

Sept. 19, 2017, 7:55-8:55 AM

4 x 6 note card

Name

KEY

Last,

First

100 points in 8 questions on 4 pages + 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. Suppose that 15 J of heat flow from the surroundings to the system while the system does 20 J of electrical work on the surroundings. During this process the system pressure is constant and is equal to the external pressure, and the volume is also constant

Find ΔU , ΔH , q , and w , using the First Law of Thermodynamics and the definitions of ΔH , q and w used by our text book. *If there is insufficient information to find any of these, then say what is missing.*

$$\Delta H = \Delta U + \Delta(PV) = \Delta U \quad (\text{if } P \text{ \& } V \text{ both const } \Delta PV = 0)$$

" " AS : reversible?

$$q \quad +15 \text{ J}$$

$$w \quad -20 \text{ J}$$

$$\Delta U \quad +5 \text{ J}$$

$$\Delta H \quad -5 \text{ J}$$

$$\Delta S \quad ?$$

- 12 pts) 2. (a) Define enthalpy (H not ΔH)

$$H = U + PV$$

- (b) Give the general equation for ΔH that comes from the definition of H

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

$$\text{or } \Delta U + \Delta(PV)$$

- (c) What 3 conditions must be met for a closed system so that $\Delta H = q$?

$P = P_{\text{ext}} = \text{constant}$ and only PV work
(against atmosphere)

(12 pts) 3. What are q , w , ΔU , ΔH , and ΔT and ΔS for an **adiabatic compression** in which 10 J of work are done reversibly on a system containing 2 moles of ideal gas if the $C_{v,m} = 2.5 R$?

Put a question mark for any item for which there is not sufficient information to calculate

$$w = \Delta U = n C_{v,m} \Delta T = 10 \text{ J}$$

$$\Delta T = \frac{10 \text{ J}}{2 \cdot 2.5 \cdot 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} =$$

$$\Delta H = n C_{p,m} \Delta T = n (C_{v,m} + R) \Delta T$$

$$\text{or } \Delta H = \Delta U + \Delta pV = \Delta U + n R \Delta T = 13.99$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = 0$$

$$q \quad 0$$

$$w \quad 10 \text{ J}$$

$$\Delta T \quad 0.24 \text{ K}$$

$$\Delta U \quad 10 \text{ J} \quad \text{given}$$

$$\Delta H \quad 13.99 \text{ J}$$

$$\Delta S \quad 0$$

$$\Delta S_{\text{surr}} \quad 0$$

$$\Delta S_{\text{universe}} \quad 0$$

(8 pts) 4. (a) For an **isothermal compression** with **constant** external pressure $p_{\text{ext}} = 4.0 \text{ bar}$, of 2 mols of ideal gas from $V_1 = 30 \text{ L}$ to $V_2 = 10 \text{ L}$ at 300 K . $C_v = 20 \text{ J mol}^{-1} \text{ K}^{-1}$ and $C_p = 29 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate q , w , ΔU , ΔH , ΔS , and ΔS_{surr} . If there is not enough information to calculate any of the properties, indicate what is missing for these.

$$w = -p_{\text{ext}} \Delta V = (-4 \text{ bar})(-20 \text{ L}) \left(100 \frac{\text{J}}{\text{L bar}}\right) = +8000 \text{ J}$$

$$q = -w \quad \text{because ideal gas}$$

$$\therefore \Delta U = \Delta H = 0$$

$$\Delta S_{\text{surr}} = -\frac{q}{T} = +\frac{8000}{300}$$

$$q \quad +8000 \text{ J}$$

$$w \quad +8000 \text{ J}$$

$$\Delta U \quad 0$$

$$\Delta H \quad 0$$

$$\Delta S \quad -18.3 \quad \text{state function from 4(b)}$$

$$\Delta S_{\text{surr}} \quad 26.67 \text{ J K}^{-1}$$

(8 pts) 4.(b) Now consider an reversible isothermal compression of 2 moles of *ideal gas* with the same initial and final states as in 4(a). Calculate q , w , ΔU , ΔH , ΔS , ΔS_{surr} and $\Delta S_{\text{universe}}$ for this process. If there is not enough information to calculate any of the properties, indicate what is missing for these.

$$w = -nRT \ln \frac{V_2}{V_1} = -2(8.3145)(300) \ln \frac{10}{30}$$

$$q = -w$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{-5481}{300} = -18.3$$

$$\Delta S_{\text{univ}} = 0 \text{ (reversible) i.e. equilibrium}$$

$$q \underline{-5481 \text{ J}}$$

$$w \underline{5481 \text{ J}}$$

$$\Delta U \underline{0} \text{ state function}$$

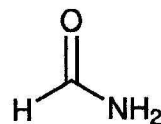
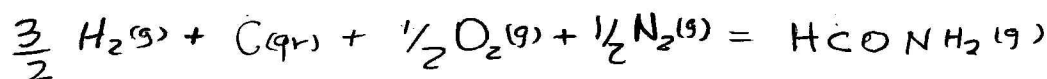
$$\Delta H \underline{0}$$

$$\Delta S \underline{-18.3 \text{ JK}^{-1}}$$

$$\Delta S_{\text{surr}} \underline{+18.3 \text{ JK}^{-1}}$$

$$\Delta S_{\text{universe}} \underline{0}$$

(12 pts) 5. Write the balanced chemical reaction whose $\Delta_r H^\circ = \Delta_f H^\circ$ for formamide (g).



(12 pts) 6. Using the Bond Dissociation table below, set up the calculation to estimate the heat of formation of formamide (g). (Write down the numbers, but don't add them up to get a final answer.)

$$\frac{3}{2} D(\text{H-H}) + D(\text{C-gr}) + \frac{1}{2} D(\text{O=O}) + \frac{1}{2} D(\text{N}\equiv\text{N})$$

$$- [D(\text{C-H}) + D(\text{C=O}) + D(\text{C-N}) + 2 D(\text{N-H})]$$

$$= \frac{3}{2} \times 436.0 + 716.7 + \frac{1}{2} (498.3) + \frac{1}{2} (945.4)$$

$$- [411 + 709 + 303 + 2(383)]$$

(12 pts) 7. (a) If the partial pressure of $N_2 = 0.8$ atm and the partial pressure of $O_2 = 0.2$ atm in a closed vessel containing liquid water at $100^\circ C$, where the vapor pressure of water is 1 atm, what is the total pressure in the vessel at equilibrium?

$$P_{\text{total}} = 0.8 + 0.2 + 1.00 = 2.0 \text{ atm}$$

(b) Suppose the volume of the vessel is decreased so that the volume of vapor is cut in half. What is the partial pressure of each gas when equilibrium is reached?

$$P_{N_2} = 2 \times 0.8 = 1.6 \text{ atm}$$

$$P_{O_2} = 2 \times 0.2 = 0.4$$

$$P_{H_2O} = 1.0 \text{ (Condenses to equilibrium)}$$

$$Total = 3.0 \text{ atm}$$

(12 pts) 8. Liquid water is converted reversibly to vapor at a constant temperature while the applied pressure is equal to the vapor pressure of water at that temperature. Tell whether q , w , ΔU , and ΔH are positive, zero, or negative, and briefly explain why.

$$q = + \text{ evaporation is endothermic (heat from bath keeps syst at const } T)$$

$$w = - (P_{\text{ext}} \Delta V) \quad \Delta V = +$$

$$\Delta U = + \text{ evaporation requires energy. } (-P_{\text{ext}} \Delta V \text{ is smaller)}$$

$$\Delta H = + = q \text{ in this case.}$$

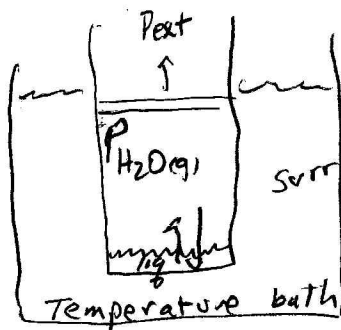


TABLE A.5 Inorganic Compounds* (cont.)

	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	$\Delta_f G^\circ$ (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 ₂ O ₃ (s)	-824.2	87.40	-742.2
H ₂ (g)	0	130.79	0
H ₂ O(g)	-241.82	188.93	-228.73
H ₂ O(l)	-285.83	69.91	-237.13
H ⁺ (aq)	0	0	0
OH ⁻ (aq)	-229.99	-10.75	-157.244
H ₂ O ₂ (aq)	-191.17	143.9	-134.03
H ₂ S(g)	-20.63	205.90	-33.56
H ₂ SO 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, $\Delta_f H^\circ$, third-law entropies, S° , and standard Gibbs free energy of formation, $\Delta_f G^\circ$, 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