

CH302 HW Week 5 Key

1. a) adiabatic  $\Rightarrow q = 0, \Delta S_{sys} = \frac{q_{sys}}{T} = 0$

b)  $\Delta T = 0$  expansion  $\Rightarrow V_f > V_i$   
 $\Delta S_{sys} = nR \ln\left(\frac{V_f}{V_i}\right) > 0$

c)  $\Delta P = 0$  cooling  $T_f < T_i$   
 $\Delta S_{sys} = C_v \ln\left(\frac{T_f}{T_i}\right) = C_p \ln\left(\frac{T_f}{T_i}\right) < 0$


d)  $\Delta P = 0$  evaporation  $\Delta S_{sys} = \frac{\Delta H_{vap}}{T_{vap}} > 0; (\Delta H_{vap} > 0)$

~~2~~d.  $\Delta S_{vap} = \frac{n \Delta H_{vap}}{T_{vap}} = \frac{(2.0 \text{ mol})(40.65 \text{ kJ/mol})}{373 \text{ K}} = 218 \text{ J/K} = \Delta S_{vap}$

$\Delta S_{vap} > 0$  because the system is becoming more disordered (i.e. has more microstates) as it moves from liquid to gas.

3. (O) vs  $\boxed{\text{CO}_2}$  more atoms  $\Rightarrow$  more disorder

$\boxed{\checkmark}$  vs  $\Delta$  more flexible, more degrees of freedom

 vs.  $\begin{array}{c} | \\ -C- \\ | \end{array}$  ditto

②

4. a)  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$  1 mole of gas on each side  $\Rightarrow$  neutral  
b)  $H_2(g) + O_2(g) \rightarrow H_2O_{2(g)}$  net loss of 2 moles of gas  $\Rightarrow$  bad  
c)  $O_2(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(l)$  net loss of 3 moles of gas  $\Rightarrow$  worse  
d)  $(s) + H_2O(g) \rightarrow (O(g) + H_2(g))$  net gain of 1 mole of gas  $\Rightarrow$  good
- $c < b < a < d$  - increasing  $\Delta S_{rxn}$



- In their pure forms, A is always surrounded by A and B is always surrounded by B. In the mixture, A could still be surrounded by A, but it now also can be surrounded by B. Moreover, A could have 1, 2, 3, 4, etc., molecules of B in its immediate vicinity. This means that both A + B have more available microstates in the mixture than in their pure forms

$$S(\text{mixture}) > S(A) \text{ or } S(B)$$

- Another way to think about this is that if A + B are miscible (i.e. will mix), we would observe this happen spontaneously, but never the reverse, spontaneous separation of A + B into their pure forms  $\rightarrow$

b) We previously explained colligative properties purely in terms of vapor pressure lowering, which we derived from Raoult's Law. However, if Raoult's Law applies, this implies the solution is ideal, and intermolecular forces in the mixture are the same as in the pure, unmixed forms. Thus in turn implies that  $\Delta H(\text{mixture}) \approx 0$ , because there is no change in internal energy of the system.

This means that the energy difference between the mixture and the pure forms (which we observe as a change in melting or boiling temperature) must be coming from entropy, not enthalpy considerations. If we make the soln. more energetically favorable by increasing its entropy (see part a), that means we have to put more energy into the system to get it to boil.

$$G. n = 3.0 \text{ mol}$$

$$C_{V,m} = 3/2 R \text{ (i.e. } C_{P,m} = 5/2 R)$$

$$P_i = 1.0 \text{ atm}$$

$$P_f = 5.0 \text{ atm}$$

$$T_i = 298 \text{ K}$$

$$T_f = 398 \text{ K}$$

Separate into two steps: 1) constant T compression

2) constant P heating  
 $\Rightarrow$  constant V heating

$$\Delta S_{\text{sys}} = nR \ln \left( \frac{V_f}{V_i} \right) + C_V \ln \left( \frac{T_f}{T_i} \right)$$

$$= nR \ln \left( \frac{P_i}{P_f} \right) + C_V \ln \left( \frac{T_f}{T_i} \right)$$

$$\boxed{-36 \text{ J/K} = \Delta S_{\text{sys}}} = (3.0 \text{ mol}) \left( \frac{8.314 \text{ J/Kmol}}{2.16 \text{ J/K}} \right) \ln \left( \frac{1.0 \text{ atm}}{5.0 \text{ atm}} \right) + \left( \frac{3}{2} \right) \left( \frac{8.314 \text{ J/Kmol}}{2.16 \text{ J/K}} \right) \ln \left( \frac{398}{298} \right)$$