

Quiz II  
CH 353 Sumer 2009

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Name: KEY

Carefully read all the problems. The exam should have 4 questions on 6 pages. The first page has potentially useful information. The last page is for extra writing space.

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad R = 8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \quad R = 8.206 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ atm} = 1.01325 \text{ bar}$$

$$T/\text{K} = T/^{\circ}\text{C} + 273.15$$

$$1 \text{ atm-L} = 101.325 \text{ J}$$

$$1 \text{ bar-L} = 100 \text{ J}$$

**Please sign at the bottom to certify that you have worked on your own.**

I certify that I have worked the following exam without the help of others, and that the work I am turning in is my own.

Signed: \_\_\_\_\_  
Signature Date

1. True/False Circle either T or F for each statement (10 points each)

T  F For an adiabatic process,  $\Delta S_{\text{SYS}}$  can never decrease.

$$q=0 \quad \Delta S_{\text{surr}} = 0$$
$$\Delta S_{\text{tot}} \text{ can't be } < 0$$

T  F Any process that spontaneously causes a decrease in the entropy of the system must be exothermic.

T  F For a perfect crystal of pure substance at  $T=0\text{K}$  the number of microstates,  $\Omega$ , is 0.

$$S=0, \Omega=1$$

T  F Given,  $dH = -TdS + VdP$  then  $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_S$

$$\left(\frac{\partial V}{\partial S}\right)_P$$

T  F For an isothermal compression of an ideal gas  $\Delta G > 0$ .

$$\Delta U=0, \Delta H=0 \quad \Delta G = \Delta H^\circ - T\Delta S$$

$S < 0$  compression

$$\therefore \Delta G > 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$\ominus = \Delta H - \oplus \ominus$$

$$\ominus + \ominus = \Delta H = \ominus \text{ exothermic}$$

2. Short Answer (25 points each)

Assuming that  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  are independent of temperature, what is  $\Delta_R G^\circ$  at 500K



	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$S^\circ$	$C_p$
$\text{NH}_3(\text{g})$	+294.1	+328.1	239	99
$\text{O}_2(\text{g})$	0	0	205	29
$\text{N}_2(\text{g})$	0	0	192	29
$\text{H}_2\text{O}(\text{g})$	-241.8	-228.6	189	33

$$\Delta_r H^\circ = 6 \Delta_f H^\circ(\text{H}_2\text{O}) - 4 \Delta_f H^\circ(\text{NH}_3) = 6(-241.8) - 4(294.1)$$

$$\Delta_r H^\circ = -2627.2 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = 6S^\circ(\text{H}_2\text{O}) + 2S^\circ(\text{N}_2) - 4S^\circ(\text{NH}_3) - 3S^\circ(\text{O}_2)$$

$$= 6(189) + 2(192) - 4(239) - 3(245) = -53 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$(500\text{K}) \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -2627.2 - (500)(10^{-3})(-53) = -2600 \text{ kJ/mol}$$

Given that

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

Would you expect the internal energy of a hard sphere gas that obeys the equation of state

$$P(V - nb) = nRT$$

where  $b > 0$ , to increase, decrease or stay the same for an isothermal expansion? Provide some math to justify your answer.

$$P = \frac{nRT}{V - nb} \quad \left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V - nb}$$

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{nR}{V - nb} \right) - P = \frac{nRT}{V - nb} - \frac{nRT}{V - nb} = 0$$

Stay the same

3. (50 points)

1 mole of an ideal gas,  $C_{v,M} = (3/2)R$ , is initially at 1 atm and 300 K. In a process that is neither isothermal nor adiabatic, the gas is simultaneously compressed by a constant external pressure of 2 atm and brought into thermal equilibrium with a constant temperature heat bath at 500 K. What is  $\Delta S_{\text{TOTAL}}$  for this process?

$$T_i = 300 \quad T_f = 500 \quad P_i = 1 \quad P_f = 2$$

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

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

$$= (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{500/2}{300/1}\right) + \frac{3}{2} R (\text{J K}^{-1} \text{ mol}^{-1})(1 \text{ mol}) \ln\left(\frac{500}{300}\right)$$

$$\Delta S_{\text{sys}} = -1.52 + 6.37 = 4.85 \text{ J K}^{-1}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{actual}}}{T} = \frac{-q_{\text{actual}}}{500 \text{ K}}$$

$$q = \Delta U - w = C_v \Delta T - (-P_{\text{ex}} \Delta V)$$

$$q = 1.5R(500 - 300) - \left(-P_f \left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)\right)$$

$$q = 300R - (-500R + 600R)$$

$$q = 200R$$

$$\Delta S_{\text{surr}} = \frac{-200(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}{500 \text{ K}} = -3.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{tot}} = (-3.32 + 4.85) \text{ J K}^{-1}$$

$$= 1.52 \text{ J K}^{-1}$$

$$\uparrow_{1 \text{ mol}} = -3.32 \text{ J K}^{-1}$$

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4. (50 points)

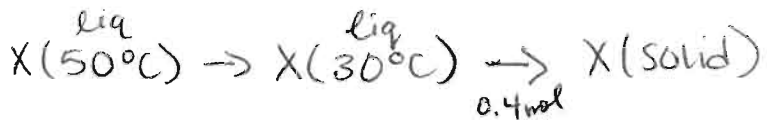
Substance X has a melting temperature of 30°C at 1 bar. A flask containing one mole of liquid X at a temperature of 50°C is submerged into a constant temperature bath at 0°C containing water and ice. After a period of time the flask is removed from the bath. After the flask is removed 0.75 moles of ice has melted in the water bath and 0.4 moles of X has frozen in the flask. (this process is at constant pressure of 1 bar). Taking the flask of X as the system and the water/ice bath as the surroundings answer the following questions

- $C_{P,M}^{\circ}(X, \text{liq}) = 70 \text{ J K}^{-1} \text{ mol}^{-1}$
- $C_{P,M}^{\circ}(X, \text{sol}) = 40 \text{ J K}^{-1} \text{ mol}^{-1}$
- $C_{P,M}^{\circ}(\text{water, liq}) = 75 \text{ J K}^{-1} \text{ mol}^{-1}$
- $C_{P,M}^{\circ}(\text{water, sol}) = 38 \text{ J K}^{-1} \text{ mol}^{-1}$
- $\Delta_{\text{FUS}}H^{\circ}(\text{water, } 0^{\circ}\text{C}) = 6 \text{ kJ mol}^{-1}$
- $S^{\circ}(X, \text{liq, } 50^{\circ}\text{C}) = 70 \text{ J K}^{-1} \text{ mol}^{-1}$

- A. What is the final temperature of the substance X in the flask?
- B. What is the heat for this process? (5 points)
- C. What is the enthalpy of fusion for X? (10 points)
- D. What is the entropy change of the system (substance X), the surroundings (the water bath), and the total entropy change? (20 points)

X is at its melting temp  $T = 303.15 \text{ K}$   $\Delta T = -20 \text{ K}$

$$q = -(0.75)(6000 \text{ J/mol}) = -4500 \text{ J}$$



$$C_p \Delta T = q = -1400 \text{ J}$$

Remaining heat 3100 J

$$\Delta H_{\text{FUS}} = \frac{3100 \text{ J}}{0.4 \text{ mol}} = 7.75 \text{ kJ/mol}$$

$$\Delta S_{\text{Surr}} = \frac{4500}{273} = \frac{-q}{T} = 16.5 \text{ J K}^{-1}$$

- $T_f = \underline{303.15 \text{ K}} \text{ (30}^{\circ}\text{C)} \text{ (5 pts)}$
- $q = \underline{-4.5 \text{ kJ}} \text{ (5 pts)}$
- $\Delta_{\text{FUS}}H = \underline{7.75 \text{ kJ/mol}} \text{ (10 pts)}$
- $\Delta_{\text{SYS}}S = \underline{-14.7 \text{ J K}^{-1}} \text{ (10 pts)}$
- $\Delta_{\text{Surr}}S = \underline{16.5 \text{ J K}^{-1}} \text{ (5 pts) 16}$
- $\Delta_{\text{Surr}}S = \underline{1.8 \text{ J K}^{-1}} \text{ (5 pts) 10}$

$$\Delta S_{\text{sys}} = C_{p, \text{liq}} \ln\left(\frac{T_f}{T_i}\right) - \left(\frac{q}{T}\right) \rightarrow \text{also } n \frac{\Delta H_{\text{FUS}}}{T}$$

$$= 70 \text{ J K}^{-1} \ln\left(\frac{303}{323}\right) - \frac{3100 \text{ J}}{303 \text{ K}}$$

$$= (-4.47 - 10.2) \text{ J K}^{-1} = -14.7 \text{ J K}^{-1}$$

$$\Delta S_{\text{tot}} = (16.5 + -14.7) \text{ J K}^{-1} = 1.8 \text{ J K}^{-1}$$