

BE.011/2.772  
Problem Set 4 Solutions  
Due March 8, 2004

Dill 8.3, 8.4, 8.5, 8.6

**8.3) The difference between the energy and enthalpy changes in expanding an ideal gas.** How much heat is required to cause the quasi-static isothermal expansion of one mole of an ideal gas at  $T = 500 \text{ K}$  from  $P_A = 0.42 \text{ atm}$ ,  $V_A = 100 \text{ L}$ , to  $P_B = 0.15 \text{ atm}$ ? To start with, we know that for an ideal gas in an isothermal process,  $dU = \delta q + \delta w = 0$ . For such a process, when it is also quasi-static, we also know that  $\delta w = -PdV$ . Therefore

$$q = \int PdV. \text{ We substitute the ideal gas law for } P \text{ and we get: } q = \int \frac{nRT}{V} dV = nRT \ln \frac{V_A}{V_B}.$$

a) What is  $V_B$ ?

$$\text{By the ideal gas law, so } \frac{P_A}{P_B} = \frac{V_B}{V_A} \text{ so } V_B = \frac{P_A V_A}{P_B} = \frac{0.42 * 100}{0.15} = 280L$$

We can use  $V_B$  to calculate the heat:

$$q = nRT \ln \frac{V_A}{V_B} = 1 \text{ mol} * 8.314 \text{ JK}^{-1} \text{ mol}^{-1} * 500 \text{ K} \ln \frac{280}{100} = 4280J$$

Since  $q$  is positive, heat is flowing into the system during the process. (Note that this corresponds to work being done *by* the system.)

b) What  $\Delta U$  for this process?

$$\Delta U = 0 \text{ for an isothermal process on an ideal gas since } \Delta U = C_V \Delta T = 0.$$

c) What  $\Delta H$  for this process?

$$H = U + PV \text{ so } \Delta H = \Delta U + \Delta(PV)$$

We already established that  $\Delta U = 0$ . For an ideal gas at constant temperature it's also true that  $PV$  is constant ( $PV = nRT$ ). So,  $\Delta H = 0$ .

**8.4) The work and the heat of boiling water.** For the reversible boiling of five moles of liquid water to steam at  $100^\circ\text{C}$  and  $1 \text{ atm}$  pressure, calculate  $q$ . Is  $w$  positive or negative?

We can get the answer from tables that give the heat of vaporization of water (the answer for  $100^\circ\text{C}$  is given in example 8.7 but you could also use Google). Also, from the periodic table we know that water weighs  $18 \text{ g/mol}$ .

$$\begin{aligned} q_{\text{boiling}} &= -q_{\text{condensation}} = 1 \Delta H_{\text{condensation}} \\ &= 540 \frac{\text{cal}}{\text{g}} 18 \frac{\text{g}}{\text{mole}} 5 \text{ moles} = 48600 \text{ cal} \end{aligned}$$

$$\text{At constant pressure, } w = - \int_{V_1}^{V_2} PdV = -P(V_2 - V_1) = -P(V_{\text{gas}} - V_{\text{liquid}})$$

And  $V_{\text{gas}} \gg V_{\text{liquid}}$ , so  $V_{\text{gas}} - V_{\text{liquid}}$  is positive, so  $w$  is negative. Note that negative  $w$  means the system is doing work on the surroundings.

**8.5) The entropy and free energy of gas expansion.** Two moles of an ideal gas undergo an irreversible isothermal expansion from  $V_A = 100$  liters to  $V_B = 300$  liters at  $T = 300\text{K}$ .

a) What is the entropy change for this process?

$$\Delta S = \int \frac{dq_{rev}}{T}$$

Since  $S$  and  $U$  are state functions, we needn't be concerned that the actual process is irreversible (read: complicated). We can choose *any* path to calculate state functions so we invent an isothermal, quasi-static process to get  $q_{rev}$ .

$$\Delta U = 0 \Rightarrow q_{rev} = -w_{rev} = nRT \ln \frac{V_2}{V_1}.$$

For an isothermal process,

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1} = (2 \text{ moles}) \left( 2 \frac{\text{cal}}{\text{molK}} \right) \ln \frac{300}{100} = 4.39 \frac{\text{cal}}{\text{K}}$$

b) What is the Gibbs free energy change?

$\Delta G = \Delta H - T\Delta S$ . For an isothermal process on an ideal gas,  $\Delta H=0$ . (Note that  $\Delta H = \Delta U + \Delta(PV)$  and for an isothermal process,  $\Delta U=0$ , and  $\Delta(PV) = \Delta(nRT) = 0$ , so  $\Delta H=0$ .)

$$\Delta G = -T\Delta S = -(300\text{K})(4.39 \frac{\text{cal}}{\text{K}}) = -1318.33\text{cal}$$

**8.6) The free energy and entropy of membrane melting.** We have a phospholipid membrane that "melts" at  $T_m = 41^\circ\text{C} = 314\text{K}$ . Reversible melting experiments indicate that  $\Delta H_m = 9 \text{ kcal mol}^{-1}$ .

a) What is the entropy of melting?

$$\Delta S_m = \frac{\Delta H_m}{T} = \frac{9 \text{ kcal} * \text{mol}^{-1}}{314\text{K}} = 28.7 \text{ cal} * \text{mol}^{-1} \text{K}^{-1}$$

b) What is the free energy of melting?

$\Delta G = 0$  because during a reversible phase transition, the two phases are in equilibrium. Also,  $\Delta G = \Delta H - T\Delta S$ , and plugging in our numbers from above,  $\Delta G=0$ .

c) Does the membrane become more or less ordered on melting?

$\Delta S_m > 0$  so the entropy increases as we melt the membrane. Thus it becomes less ordered during melting.

d) If there are 32 rotatable bonds in each phospholipid molecule, what is the increase in multiplicity on melting one mole of bonds?

First, if there are 32 rotatable bonds in each molecule, then one mole of phospholipid corresponds to 32 moles of bonds. Thus, the entropy change per mole of bonds during melting is  $28.7/32 = 0.897 \text{ cal mol}^{-1} \text{K}^{-1}$ .

$$\ln \frac{W_2}{W_1} = \frac{\Delta S}{K} = \frac{0.897}{3.30e-24} = 2.71e23$$