

## Chem 531: Problem Set #2

Due in class: Thurs, Sept. 14th

(1) The heat capacities of a gas are often represented by expressions such as:

$$\bar{C}_p = \alpha + \beta T + \gamma T^2 + \delta T^3$$

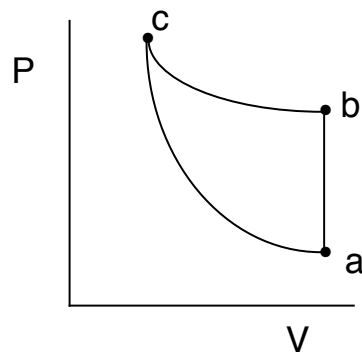
For  $\text{N}_2$ ,  $\alpha = 28.883 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\beta = -1.57 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$ ,  $\gamma = 0.808 \times 10^{-5} \text{ J K}^{-3} \text{ mol}^{-1}$ , and  $\delta = -2.871 \times 10^{-9} \text{ J K}^{-4} \text{ mol}^{-1}$ . How much heat is required to heat a mole of  $\text{N}_2$  from 200 to 1000 K at a constant pressure of 1 bar?

$$\begin{aligned} q_p &= n \int_{T_i}^{T_f} \bar{C}_p dT = n \int_{T_i}^{T_f} (\alpha + \beta T + \gamma T^2 + \delta T^3) dT \\ &= n \left[ \alpha T + \frac{1}{2} \beta T^2 + \frac{1}{3} \gamma T^3 + \frac{1}{4} \delta T^4 \right]_{T_i}^{T_f} \\ &= n \left[ \alpha \Delta T + \frac{1}{2} \beta (T_f^2 - T_i^2) + \frac{1}{3} \gamma (T_f^3 - T_i^3) + \frac{1}{4} \delta (T_f^4 - T_i^4) \right] \end{aligned}$$

$$\text{for } n = 1.0 \text{ mol}, T_i = 200 \text{ K}, T_f = 1000 \text{ K}$$

$$q_p = 24308 \text{ J} = 24.3 \text{ kJ}$$

- (2) Compressing the system represented in the figure along the adiabatic path  $a \rightarrow c$  requires 1000 J of work. Compressing the system along the isothermal line  $b \rightarrow c$  requires 1500 J of work but 600 J of heat flows out of the system. Fill in the table below, paying close attention to signs.



	Process	w	q	$\Delta U$
①	a $\rightarrow$ b	0	100	100
②	b $\rightarrow$ c	1500	-600	900
③	c $\rightarrow$ a	-1000	0	-1000
④	cycle abca	500	-500	0

- ① isochoric, so  $w = 0$  since  $dw = -P_{\text{ext}}dV$  &  $dV = 0$
- ②  $w$  &  $q$  are as stated in problem  $\Delta U = q + w$
- ③ adiabatic, so  $q = 0$ ;  $w$  is opposite as stated
- ④  $\Delta U = 0$  since it's a state function. This gives the result for  $\Delta U$  in ① since  $① + ② + ③ = 0$

(3)

(a) Show that

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{noting that } \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

(b) Evaluate this for an ideal gas.

$$\textcircled{a} \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V, \quad \text{so } \left(\frac{\partial C_v}{\partial V}\right)_T = \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right]_T$$

but  $U$  is a state function ( $dU$  is an exact differential)  
so its mixed 2nd partial derivatives are equal:

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

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

$$\begin{aligned} \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right]_V &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V \\ &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \end{aligned}$$

$$\text{(b)} \quad P = \frac{nRT}{V} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

hence  $\left(\frac{\partial C_v}{\partial V}\right)_T = 0$  for an ideal gas

- (4) The standard enthalpy of dissociation  $\Delta H_{diss}^{\circ}$  for hypobromous acid, i.e.,  $\Delta H_r^{\circ}$ , for the reaction  $\text{HOBr(g)} \rightarrow \text{OH(g)} + \text{Br(g)}$ , has been measured to be 206.8 kJ/mol at 25°C.
- (a) Determine the standard internal energy change  $\Delta U_r^{\circ}$  for this reaction at 25°C.
- (b) Determine the standard enthalpy of formation,  $\Delta H_f^{\circ}$ , of HOBr at 25°C [Note: you'll need to look up appropriate thermodynamic data for OH(g) and Br(g). See: <https://atct.anl.gov>]

$$(a) \quad H = U + PV \quad \text{hence} \quad \Delta U_r^{\circ} = \Delta H_r^{\circ} - \Delta(PV)$$

$$\Delta(PV) = \Delta(nRT) = \Delta n_{\text{gas}} RT$$

$$\Delta U_r^{\circ} = 206.8 \text{ kJ} - (2-1)(8.3145)(298.15) / 1000$$

$$= 204.3 \text{ kJ}$$

(b) from the ATcT:

$$\Delta H_f^{\circ}(\text{OH(g)}) \text{ at } 298\text{K} = 37.518 \text{ kJ/mol}$$

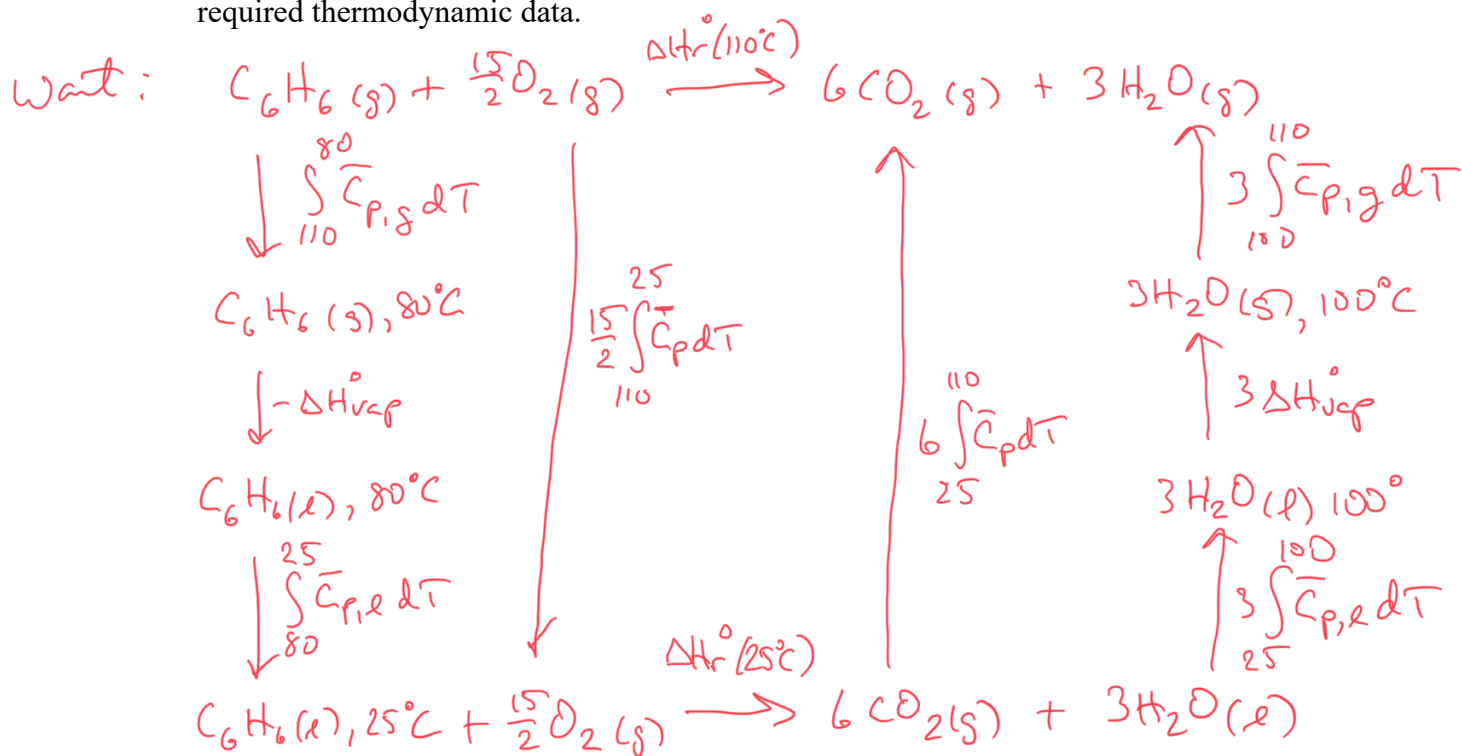
$$\Delta H_f^{\circ}(\text{Br(g)}) \text{ at } 298\text{K} = 111.848 \text{ kJ/mol}$$

$$\Delta H_{diss} = \Delta H_f^{\circ}(\text{OH(g)}) + \Delta H_f^{\circ}(\text{Br(g)}) - \Delta H_f^{\circ}(\text{HOBr(g)})$$

$$\Delta H_f^{\circ}(\text{HOBr}) = 37.518 + 111.848 - 206.8$$

$$= -57.4 \text{ kJ/mol}$$

- (5) The standard enthalpy of combustion for liquid benzene at 25°C is -3268 kJ/mol. Determine the enthalpy of combustion of gaseous benzene at 110°C. Please note your sources for the required thermodynamic data.



data from NIST WebBook

Benzene:  $\bar{C}_{p,g} = 104 \text{ J/mol}\cdot\text{K}$  at 368 K (avg of 80°C and 110°C)

$\bar{C}_{p,l} = 140 \text{ J/mol}\cdot\text{K}$  at 322 K (~avg of 80 → 25°C)

$\Delta H_{vap} = 33.9 \text{ kJ/mol}$  at 353.3 K ~ 80°C

other data from Noggle, 2nd ed., Physical Chemistry at 298.15 K  
 - ignoring T dependence since that is too much for this problem.  
 my apologies for not specifying this in the problem

$O_2(g)$ :  $\bar{C}_p = 29.355 \text{ J/mol}\cdot\text{K}$

$CO_2(g)$   $\bar{C}_p = 37.11 \text{ J/mol}\cdot\text{K}$

$H_2O(g)$   $\bar{C}_p = 33.577 \text{ J/mol}\cdot\text{K}$       $H_2O(l)$   $\bar{C}_p = 75.291 \text{ J/mol}\cdot\text{K}$

$\Delta H_{vap}(H_2O, 373 \text{ K}) = 40.66 \text{ kJ/mol}$

$$\begin{aligned}
 \Delta H_r(110^\circ\text{C}) &= \int_{110}^{80} \bar{C}_{P,g}(\text{C}_6\text{H}_6) dT - \Delta H_{\text{vap}}^\circ(\text{C}_6\text{H}_6) + \int_{80}^{25} \bar{C}_{P,l}(\text{C}_6\text{H}_6) dT \\
 &+ \frac{15}{2} \int_{110}^{25} \bar{C}_{P,g}(\text{O}_2) dT + \Delta H_r^\circ(25^\circ\text{C}) \\
 &+ 6 \int_{25}^{110} \bar{C}_p(\text{CO}_2) dT + 3 \int_{25}^{100} \bar{C}_{P,l}(\text{H}_2\text{O}) dT + 3 \Delta H_{\text{vap}}^\circ(\text{H}_2\text{O}) \\
 &+ 3 \int_{100}^{110} \bar{C}_{P,g}(\text{H}_2\text{O}(g)) dT
 \end{aligned}$$

$$= 104(80-110) - 33.9 \times 10^3 + 140(25-80)$$

$$+ 7.5(29.355)(25-110) + -3268 \times 10^3$$

$$+ 6(37.11)(110-25) + 3(75.291)(100-25) + 3(40.66 \times 10^3)$$

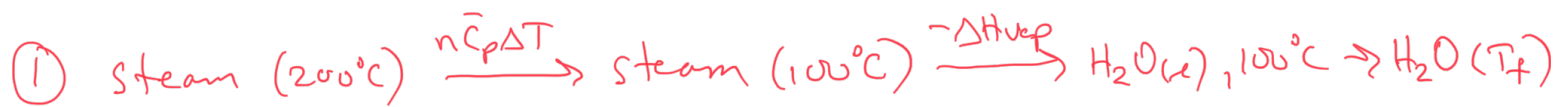
$$+ 3(33.577)(110-100)$$

$$= -3172 \text{ kJ/mol} \sim -3170 \text{ kJ/mol}$$

- (6) Two moles of superheated steam at 200°C is injected into 50 moles of 25°C water at a constant pressure of 1.0 bar under adiabatic conditions. Calculate the final temperature ( $T_f$ ) of the system. The constant pressure molar heat capacities of  $\text{H}_2\text{O}(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are 33.6 and 75.3  $\text{J K}^{-1} \text{mol}^{-1}$ , respectively, and can be assumed to be independent of temperature. The enthalpy of vaporization at 100°C and 1 bar for  $\text{H}_2\text{O}$  is 40.66  $\text{kJ mol}^{-1}$ .

adiabatic, so  $q = 0 \quad \therefore q_{\text{steam}} + q_{\text{H}_2\text{O}} = 0$

① ②



$$2(33.6)(100 - 200) + 2(-40.66 \times 10^3) + 2(75.3)(T_f - 100)$$

$$+ 50(75.3)(T_f - 25) = 0$$

$$T_f = 50^\circ\text{C}$$