**In-class Thermodynamics exam : Chem 6854 Spring 2013 (30 points)**

**Your name: \_\_\_\_\_\_\_answers\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

1. **Which statement is true concerning the sign conventions for heat (Q) and work (W) assumed in your text ?**
2. Q is positive if it flows to the surroundings.
3. W is negative if the surroundings does work on the system.
4. W is positive if the system does work on the surroundings.
5. **Q is negative if the system gives up heat to the surroundings.**
6. **In an adiabatic process:**
7. A piston will expand by raising system temperature while converting internal heat to work .
8. The surroundings can only do work, on the system while the system can pass only heat to the surroundings.
9. **The surroundings and system can only pass work back and forth to each other.**
10. A piston will cool when compressed since no heat is passed from surroundings to system.
11. **Expand the perfect differential U(T,V) as a function of partial derivatives and the perfect differentials dT and dV**

**dU(T,V) =**

1. **Given that df(x,y) = M(x,y) dx + N(x,y) dy what condition for M(x,y) and N(x,y) must be true for df to be a path independent, perfect differential ?**
2. **Given the thermodynamic data below, find the heat of reaction for :**

**Ca(s) + O2(g) + H2(g) 🡪 Ca(OH)2(s) \_\_\_\_\_\_\_\_ = ΔrH (kcal) (2 pts)**

Reaction ΔrH (kcal/mol reactant)

CaO(s) 🡪 Ca(s) + ½ O2(g) 151.8 Ca(s) + ½ O2(g)🡪 CaO(s) -151.8 kJ

H2O(l) 🡪 H2(g) + ½ O2(g) +68.4 H2(g) + ½ O2(g) 🡪 H2O(l) -68.4

CaO(s) +H2O(l) 🡪 Ca(OH)2(s) -15.3 CaO(s) +H2O(l) 🡪 Ca(OH)2(s) -15.3

 Sum **Ca(s) + O2(g) + H2(g) 🡪 Ca(OH)2(s) -235.5 Kj**

1. The enthalpy of formation of HF is -273 kJ/mol HF. Given the bond enthalpies below

 Compute the bond energy ε(H-F) in kJ/mol bond

Bond enthalpy (kJ/mol) per product atom

H2🡪 2H 217.9 F(g) H(g) +F(g)

F2🡪 2F 79.39 217.9 kJ

 H(g)

 ε(H-F) 79.39 kJ

---------- ½ H2 + ½ F2 ------------------0

 +273 kJ

 570.29 kJ =ε(H-F)

 HF(g)

1. Consider the set of steps carried out on a mole of ideal gas in a piston initially at a temperature = T1

Step 1: reversible expansion at constant P1 from V1🡪V2 P

Step 2: reversible adiabatic compression from V2 to V3 < V1. (P2,V3)

Step 3: reversible isothermal expansion from V3 back to V2 step 3

 Step 4: reversible adiabatic de-pressurization back to (P1,V2) step 2 (P3,V2)

 step 4

1. **In which step(s) does the temperature rise ?**

**Steps 1, 2**

1. **In which step(s) does no work get done ?**

**Step 4 ( no volume change)**

 step 1

(P1,V1) (P1,V2)

 V

1. In the previous problem, given that n=1, P1=1 atm, V1 = 1 L and T1 = 300 K: (2 pts each)
2. **Compute the temperature T2  reached during step 1 to achieve a new volume V2 = 2 L.**

**Only n,P constant=> P1V1  = P1 V2 => V2 = T2  Plugging in givens: 2= T2 => T2 = 2\*300=600 K**

 T1  T2 V1 T1  1 300

1. **Compute W for step 1 in atm\*L units (include correct sign for W !!!! )**

P1ΔV = 1\*(2-1) = 1 atm\*L (work done on surroundings) => -1 atm\*L =W

1. **Compute Q by the system to achieve step 1 given that Cp = 5R/2**

**In this step, volume is constant so Qrev = = (5R/2 ) (600-300) = 750 R**

1. **Compute ΔSsystem for step 1.**

**ΔS =**

1. **In a reversible, adiabatic expansion the following is not true:**
2. The process takes infinite amounts of time.
3. **The temperature of the surroundings and system both remain the same.**
4. ΔStotal = ΔSsystem + ΔSsurroundings =0
5. ΔSsystem = ΔSsurroundings  = 0
6. **Given Cv = 3R/2 for an ideal monatomic gas, compute the change in entropy for an isothermal expansion of 1 mole of ideal monatomic gas from 20 to 40 L at T= 300 K. (2 pts)**

In an isothermal expansion, ΔU=Wrev +Qrev = 0 => dQrev =-dWrev = pdV ( a positive number for dV > 0)

 Thus, dS = dQrev/T = p dV/T = (RT/V)/T dV = R/V dV

 ΔS = R ln (V2/V1) = R ln (40/20) = R ln 2

1. **The reason enthalpy, ΔHp , is commonly used by chemists is:**
2. At constant pressure, chemical reaction heat Qreaction = ΔHp is a state function.
3. ΔHp = ΔU and we can measure energy changes of systems directly at constant pressure.
4. It allows us to easily compute the entropy change of a gas phase reaction, ΔSgas = ΔHp/T.
5. We can deduce the maximum work from a reaction since Wrev = **ΔHp.**
6. **For any irreversible process, even an adiabatic one, it is inevitable that the process:**
7. Conserves entropy
8. Makes work
9. **Causes a transient temperature change**
10. Causes entropy to decrease
11. Causes energy to increase