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Lecture: Tue, 2.10-3.25 pm & Fri 2.10-3.25 pm, **C111**
Office hours: Wed, 4-6 pm, **HN-1321B**

Problem 1   CH3/5pts

Using definitions o heat capacities at constant volume and pressure, cyclic rule (equations a/P3.32 and b/P3.37) and expression for $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ (equation c/P3.38), prove that:

$$C_P = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_H} \tag{1a}$$

$$C_V = -\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_U \tag{1b}$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \tag{1c}$$

Show that the equation 1c simplifies to 0 for ideal and van der Waals gas (P3.39).
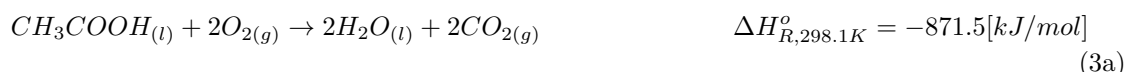
Problem 2 (P4.14 and P4.21)   CH4/5pts

1. From the following data, compute the $\Delta_f H^o$ of $CaC_{2(s)}$ at 298 K.

$$CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + C_2H_{2(g)} \qquad \Delta H^o_R = -127.9[kJ/mol] \tag{2a}$$

$$Ca_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CaO_{(s)} \qquad \Delta H^o_R = -635.1[kJ/mol] \tag{2b}$$

$$CaO_{(s)} + H_2O(l) \rightarrow Ca(OH)_{2(s)} \qquad \Delta H^o_R = -65.2[kJ/mol] \tag{2c}$$

The combustion enthalpies of $C_{(s)}$ and $C_2H_{2(g)}$ are -393.5 and -1299.8 kJ/mol respectively.

2. From the following data, compute $\Delta H^o_{R,391.4K}$ for the $CH_3COOH_{(g)} + 2O_{2(g)} \rightarrow 2H_2O_{(g)} + 2CO_{2(g)}$:

$$CH_3COOH_{(l)} + 2O_{2(g)} \rightarrow 2H_2O_{(l)} + 2CO_{2(g)} \qquad \Delta H^o_{R,298.1K} = -871.5[kJ/mol] \tag{3a}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H^o_{R,298.1K} = 40.6[kJ/mol] \tag{3b}$$

$$CH_3COOH_{(l)} \rightarrow CH_3COOH_{(g)} \qquad \Delta H^o_{R,391.4K} = 24.4[kJ/mol] \tag{3c}$$

The molar $\frac{C_P}{R}$ are equal 14.9, 3.53, 4.46, 9.055 and 4.048 for $CH_3COOH_{(l)}$, $O_{2(g)}$, $CO_{2(g)}$, $H_2O_{(l)}$ and $H_2O_{(g)}$ respectively ($C_P = \frac{C_P}{R} \cdot R$).

Problem 3 (variation of P5.7)   CH5/5pts

Consider a classical reversible Carnot cycle with 1.0 mole of an ideal gas with $C_V = \frac{5}{2}R$ as a working substance that undergoes, as we discussed in the lecture (figure 5.2 in the book), following transitions:

1. $(a \rightarrow b)$ Isothermal expansion from V_a=2.5 L to V_b=10 L at $T_{hot} = 640$ K

2. $(b \rightarrow c)$ Adiabatic expansion until system reaches $T_{cold} = 240$ K

3. $(c \rightarrow d)$ Isothermal compression at $T_{cold} = 240$ K.

4. $(d \rightarrow a)$ Adiabatic compression until gas reaches the T_{hot} and V_a=2.5 L.

Please calculate:

1. Volume at points c and d (V_c and V_d).

2. Work for the each step of the cycle and the total work.

3. The efficency θ of the cycle and the amount of heat that needs to be extracted from the reservoir T_{hot} to provide 1.5 kJ of work in the surroundings.

Problem 4 (P5.39) CH5/5pts

1. Calculate ΔS if 1.00 mol of liquid water is heated from 0.00^oC to 10.00^oC under constant pressure and $C_{P,m}$=75.3 [J/mol·K].

2. The melting point of water at the pressure of interest is 0.00^oC and the enthalpy of fusion is 6.010 [kJ/mol]. The boling point is 100^oC and the enthalpy of vaporization is 40.65 [kJ/mol]. Calculate ΔS for the transformation from ice to vapor: $H_2O(s, 0^oC) \rightarrow H_2O(g, 100^oC)$

Problem 5 CH5/5pts

Using the thermodynamic cycles, explain the difference between the heat engine (Carnot cycle) and Otto and diesel engines. Why diesel engine requires different type of fuel than regular (Otto) engine? Finally, what is your opinion on Volkswagen emission scandal?