

APS 104S, Final Exam – Chemistry portion, Feb. 26, 2009, 6:10 PM

1. (20 pts) At intermediate specific volumes, the Van der Waals (VdW) equation can be simplified as: $P = \frac{RT}{V} - \frac{a}{V^2}$.
 - (a) Develop an equation to calculate the reversible isothermal work of compression for a gas that complies with this modified VdW equation.
 - (b) Compare your equation and the equation for isothermal work of compression of an ideal gas and argue if compressing this real gas to half of its original volume requires more or less work than the ideal case.
2. (20 pts) You are asked to conduct a preliminary design of a “gas-driven elevator”. Assume that the elevator always moves slowly (no friction losses) and at a constant pressure of 1.1 bar. When the elevator is in the basement, the temperature of the gas is 30°C, and its volume is 2m³. When the elevator reaches the last floor, the volume of the gas is 20 m³. Consider that the system is closed (constant number of moles). In order to expand the gas, and reach the last floor, the gas is heated using a certain heat source. Then:
 - (a) Calculate the final temperature of the gas
 - (b) Calculate the heat required for this expansion
 - (c) Could there be a problem in implementing this idea?
 - (d) What is the minimum temperature that the heat source needs to have in order to accomplish the desired expansion?Assume that the gas is ideal and monoatomic, such that $C_v = 1.5*R$
3. (20 pts) You are planning to completely evaporate 1kg of water, initially at 25°C. To this end you put this water in a 200g aluminum pan that also heats up from 25°C to 100°C. To accomplish this, you introduced an electrical resistance that consumes of 1600 watts (Joule/second) of electricity. Knowing that the C_p of liquid water is 4.19 kJ/kg°C, the enthalpy of vaporization of water is 2260 kJ/kg, and C_p of aluminum is 0.93 kJ/kg°C. Assuming that this pan is placed in an insulated room (no heat transfer with the surroundings), calculate:
 - (a) The time that it takes for the liquid water to start boiling;
 - (b) The time that it takes for all the water to boil;
 - (c) The total (universe) change of entropy when all the water is boiled;
 - (d) Is there any way to make this process reversible?

4. (20 pts) Molecular bromine is 24 per cent dissociated at a temperature of 1600 K and a pressure of 1.00 bar in the equilibrium: $\text{Br}_2(\text{g}) \leftrightarrow 2\text{Br}(\text{g})$. Calculate:
- (a) K at 1600 K
 - (b) ΔrG^\ominus (free energy of the reaction at 25°C)
 - (c) K at 2000 K given that $\Delta rH^\ominus = +112 \text{ kJ/mol}$, assuming that it does not change with temperature.
5. Consider the dissociation of methane: $\text{CH}_4(\text{g}) \leftrightarrow 2\text{H}_2(\text{g}) + \text{C}(\text{s})$.
- (a) Given $\Delta H_f^\ominus(\text{CH}_4, \text{g}) = -74.85 \text{ kJ/mol}$ and $\Delta S_f^\ominus(\text{CH}_4, \text{g}) = -80.97 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 298 K, calculate the value of the equilibrium constant for the dissociation of methane at 298 K.
 - (b) Calculate the extent of reaction (ξ), for the dissociation of one mol of methane at 25 °C and a total pressure of 0.010 bar.
 - (c) Assuming that $\Delta H_f^\ominus(\text{CH}_4, \text{g})$ is independent of temperature, calculate the equilibrium constant at 50 °C. (d) Should you be worried about carbon build up in a storage tank designed to hold methane at either 25 °C or 50 °C: yes or no and why or why not?

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<p>Idea gas equation of state: $PV = nRT$</p> <p>Compressibility factor: $Z = \frac{PV}{nRT}$</p> <p>Virial equation of state:</p> $Z = \frac{PV}{nRT} = 1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \dots$ <p>Van der Waals equation of state:</p> $P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$ $a = \frac{27R^2T_c^2}{64P_c}$ $b = \frac{RT_c}{8P_c} = \frac{V_c}{3}$	$H \equiv U + PV$ $dH = nC_p dT$ <p>For ideal gases, $C_p = C_v + R$</p> <p>Adiabatic reversible compression or expansion of an ideal gas:</p> $\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{-R/C_v}$ $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_p}$ $P_1 V_1^\gamma = P_2 V_2^\gamma \quad \gamma = \frac{C_p}{C_v}$
<p>$dW = -P_{\text{ext}} dV$</p> <p>First law, closed systems</p> $\Delta U = Q + W \quad \text{or} \quad dU = dQ + dW$ <p>$dU = nC_v dT$</p> <p>For an isothermal 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>Extent of reaction (ξ) $\Rightarrow \Delta n_i = v_i * \xi$</p> <p>$v_i$: 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</p> <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>$dS \equiv \frac{dQ_{\text{reversible}}}{T}$ 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>Clausius-Clapeyron equation for L-V transition = $\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$</p>	

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

$$\Delta_r H^\ominus = \left[\sum_{i=1}^n \nu_i H_{i,m}^\ominus (\text{products}) - \sum_{i=1}^n \nu_i H_{i,m}^\ominus (\text{reactants}) \right] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r C_p^\ominus = \left[\sum_{i=1}^n \nu_i C_{p,i,m}^\ominus (\text{products}) - \sum_{i=1}^n \nu_i C_{p,i,m}^\ominus (\text{reactants}) \right] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S^\ominus = \left[\sum_{i=1}^n \nu_i S_{i,m}^\ominus (\text{products}) - \sum_{i=1}^n \nu_i S_{i,m}^\ominus (\text{reactants}) \right] \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r G^\ominus = \left[\sum_{i=1}^n \nu_i G_{i,m}^\ominus (\text{products}) - \sum_{i=1}^n \nu_i G_{i,m}^\ominus (\text{reactants}) \right] \text{ kJ} \cdot \text{mol}^{-1}$$

$\Delta G = \Delta H - T\Delta S$, For reactions, $\Delta_r G = \Delta_r G^\ominus + RT \ln(K)$, where $K = \left[\frac{a_C^c a_D^d}{a_A^a a_B^b} \right]$ for a reaction $aA + bB = cC + dD$ and "a" is the activity of each specie.

For gasses, $a_i = P_i/P^\ominus = (y_i P)/P^\ominus$ where P^\ominus is the reference pressure, 1 bar

For liquids, $a_i = C_i/C^\ominus = [i]/C^\ominus$ where C^\ominus is the reference concentration, 1 mol·dm⁻³

For solids, $a_i = 1$

$$\mu_j = \mu_j^\ominus + RT \ln a_j$$

$$\ln K_2 - \ln K_1 = \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

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

STP = Standard Temperature and Pressure: 1 atm, 0 °C (273 K)

NTP = Normal Temperature and Pressure: 1 atm, 15 °C (288 K)

SATP = Standard Ambient Temperature & Pressure: 25 °C, 1 bar