Sept. 16, 2014, 7:55-8:55 AM   Name _____ KEY _____ _____

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*100 points in **9 questions on 4 pages including Tables 2.3 and A.5***
For full credit show all work and put correct units on final answers. Note: information that is not needed may be present in some problems.

(12 pts)   **1.**   If a system composed of *unknown* material goes from state 1 to state 2 such that:
$P_1 = 5$ bar, $V_1 = 20$ L, and $T_1 = 300$ K
$P_2 = 2$ bar, $V_2 = 30$ L, and $T_2 = 250$ K
heat <u>given off</u> by the system = 10 kJ,   work *done on* the system = 15 kJ

$$q = -10 \, kJ \qquad w = +15 \, J$$

Find ΔU, ΔH, q, and w, using the First Law of Thermodynamics, and definitions of q and w used by our text book. If insufficient information is given to find some of these, please indicate what is missing.

$$\Delta U = q + w$$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$= 5 \, kJ + \left[2(30) - 5(20) \right] L \, bar \times \frac{100 \, J}{L \, bar}$$

$$= 5000 \, J + (60 - 100) \times 100 \, J$$

$$5000 - 4000 = 1000 \, J$$

$$= 1 \, kJ$$

q -10 kJ

w $+15$ kJ

ΔU $+5$ kJ

ΔH $+1$ kJ

(6 pts)   **2.**   Under what conditions is $\Delta H = q$?

$$P_{ext} = P = constant \quad and \quad no \; non\text{-}PV \; work$$

(16pts)3. (a) Consider the *isothermal* expansion of *2 moles* of *ideal gas* from $V_1 = 25$ L to $V_2 = 75$ L at 300 K. $C_v = 20$ J mol^{-1} K^{-1} and $C_p = 29$ J mol^{-1} K^{-1}. The *external pressure is held constant* at 2 bar during the process. Calculate q, w, ΔU, ΔH, ΔS, and ΔS_{surr} for this process. ← irreversible

$$W = -P_{ext}\,\Delta V = -2\,bar \times (75-25)L \times \frac{100\,J}{L\,bar}$$

$$= -100\,L\,bar \times 100\,J/_{L\,bar}$$

Irreversible so $q/T \neq \Delta S$

$$\Delta S_{surr} = \frac{-q}{T} = \frac{-10000}{300} = -33.3\,J/_K$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{nRT\,\ln(V_2/V_1)}{T} \leftarrow \left(\begin{array}{c}\text{If you did it}\\\text{reversibly}\end{array}\right)$$

$$= 2 \times 8.3145\,\ln 3$$

$$= 18.3\,J/_K$$

q $+10,000$ J

w $-10,000$ J

ΔU 0

ΔH 0

ΔS 18.3 J/K

ΔS_{surr} -33.3 J/K

(b) Is the process in part (a) allowed according to the Second Law of Thermodynamics? Explain your answer.

NO! $\Delta S + \Delta S_{surr} < 0$

(14 pts) 4. In the cylinder of a diesel engine, the fuel + air mixture is ignited solely by the temperature rise caused by adiabatic compression. (It is adiabatic because there is not time for heat to conduct out of the cylinder during the compression.)
What will be q, w, ΔU, ΔH, ΔS, and ΔS_{surr} for *3 moles* of an ideal diatomic gas ($C_{p,m} = 7/2\,R$) if its *temperature increases by 500 K* during the compression, assuming the expansion is *reversible* and *adiabatic*? $C_{v,m} = C_{p,m} - R = 5/2\,R$

$$\Delta U = nC_{v,m}\Delta T = 3 \times \frac{5}{2}(8.3145)\,500\,K$$

$$\Delta H = nC_{p,m}\Delta T = 3 \times \frac{7}{2}(8.3145) \times 500$$

$$= 43651\,J$$

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = 0 \quad \text{because each } \; dq_{rev} = 0$$

q 0

w 31.18 KJ

ΔU 31.181 kJ

ΔH 43.65 kJ

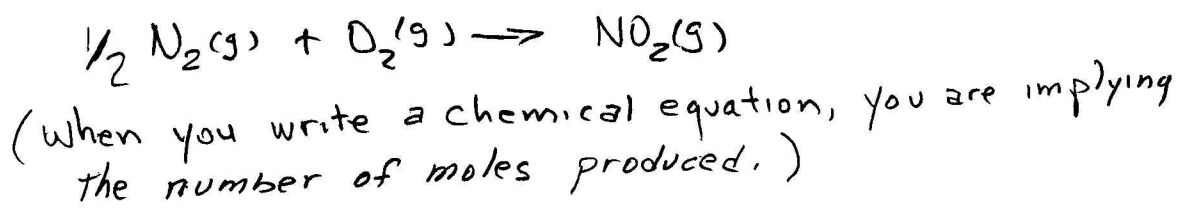ΔS 0

ΔS_{surr} 0

2

(10 pts) 5. If the molar concentration of O_2 gas is 0.2 M and that of N_2 gas is 0.8 M in a closed container at T=300 K, what is its partial pressure of the N_2?

$$P V = n R T \qquad P = \frac{n}{V} R T$$

$$P_{N_2} = [N_2] R T = 0.8 \frac{mol}{L} \; 0.083145 \frac{L \cdot bar}{mol \cdot K} \times 300 K$$

$$= 19.95 \; bar.$$

$$= 19.95 \; bar \times \frac{10^5 \; Pa}{bar} = 1.995 \times 10^6 \; Pa$$

(11 pts) 6. Define "vapor pressure" of a liquid.

The partial pressure of the liquid's vapor that is in dynamic equilibrium with the liquid.

(11 pts) 7. Write the balanced chemical reaction whose $\Delta_r H^0 = \Delta_f H^0$ for NO_2 (g).

$$\tfrac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g)$$

(when you write a chemical equation, you are implying the number of moles produced.)

(10 pts) 8. With the aid of the Bond Dissociation table below, explain why the N_2 gas of the atmosphere is does not catch on fire when we light a match in it. Assume the chemical reaction for the burning is $N_2 + O_2 \rightarrow 2NO$. (D for N-O is 630 kJ.mol.)

$$\Delta H \cong D_{N_2} + D_{O_2} - 2 D_{N-O}$$

$$= 945 + 498 - 2(630)$$

$$= 1443 - 1260 = +183$$

VERY ENDOTHERMIC   SO WILL   NOT

GIVE OFF HEAT.

3

(10 pts) 9. The vapor pressure of $H_2O(l)$ at 298 K is 0.0313 atm. At what temperature will water boil in a vessel in which the air pressure is 0.0313 atm?

Boiling point is when applied pressure = vapor pressure

so will boil at 298 K = 25°C (Really!)

TABLE A.5 Inorganic Compounds* (cont.)

	$\Delta_f H$ (kJ mol^{-1})	S (J K^{-1} mol^{-1})	$\Delta_f G$ (kJ mol^{-1})
$HCO_3^-(aq)$	−691.99	91.2	−586.77
$CO_3^{2-}(aq)$	−677.14	−56.9	−527.81
$Fe(s)$	0	27.28	0
$Fe_2O_3(s)$	−824.2	87.40	−742.2
$H_2(g)$	0	130.79	0
$H_2O(g)$	−241.82	188.93	−228.73
$H_2O(l)$	−285.83	69.91	−237.13
$H^+(aq)$	0	0	0
$OH^-(aq)$	−229.99	−10.75	−157.244
$H_2O_2(aq)$	−191.17	143.9	−134.03
$H_2S(g)$	−20.63	205.90	−33.56
$H_2SO_4(g)$	−735.13	298.8	−653.37
$N_2(g)$	0	191.72	0
$NH_3(g)$	−46.11	192.56	−16.78
$NH_3(aq)$	−80.29	111.3	−26.50
$NH_4^+(aq)$	−132.51	113.4	−79.31
$NO(g)$	90.25	210.87	86.55
$NO_2(g)$	33.18	240.17	51.47
$NO_3^-(aq)$	−205.0	146.40	−108.74
$Na^+(aq)$	−240.12	59.0	−261.90
$NaCl(s)$	−411.15	72.13	−384.14
$NaCl(aq)$	−407.27	115.5	−393.13
$NaOH(s)$	−425.61	64.46	−379.49
$O_2(g)$	0	205.25	0
$O_3(g)$	142.7	239.04	163.4
$S(rhombic)$	0	31.80	0
$SO_2(g)$	−296.83	248.33	−300.19
$SO_3(g)$	−395.72	256.87	−371.22

* Standard thermodynamic values at 25°C (298.15 K) and 1 bar pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation, $\Delta_f H°$, third-law entropies. $S°$, and standard Gibbs free energy of formation, $\Delta_f G°$, are given.
† The standard state for all ions and for species labeled (aq) is that of a solute on the molarity scale.
(Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., eds., *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982), corrected to 1 bar pressure.)

Table 2.3 Bond Dissociation Energies

Bond	D (kJ mol^{-1})
C—C	359
C=C	611
C≡C	827
C—H	411
C—N	303
C—O	361
C=O	709
C—S	294
N—H	383
O—H	452
S—H	359
H—H	436.0
N≡N	945.4
O=O	498.3
C (graphite)	716.7
S (rhombic sulf	277.0