

APS104 2010 chemistry section - Mock mid-term exam

Question 1 (25 Marks)

- 1) The sudden deflation of a balloon can be simulated as an adiabatic expansion against a constant pressure, defining the system as the mass of air that was initially in the balloon before deflation. Assume air is an ideal gas, $C_v = 2R$. At initial conditions, $P_i = 1.003 \text{ atm}$, $V_i = 4.000 \text{ L}$, $T_i = 298 \text{ K}$. External pressure (constant = 1.000 atm). Using these assumptions:
 - a) Demonstrate that $T_f/T_i = (1+(R/C_v)(P_f/P_i))/(1+(R/C_v))$, why couldn't you use $T_f/T_i = (P_f/P_i)^{(R/C_p)}$?
 - b) Calculate the final volume, V_f (L). Is this the final volume inside the balloon?
 - c) Calculate the amount of work produced by the system. What did the system do with that work?

Question 2 (20 Marks)

- a) Calculate the enthalpy of formation of NO_2 at 57°C given the following information.

	$\Delta H_f^\circ \text{ (kJ/mol)}$	$C_p \text{ (J/(mol K))}$
$\text{NH}_3 \text{ (g)}$	-57.5	35.1
$\text{H}_2\text{O} \text{ (l)}$	-43.7	75.3
NO_2		37.2
$\text{NH}_3 \text{ (g)} + 2\text{H}_2\text{O} \text{ (l)} \rightarrow \text{NO}_2 \text{ (g)} + 3.5\text{H}_2 \text{ (g)}$	71.25	
$\text{O}_2 \text{ (g)}$		29.4
$\text{N}_2 \text{ (g)}$		29.1

- b) Could you use a similar strategy as used for part a to calculate the total heat produced during the formation of NO_2
- c) If given the enthalpy of formation of $\text{H}_2\text{O} \text{ (g)} = -37.3 \text{ kJ/mol}$ calculate the heat of vapourization

Question 3: (20 Marks)

- a) Under standard conditions predict whether the entropy change is positive or negative for each of the following processes. Briefly justify your predictions:
 - i) $\text{NH}_4\text{NO}_3 \text{ (s)} \rightarrow \text{N}_2 \text{ (g)} + 2\text{H}_2\text{O} \text{ (g)} + \frac{1}{2}\text{O}_2 \text{ (g)}$
 - ii) $\text{H}_2\text{O} \text{ (g)} \rightarrow \text{H}_2\text{O} \text{ (l)}$
 - iii) $\text{CaCO}_3 \text{ (s)} \rightarrow \text{CaO} \text{ (s)} + \text{CO}_2 \text{ (g)}$
- b) 1 mole of a gas with a C_v of $3/2R$ is adiabatically compressed reversibly from 17L to 8L at a constant pressure of 100kPa . If the gas starts at 25°C calculate ΔS , $\Delta S_{\text{surroundings}}$, and ΔS^{total} .
- c) How would your answer differ if you compressed the gas irreversibly?

Question 4: (20 Marks)

At this moment there is a race to produce the first fuel cell that works with natural gas (mostly methane, CH₄). The overall reaction for this fuel cell would be CH_{4(g)} + 2O_{2(g)} => CO_{2(g)} + 2H₂O_(l). For this reaction, calculate:

- a) The theoretical efficiency of this reaction ($\Delta G^\circ_{rxn}/\Delta H^\circ_{rxn}$) at standard conditions, and discuss why this efficiency is larger than the efficiency of gas turbines (~ 40%)
- b) Should we feed oxygen to the anode or the cathode of the cell?
- c) Based on the “lnQ” term of the free energy, explain what could you do to increase the amount of work you can get out of the fuel cell?
- d) Estimate the standard potential of this fuel cell (E°). Consider that in this reaction every oxygen atom gains 2 electrons in the process.

Other Data:

$$\Delta H^\circ_f \text{CH}_4(\text{g}) = -74.6 \text{ kJ/mol} ; \Delta G^\circ_f \text{CH}_4(\text{g}) = -50.5 \text{ kJ/mol}$$

$$\Delta H^\circ_f \text{O}_2(\text{g}) = 0 \text{ kJ/mol} ; \Delta G^\circ_f \text{O}_2(\text{g}) = 0 \text{ kJ/mol}$$

$$\Delta H^\circ_f \text{CO}_2(\text{g}) = -393.5 \text{ kJ/mol} ; \Delta G^\circ_f \text{CO}_2(\text{g}) = -394.4 \text{ kJ/mol}$$

$$\Delta H^\circ_f \text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ/mol} ; \Delta G^\circ_f \text{H}_2\text{O}(\text{l}) = -237.1 \text{ kJ/mol}$$

Question 5: (15 Marks)

- a) Draw a typical phase diagram for a substance in which the volume of the solid is greater than the volume of the liquid (e.g. water). On the diagram label i) the critical point, ii) the different phase regions.
- b) Explain what the critical point corresponds to.
- c) Draw a line that corresponds freezing a liquid to into a solid at constant pressure on the diagram.
- d) Explain what the boundary line between the solid and liquid phases represents.

APS 104S, Formula sheet, February 2010

<p>Idea gas equation of state: $PV = nRT$</p> <p>Van der Waals equation of state:</p> $P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$ <p>First law, closed systems</p> $\Delta U = Q + W \quad \text{or} \quad dU = dQ + dW$ $dW = -P_{\text{ext}} \cdot dV$ $dU = nC_V dT$	$H \equiv U + PV$ $dH = nC_p dT$ <p>For ideal gases, $C_p = C_v + R$ Solids, Liquids, $C_p = C_v$</p> $G \equiv H - TS$ $dS \equiv \frac{dQ_{\text{reversible}}}{T}$ <p>For a process at constant temperature $\Delta G = \Delta H - T\Delta S$</p>
<p>For an isothermal reversible process (ideal gas):</p> $W_{\text{rev}} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$ <p>Adiabatic reversible process (ideal gas):</p> $\frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{-R/C_v} ; \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{R/C_p}$	<p>Extent of reaction (ξ) $\Rightarrow \Delta n_i = v_i * \xi$ v_i: stoichiometric coefficient</p> $\Delta H^\circ_{\text{rxn}} = \sum v_i * \Delta H^\circ_{f,i} + \Delta C_p * (T - 25^\circ\text{C})$ $\Delta C_p = \sum v_i * C_{p,i}$ <p>Assuming no phase change, constant C_p First law for closed systems, with reaction:</p> $\Delta H + \xi * \Delta H_{\text{rxn}} = Q + W_{\text{shaft}} + V * \Delta P$ <p>W_{shaft} does not include expansion ($-P\Delta V$)</p>
<p>For solids or liquids, $\Delta \bar{S} = C \ln \left(\frac{T_2}{T_1} \right)$; Phase transition $\Delta \bar{S}_{\text{trans}} = \frac{\overline{\Delta H}_{\text{trans}}}{T_{\text{trans}}}$</p> <p>For ideal Gases: $\Delta \bar{S} = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$ or $\Delta \bar{S} = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$</p> <p>Clausius equation for phase transition: $\left(\frac{dP}{dT} \right)_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T(\Delta V_{\text{transition}})}$</p> <p>Standard entropy of the reaction $\Delta S^\circ_{\text{rxn}} = \sum v_i * S^\circ_i$</p> <p>Standard free energy of a reaction: $\Delta G^\circ_{\text{rxn}} = \sum v_i * \Delta G^\circ_{f,i}$ or $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$</p> <p>Total free energy of the reaction $aA + bB \Rightarrow cC + dD$</p> $\Delta_r G = \Delta_r G^\emptyset + RT \ln(Q), \text{ where } Q = \begin{bmatrix} y_C^c y_D^d \\ y_A^a y_B^b \end{bmatrix}$ <p>$E^\circ = \Delta G^\circ_{\text{rxn}} / (-n_e F)$; n_e = moles of electrons transferred, F = Faraday's constant = 9.65E+4 C/mol</p>	

$$R = 8.3145 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1} = 0.0820574587 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1} \text{ mol}^{-1} = 0.083145 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ atm} = 101.325 \text{ kPa} = 1.01325 \text{ bar} = 14.696 \text{ psi} = 760 \text{ Torr} = 760 \text{ mmHg}$$