

Sept. 20, 2016, 7:55-8:55 AM

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Name

KEY

Last,

First

100 points in 7 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.

- (14 pts) 1. If a system composed of *unknown* material goes from state 1 to state 2 such that:  
 $P_1 = 10 \text{ bar}$ ,  $V_1 = 10 \text{ L}$ , and  $T_1 = 300 \text{ K}$ ,  
 $P_2 = 20 \text{ bar}$ ,  $V_2 = 20 \text{ L}$ , and  $T_2 = 200 \text{ K}$ ,  
 the heat *absorbed* by the system = 20 kJ, and the work *done* by the system = 30 kJ and  
 includes some electrical work.

Find  $\Delta U$ ,  $\Delta H$ ,  $q$ ,  $w$ , 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.

$$\Delta U = q + w$$

$$\Delta H = \Delta U + \Delta(PV)$$

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

$$= -10 \text{ kJ} + (20 \cdot 20 - 10 \cdot 10) \text{ L bar}$$

$$\times 100 \frac{\text{J}}{\text{L bar}} \times 10^{-3} \frac{\text{kJ}}{\text{J}}$$

$$= -10 + 30 = 20 \text{ kJ}$$

$$q \quad +20 \text{ kJ}$$

$$w \quad -30 \text{ kJ}$$

$$\Delta U \quad -10 \text{ kJ}$$

$$\Delta H \quad 20 \text{ kJ}$$

(16 pts) 2. What are  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for a reversible adiabatic expansion in which 3 moles of ideal gas cools by 20 K, if the  $C_{v,m} = 2.5 R$ ?

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

$$= (3 \text{ mol}) (2.5 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times -20 \text{ K})$$

$$= -1247 \text{ J}$$

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

$$= 3 \text{ mol} (3.5 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (-20 \text{ K})$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = 0 \quad q_{\text{rev}} = 0$$

$$q \quad 0$$

$$w \quad -1247 \text{ J}$$

$$\Delta U \quad -1247 \text{ J}$$

$$\Delta H \quad -1746 \text{ J}$$

$$\Delta S \quad 0$$

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

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

(22pts) 3. (a) Consider the *isothermal reversible expansion* of 2 moles of *ideal gas* from  $V_1 = 10 \text{ L}$  to  $V_2 = 20 \text{ L}$  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  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta S_{\text{surr}}$  for this process. If there is not enough information to calculate any of the properties, indicate what is missing for these.

$$w = -nRT \ln \frac{V_2}{V_1} = -(2 \text{ mol}) (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \ln 2$$

$$= -3458 \text{ J}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{3458 \text{ J}}{300} = 11.52$$

$$\Delta S_{\text{surr}} = -q/T = -11.52$$

$$\Delta U \quad 0 \quad \text{ideal gas}$$

$$\Delta H \quad 0$$

$$\Delta S \quad 11.52 \text{ J/K}$$

$$\Delta S_{\text{surr}} \quad -11.52 \text{ "}$$

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

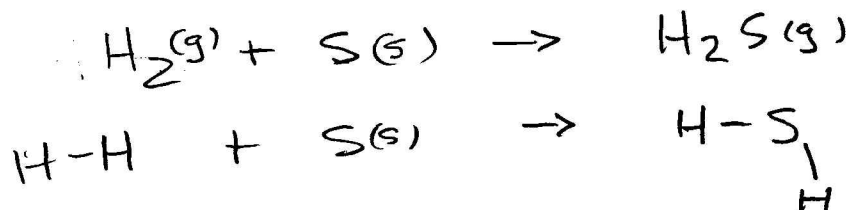
3. (b) For the *same* initial and final states as in 3(a) reached by an *isothermal expansion* with **constant** external pressure of  $p_{\text{ext}} = 2.5 \text{ bar}$ , calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta S_{\text{surr}}$ . If there is not enough information to calculate any of the properties, indicate what is missing for these.

$$\begin{aligned}
 w &= -p_{\text{ext}} \Delta V = -2.5 \text{ bar} \times 10 \text{ L} & q & \underline{2500 \text{ J}} \\
 &= -25 \text{ L bar} \times \frac{100 \text{ J}}{\text{L bar}} & w & \underline{-2500 \text{ J}} \\
 &= -2500 \text{ J} & \Delta U & \underline{0} \\
 \Delta S_{\text{surr}} &= -\frac{2500 \text{ J}}{300 \text{ K}} = & \Delta H & \underline{0} \\
 & & \text{From 3(a)} \rightarrow \Delta S & \underline{11.52 \text{ J/K}} \\
 & & \Delta S_{\text{surr}} & \underline{-8.33 \text{ J/K}}
 \end{aligned}$$

(10 pts) 4. Write the balanced chemical reaction whose  $\Delta_f H^\circ = \Delta_f H^\circ$  for  $\text{N}_2\text{O}_5(\text{g})$  at room temperature.



(12 pts) 5. Using the Bond Dissociation table below, estimate the heat of formation of  $\text{H}_2\text{S}(\text{g})$ , and compare with the value found in Table A.5.



$$\Delta H_f^\circ \approx 436 + 277 - 2(359) = \boxed{-5 \text{ kJ/mol}}$$

Not far from  $-20 \text{ kJ/mol}$  in Table.

(14 pts) 6. In a mixture of gases, A, B, and C at 300 K: if the molar concentration of each gas is 0.2 molar, what is the partial pressure of gas A?

$$P_A = [A]RT = 0.2 \frac{\text{mol}}{\text{L}} \cdot 0.082145 \frac{\text{L bar}}{\text{mol K}} \cdot 300 \text{ K}$$
$$= \boxed{5.0 \text{ bar}}$$

(12 pts) 7. Using the concept of vapor pressure and boiling point in a knowledgeable and accurate manner, describe what happens and why it happens as one raises the temperature of a beaker of water from just below the boiling point to just above the boiling point:

(a) if there are absolutely no gas bubbles in the water.

The water will super heat but NOT boil

← full credit

For your information: Cold water from the tap has dissolved air. As the temperature rises, the air is less soluble and air bubbles form on the bottom. Where the water vapor pressure just exceeds  $P_{\text{ext}}$ , water evaporation expands the air bubbles and new bubbles form.

(b) if there are gas bubbles in the water.

Boiling begins when  $T$  is slightly higher than the boiling point as evaporation into the bubbles becomes fast enough that they rise to the surface. In boiling, when a bubble becomes large enough, it will break away from the bottom, leaving a small piece of itself behind — which then grows large, breaks off, leaves a small piece of itself, which.....

After the first air bubble leave the bubbles become pure water vapor. But they are the ancestors of what were air bubbles.

TABLE A.5 Inorganic Compounds\* (cont.)

	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )
HCO <sub>3</sub> <sup>-</sup> (aq)	-691.99	91.2	-586.77
CO <sub>3</sub> <sup>2-</sup> (aq)	-677.14	-56.9	-527.81
Fe(s)	0	27.28	0
Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	87.40	-742.2
H <sub>2</sub> (g)	0	130.79	0
H <sub>2</sub> O(g)	-241.82	188.93	-228.73
H <sub>2</sub> O(l)	-285.83	69.91	-237.13
H <sup>+</sup> (aq)	0	0	0
OH <sup>-</sup> (aq)	-229.99	-10.75	-157.244
H <sub>2</sub> O <sub>2</sub> (aq)	-191.17	143.9	-134.03
H <sub>2</sub> S(g)	-20.63	205.90	-33.56
H <sub>2</sub> SO <sub>4</sub> (g)	-735.13	298.8	-653.37
N <sub>2</sub> (g)	0	191.72	0
NH <sub>3</sub> (g)	-46.11	192.56	-16.78
NH <sub>3</sub> (aq)	-80.29	111.3	-26.50
NH <sub>4</sub> <sup>+</sup> (aq)	-132.51	113.4	-79.31
NO(g)	90.25	210.87	86.55
NO <sub>2</sub> (g)	33.18	240.17	51.47
NO <sub>3</sub> <sup>-</sup> (aq)	-205.0	146.40	-108.74
Na <sup>+</sup> (aq)	-240.12	59.0	-261.90
NaF(s)	-411.15	72.13	-344.14
NaCl(aq)	-407.27	115.5	-393.13
NaOH(s)	-425.61	64.46	-379.49
O <sub>2</sub> (g)	0	205.25	0
O <sub>3</sub> (g)	142.7	239.04	163.4
S(rhombic)	0	31.80	0
SO <sub>2</sub> (g)	-296.83	248.33	-300.19
SO <sub>3</sub> (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,  $S^\circ$ , 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 <sup>-1</sup> )
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