o = -RT \ln K_p$$

$$\frac{-\Delta \bar{G}_{rxn}^o}{RT} = \ln K_p$$

$$\frac{\partial \left( \frac{-\Delta \bar{G}_{rxn}^o}{RT} \right)}{\partial T} = \frac{\partial \ln K_p}{\partial T}$$

$$\frac{(\Delta \bar{H}_{rxn}^o)}{RT^2} = \frac{\partial \ln K_p}{\partial T}$$

Since the problem states that we can assume the enthalpy change of reaction is independent of temperature, we can re-arrange this expression and integrate:

$$\frac{(\Delta \bar{H}_{rxn}^{\circ}) dT}{RT^2} = d \ln K_p$$

$$\int \frac{(\Delta \bar{H}_{rxn}^{\circ}) dT}{RT^2} = \int d \ln K_p$$

$$\frac{\Delta \bar{H}_{rxn}^{\circ}}{R} \int \frac{dT}{T^2} = \Delta \ln K_p$$

$$\frac{\Delta \bar{H}_{rxn}^{\circ}}{R} \left( \frac{-1}{T} \right) \Big|_{700}^{298} = \Delta \ln K_p = \ln K_p(T = 298K) - \ln K_p(T = 700K)$$

$$\frac{-42,100}{8.3144} (-0.00193) = \ln K_p(T = 298K) - 1.35$$

$$\therefore \ln K_p(T = 298K) = 11.11$$

$$\Delta \bar{G}_{rxn}^{\circ}(T = 298K) = -RT \ln K_p(T = 298K) = -27.5 \frac{kJ}{mole}$$

b. Engel and Reid problem 6.29.

(a) What is  $K_p$  for the reaction? We can solve this using only the partial pressure information and the stoichiometry of the reaction. The total pressure is given, thus

$$(i) P_{H_2O} + P_{CO_2} = 0.115 \text{ bar}$$

From the given reaction equation, we know that  $K_p$  is given by:

$$K_p = \left( \frac{P_{H_2O}}{P^{\circ}} \right) \left( \frac{P_{CO_2}}{P^{\circ}} \right) = (P_{H_2O}) P_{CO_2}$$

...and we also know from the reaction equation that for every mole of  $H_2O$  produced, we must produce one mole of  $CO_2$ . This guarantees that:

$$(ii) P_{H_2O} = P_{CO_2}$$

Combining (i) and (ii):

$$P_{H_2O} = P_{CO_2} = \frac{0.115}{2} \text{ bar} = 0.0575 \text{ bar}$$

$$K_p = 3.31 \times 10^{-3}$$

(b) With some water vapor initially present, the partial pressures after some extent of reaction  $\xi$  are:

$$P_{H_2O} = 0.225 + \xi$$

$$P_{CO_2} = \xi$$

...and the equilibrium constant is thus:

$$K_p = 3.31 \times 10^{-3} = (P_{H_2O})P_{CO_2} = (0.225 + \xi)\xi$$

Solving this quadratic equation for  $\xi$  gives us:

$$\xi = P_{CO_2} = 0.0139 \text{ bar}$$

## Problem Set 4 - Bonding

1. Recall: a wavefunction  $\psi(\vec{r}_1, \vec{r}_2)$  is symmetric if  $\psi(\vec{r}_1, \vec{r}_2) = +\psi(\vec{r}_2, \vec{r}_1)$ . It is antisymmetric if  $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$  (note that it is possible for a wavefunction to be neither symmetric nor antisymmetric).

Here due to the facts that  $|\vec{r}_1 - \vec{r}_2| = |\vec{r}_2 - \vec{r}_1|$  and  $|\vec{r}_1 + \vec{r}_2| = |\vec{r}_2 + \vec{r}_1|$ , all the wavefunctions are symmetric.

2. a. 1) Hamiltonian for  $H_2=2$  protons + 2 electrons (Born-Oppenheimer approximation):

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 && \text{(electron kinetic terms)} \\ & -\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_B|} && \text{(Coulomb interaction between the first electron and the nuclei)} \\ & -\frac{e^2}{4\pi\epsilon_0|\vec{r}_2-\vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_2-\vec{r}_B|} && \text{(Coulomb interaction between the second electron and the nuclei)} \\ & +\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|} && \text{(Coulomb interaction between the electrons - repulsive)} \end{aligned} \quad (1)$$

b. When the internuclear distance goes to 0 Å, the LCAO trial set (linear combination of hydrogen 1s orbitals) is unable to reproduce the exact ground-state. In this limit,  $H_2$  can be assimilated to a helium atom He. Consequently, a better approximation of the ground-state is obtained by replacing the hydrogen 1s orbital,  $\Psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$  by the helium 1s orbital,  $\Psi_{1s}^{\text{He}}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r}{a_0}}$  in the expressions of  $\varphi_\alpha$  and  $\varphi_\beta$

3. a. The wavefunctions  $|\varphi_i\rangle$  are the eigenfunctions of the same Hermitian operator  $\hat{A}$ . Thus (Lecture 5), they are orthogonal:

(i)  $\langle\varphi_i|\varphi_j\rangle = 0$  if  $i \neq j$

Moreover:

(ii)  $|\Psi\rangle = c_1|\varphi_1\rangle + c_2|\varphi_2\rangle + c_3|\varphi_3\rangle + \dots$

Besides, since  $|\Psi\rangle$  is orthogonal to  $|\varphi_2\rangle$ :

(iii)  $\langle\varphi_2|\Psi\rangle = 0$

Combining (ii) and (iii), we obtain:  $\langle\varphi_2|\Psi\rangle = c_1\langle\varphi_2|\varphi_1\rangle + c_2\langle\varphi_2|\varphi_2\rangle + c_3\langle\varphi_2|\varphi_3\rangle + \dots = 0$ .

Using the orthogonality relations (i) results in:  $c_2\langle\varphi_2|\varphi_2\rangle = 0$ .

As a consequence, since  $\langle\varphi_2|\varphi_2\rangle = \int_{space} \varphi_2^*(\vec{r})\varphi_2(\vec{r})d\vec{r}$  is not zero (otherwise,  $\varphi_2(\vec{r})$  would be zero everywhere), we conclude that  $c_2 = 0$ . Nothing can be said about  $c_1$ .

b. The wavefunctions  $|Y_l^m\rangle$  are, by definition, the normalized eigenfunctions of the same Hermitian operator  $\hat{L}^2$  with eigenvalues  $\hbar^2 l(l+1)$ . Consequently:

- (i)  $\hat{L}^2|Y_l^m\rangle = \hbar^2 l(l+1)|Y_l^m\rangle$
- (ii)  $\langle Y_l^m|Y_{l'}^{m'}\rangle = 0$  if the labels are different
- (iii)  $\langle Y_l^m|Y_l^m\rangle = 1$  (same labels)
- $|\Omega\rangle$  is a linear combination of  $|Y_1^0\rangle$  and  $|Y_2^0\rangle$ :
- (iv)  $|\Omega\rangle = c_1|Y_1^0\rangle + c_2|Y_2^0\rangle$  (and, correspondingly,  $\langle\Omega| = c_1^*\langle Y_1^0| + c_2^*\langle Y_2^0|$ )

We have to calculate and minimize  $\langle\Omega|\hat{L}^2|\Omega\rangle$ . Substituting (iv) in  $\langle\Omega|\hat{L}^2|\Omega\rangle$  and using (i), (ii), (iii), we obtain:  $\langle\Omega|\hat{L}^2|\Omega\rangle = c_1^*c_1\hbar^2 1(1+1) + c_2^*c_2\hbar^2 2(2+1) = |c_1|^2 2\hbar^2 + |c_2|^2 6\hbar^2$ . Similarly  $\langle\Omega|\Omega\rangle = |c_1|^2 + |c_2|^2$ .

Consequently, minimizing  $\langle\Omega|\hat{L}^2|\Omega\rangle$  with respect to  $c_1$  and  $c_2$  under the constraint  $\langle\Omega|\Omega\rangle = 1$  amounts to minimizing  $|c_1|^2 2\hbar^2 + |c_2|^2 6\hbar^2$  with respect to  $c_1$  and  $c_2$  under the constraint  $|c_1|^2 + |c_2|^2 = 1$ . After inspection, it can be concluded that the minimum is reached when  $|c_1| = \pm 1$  and  $|c_2| = 0$ . The corresponding minimal value is  $2\hbar^2$ .

4. The stability of methane, ammonia and water is related to two principal intermolecular interactions:

- (1) dipole-dipole interactions between the polar molecules<sup>1</sup>;
- (2) hydrogen bonds between the hydrogen ligand of one molecule and the electron lone pair of another molecule<sup>2</sup>.

The dipole moments of CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O (all characterized by tetrahedral  $sp^3$  hybridizations) are mainly related to the presence of electron lone pairs: the magnitude of the moment increases with the number of electron pairs (Lecture 10). The ordering of the dipole moments is thus  $\mu(\text{CH}_4) < \mu(\text{NH}_3) < \mu(\text{H}_2\text{O})$ .

From the preceding, it can be concluded that the boiling points of CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O are ordered as follows:

$$\underline{T_{bp}(\text{CH}_4) < T_{bp}(\text{NH}_3) < T_{bp}(\text{H}_2\text{O})}.$$

	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O
number of lone pairs	0	1	2
dipole moment $\mu$ (Debye)	0	1.5	1.8
boiling point $T_{bp}$ (Celsius)	-162	-33	100
dipole-dipole interactions	no	yes	yes
hydrogen bonds	no	no	yes

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<sup>1</sup>Non-polar molecules can also exhibit temporary dipole moments resulting from the fluctuations of their electron charge densities. The resulting temporary intermolecular interaction are called "London dispersion forces".

<sup>2</sup>Hydrogen bond are generally stronger than dipole-dipole interactions.

5. The molecular HOMO's of N<sub>2</sub> and O<sub>2</sub> are the following (Lecture 11 and Engel, Reid 24.5):

(1) the orbitals  $\sigma_g 2p_z \times (\text{spin } \uparrow)$  and  $\sigma_g 2p_z \times (\text{spin } \downarrow)$  for N<sub>2</sub>.

(2) the orbitals  $\pi_g^* 2p_x \times (\text{spin } \uparrow)$  and  $\pi_g^* 2p_y \times (\text{spin } \uparrow)$  for O<sub>2</sub> (we could also have chosen the orbitals  $\pi_g^* 2p_x \times (\text{spin } \downarrow)$  and  $\pi_g^* 2p_y \times (\text{spin } \downarrow)$ , the only requirement is that the spins have the same orientations - Hund's rule)

Refer to Lecture 11 or Engel, Reid 24.5, for the plots of the radial parts and their symmetries.

6. The energy of the orbital is indicated in the top-left corner:

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The HOMO-LUMO gaps are listed below:

	$E(\text{HOMO})$	$E(\text{LUMO})$	$E_{gap} = E(\text{LUMO}) - E(\text{HOMO})$
benzene	$\alpha -  \beta $	$\alpha +  \beta $	$\frac{2 \beta }{}$
naphthalene	$\alpha - 0.618 \beta $	$\alpha + 0.618 \beta $	$\frac{1.236 \beta }{}$
anthracene	$\alpha - 0.414 \beta $	$\alpha + 0.414 \beta $	$\frac{0.828 \beta }{}$

The HOMO-LUMO gap diminishes as the molecule becomes longer.

The energy levels for ethene are obtained by solving the following determinant equation

(Lecture 12 and Engel, Reid 25.7):  $\det \begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} = 0$ . As a result,  $(\alpha - E)^2 - \beta^2 = 0$ , which implies  $E = \alpha \pm |\beta|$ .

Thus, we obtain:  $E(HOMO) = \alpha - |\beta|$  (bonding orbital),  $E(LUMO) = \alpha + |\beta|$  (anti-bonding orbital) and  $E_{gap} = E(LUMO) - E(HOMO) = 2|\beta|$ .