Chemistry 231 **Assignment #3** (due Tuesday, 04 October, in class)

1. [5] The molar heat capacity of CO_2 gas at 1.00 bar pressure and temperature T is given by the polynomial expression

$$C_{pm} / (\mathrm{J\ K^{-1}\ mol^{-1}}) = a_0 + a_1(T/\mathrm{K}) + a_2(T/\mathrm{K})^2$$

with constants $a_0 = 18.86$, $a_1 = 0.07937$ and $a_2 = -0.00006783$.

5.00 moles of CO_2 is heated from 300 K to 450 K at 1.00 bar. Assuming the gas is ideal, an excellent approximation at this pressure, calculate q, w, ΔU and ΔH.

2. [1] Jet aircraft cruise at altitudes of about 10 km where air is very cold, about −40 °C. But the air pumped into the cabin for passengers and crew to breathe must be "air conditioned", *i.e.* cooled! Why is it necessary to cool the air?

3. [5] Assuming ideal gas behavior, calculate q, w, ΔU and ΔH for the reaction

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$$

carried out at 25.0 °C and 1.00 bar. Use the following standard enthalpies of formation:

$\Delta H_{fm}°(CH_4, g) = -74.81\ \mathrm{kJ\ mol^{-1}}$ $\Delta H_{fm}°(CO_2, g) = -393.509\ \mathrm{kJ\ mol^{-1}}$
$\Delta H_{fm}°(O_2, g) = 0$ $\Delta H_{fm}°(H_2O, l) = -285.830\ \mathrm{kJ\ mol^{-1}}$

(Note that the molar volume of liquid H_2O is negligible compared to the gas molar volumes.)

4. [3] 10.0 moles of helium ($C_{Vm} = 3R/2$) initially at 1.00 bar and 300 K is adiabatically compressed to a final pressure of 9.00 bar using a constant 9.00 bar external pressure. Calculate the final temperature, ΔU and ΔH.

5. [3] Suppose you want to produce liquid nitrogen at 1.00 bar pressure by reversibly and adiabatically expanding compressed N_2 gas initially at 300 K. Estimate the minimum initial pressure of N_2 that must be used.

Data: $C_{Vm} = 5R/2$. Nitrogen gas at 1.00 bar condenses to form liquid N_2 at 77 K, the standard boiling point.

6. [3] In class we used the test for an exact differential to show that $dq = C_V dT + p dV$ for an ideal gas <u>is not</u> the differential of a function, illustrating that the heat q is path-dependent (not a state function). Use the test for an exact differential to decide if S defined by

$$dS = \frac{C_V}{T} dT - \frac{p}{T} dV$$

is a state function or path-dependent for an ideal gas.

Chemistry 231 Assigment #3 (2016)

Ⓠ1 heat 5.00 mol CO_2 gas from 300 K to 450 K at 1 bar $\Longrightarrow$ $dq = dH = C_p dT$

$$q = \Delta H = \int_{T_i}^{T_f} C_p\, dT$$

per mole $\quad q_m = \Delta H_m = \int_{T_i}^{T_f} C_{pm}\, dT$

$$q_m = \Delta H_m = \int_{T_i}^{T_f} \left(a_0 + a_1 T + a_2 T^2\right) dT$$

$$= a_0 \int_{T_i}^{T_f} dT + a_1 \int_{T_i}^{T_f} T\, dT + a_2 \int_{T_i}^{T_f} T^2\, dT = \left(a_0 T + \frac{a_1}{2} T^2 + \frac{a_2}{3} T^3\right)\Big|_{T_i}^{T_f}$$

$$= a_0 (T_f - T_i) + \frac{a_1}{2}(T_f^2 - T_i^2) + \frac{a_2}{3}(T_f^3 - T_i^3)$$

$$= 18.86(450-300) + \frac{0.07937}{2}(450^2 - 300^2) - \frac{0.00006783}{3}(450^3 - 300^3)$$

$$= (2829 + 4464 - 1450)\frac{J}{mol} = 5844 \frac{J}{mol}$$

$$\boxed{q = \Delta H = (5.00\ mol)\left(5844 \frac{J}{mol}\right) = 29220\ J}$$

$$\Delta H = \Delta(U + pV) = \Delta(U + nRT) = \Delta U + nR\Delta T$$

$$\Delta U = \Delta H - nR\Delta T = 29220\,J - 5.00\,mol\ 8.314 \frac{J}{K \cdot mol}(450-300)K$$

$$= (29220 - 6236) J$$

$$\boxed{\Delta U = 22980\ J}$$

$$\Delta U = q + w$$

$$w = \Delta U - q = (22980 - 29220) J$$

$$\boxed{w = -6240\ J}$$

Or ll

$$w = -\int p_{ext}\, dV$$

$$= -p \int dV$$

$$= -pV_f + pV_i$$

$$= nR(T_i - T_f)$$

Ⓠ2 Air at an altitude of 10 km is cold ($\simeq -40\ °C$) and at a <u>pressure too low</u> to breathe ($\simeq 0.2$ bar).

Air pumped into the cabin is <u>adiabatically compressed</u> from about 0.2 bar to 1.0 bar for passengers and crew to breathe.

Compressing the air adiabatically makes it too hot to breathe, so it must be cooled.

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react at constant pressure ($q = \Delta H$)

Ⓠ3

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H = \Delta H_f\,(\text{products}) - \Delta H_f\,(\text{reactants})$$

$$= (1\,mol)\Delta H^\circ_{fm}(CO_2,g) + (2\,mol)\Delta H^\circ_{fm}(H_2O,l) - (1\,mol)\Delta H^\circ_{fm}(CH_4,g) - (2\,mol)\Delta H^\circ_{fm}(O_2,g)$$

$$= \left[(1)(-393.509) + (2)(-285.830) - (1)(-74.81) - (2)(0)\right] kJ$$

$$\boxed{\Delta H = -890.359\ kJ = q}$$

$$\boxed{\begin{aligned} V_m(H_2O,l) &\simeq 18\ cm^3\,mol^{-1} \\ V_m(\text{gas}) = \frac{RT}{P} &\simeq 25\ L\,mol^{-1}\end{aligned}}$$

$\boxed{P \text{ constant}}$

$$w = -\int_{V_i}^{V_f} P_{ext}\,dV = -P\int_{V_i}^{V_f} dV = -P(V_f - V_i)$$

$$= -P(V_{products} - V_{reactants})$$

$$= -P\left[(1\,mol)V_m(CO_2,g) + (2\,mol)V_m(H_2O,l) - (1\,mol)V_m(CH_4,g) - (2\,mol)V_m(O_2,g)\right]$$

$$= -P\left[(1\,mol)\frac{RT}{P} + (2\,mol)(0) - (1\,mol)\frac{RT}{P} - (2\,mol)\frac{RT}{P}\right]$$

$$= (2\,mol)\,RT$$

negligible

$$w = (2\,mol)(8.314\ J\,K^{-1}\,mol^{-1})(298.15\ K)$$

$$\boxed{w = 4960\ J}$$

$$\Delta U = q + w$$

$$= -890.359\ kJ + 4.960\ kJ$$

$$\boxed{\Delta U = -885.401\ kJ}$$

$C_{vm} = 3R/2$ (constant)

Q4 Adiabatic compression of 10.0 mol He(g)

$\boxed{\begin{array}{l} P_i = 1.00 \text{ bar} \\ T_i = 300 \text{ K} \end{array}} \xrightarrow[\substack{P_{ext} = 9.00 \text{ bar} \\ \text{(constant)}}]{\substack{\text{adiabatic} \\ (q=0)}} \boxed{\begin{array}{l} P_f = 9.00 \text{ bar} \\ T_f = ? \end{array}}$

$$dU = \cancel{dq}^{\,0} + dw \quad (1^{ST} \text{ Law})$$

$$C_v dT = -P_{ext} dV \quad \left(\begin{array}{c}\text{ideal gas: } U \text{ depends} \\ \text{only on } T\end{array}\right)$$

$$\Delta U = \int \overset{\text{const.}}{C_v} dT = -\int \overset{\text{const.}}{P_{ext}} dV = w$$

$$C_v \int_{T_i}^{T_f} dT = -P_{ext} \int_{V_i}^{V_f} dV \quad (P_{ext} = 9.00 \text{ bar} = P_f)$$

$C_v = nC_{vm}$

$$\boxed{nC_{vm}(T_f - T_i) = -P_{ext}(V_f - V_i)} = -P_f(V_f - V_i)$$

$$n\frac{3}{2}R(T_f - T_i) = -P_fV_f + P_fV_i = -\underbrace{P_fV_f}_{nRT_f} + \frac{P_f}{P_i}\underbrace{P_iV_i}_{nRT_i}$$

$$\cancel{n}\frac{3}{2}\cancel{R}T_f - \cancel{n}\frac{3}{2}\cancel{R}T_i = -\cancel{nR}T_f + \frac{P_f}{P_i}\cancel{nR}T_i$$

$$\frac{3}{2}T_f - \frac{3}{2}T_i = -T_f + \frac{P_f}{P_i}T_i \Longrightarrow \frac{5}{2}T_f = \left(\frac{3}{2} + \frac{P_f}{P_i}\right)T_i$$

$$T_f = \frac{2}{5}\left(\frac{3}{2} + \frac{P_f}{P_i}\right)T_i = \frac{2}{5}\left(\frac{3}{2} + \frac{9.00 \text{ bar}}{1.00 \text{ bar}}\right)300 \text{ K} = \boxed{\overset{T_f}{1260 \text{ K}}}$$

$$\Delta U = nC_{vm}(T_f - T_i) = 10.0 \text{ mol } \frac{3}{2} 8.314 \frac{\text{J}}{\text{K·mol}}(1260-300)\text{K} = \boxed{119.7 \text{ kJ}}$$

$$\Delta H = nC_{pm}(T_f - T_i) = 10.0 \text{ mol } \frac{5}{2} 8.314 \frac{\text{J}}{\text{K·mol}}(1260-300)\text{K} = \boxed{199.5 \text{ kJ}}$$

use $C_{pm} = C_{vm} + R = \left(\frac{3}{2} + \frac{2}{2}\right) = \frac{5}{2}R$

not reversible: $P_{gas} \neq P_{ext} \Longrightarrow$ do not use $C_{vm} \ln\left(\frac{T_f}{T_i}\right) = -R\ln\left(\frac{V_f}{V_i}\right)$

$C_{vm} = \frac{5}{2}R$

Ⓠ5 Reversible adiabatic expansion of N_2 gas.

$$\boxed{\begin{matrix} p_i = ? \\ T_i = 300\,K \end{matrix}} \xrightarrow[p = p_{ext}]{q=0} \boxed{\begin{matrix} p_f = 1.00\text{ bar} \\ T_f = 77\,K \end{matrix}}$$

$$dU = \overset{\text{adiabat}}{\cancel{dq}}^{\,0} + dw \qquad 1^{ST}\text{ Law} \qquad \text{ideal gas, so } dU = C_v dT$$

$$C_v dT = -p_{ext} dV \xRightarrow[(p=p_{ext})]{\text{reversible}} C_v dT = -p dV$$

$$C_v dT = nC_{vm} dT = -p dV = -\frac{nRT}{V} dV$$

$$nC_{vm} dT = nRT\frac{dV}{V} \Rightarrow \cancel{n}\frac{5}{2}R\,dT = -\cancel{n}RT\frac{dV}{V}$$

$$\frac{5}{2}\frac{dT}{T} = -\frac{dV}{V} \Rightarrow \frac{5}{2}\int_{T_i}^{T_f}\frac{dT}{T} = -\int_{V_i}^{V_f}\frac{dV}{V}$$

$$\frac{5}{2}\int_{\ln T_i}^{\ln T_f} d\ln T = -\int_{\ln V_i}^{\ln V_f} d\ln V$$

$$\frac{5}{2}(\ln T_f - \ln T_i) = -(\ln V_f - \ln V_i) \Rightarrow \underbrace{\frac{5}{2}\ln\left(\frac{T_f}{T_i}\right) = \ln\left(\frac{T_f}{T_i}\right)^{5/2} = \ln\left(\frac{V_f}{V_i}\right)^{-1}}_{\text{ok: but not convenient (don't know } V_f \text{ or } T_f)}$$

[[or]] Just use $C_{vm}\ln(T_f/T_i) = -R\ln(V_f/V_i)$ from equation sheet!

"exponentiate":

$$\left(\frac{T_f}{T_i}\right)^{5/2} = \left(\frac{V_f}{V_i}\right)^{-1} = \frac{V_i}{V_f} = \frac{\frac{nRT_i}{p_i}}{\frac{nRT_f}{p_f}} = \frac{T_i}{T_f}\frac{p_f}{p_i}$$

$$\frac{T_f}{T_i}\left(\frac{T_f}{T_i}\right)^{5/2} = \frac{p_f}{p_i} = \left(\frac{T_f}{T_i}\right)^{7/2} \Longrightarrow \frac{T_f}{T_i} = \left(\frac{p_f}{p_i}\right)^{2/7}$$

$$\frac{p_f}{p_i} = \left(\frac{77\,K}{300\,K}\right)^{7/2} = 0.00857 \qquad p_i = \frac{p_f}{0.00857} = \frac{1.00\text{ bar}}{0.00857}$$

$$\boxed{p_i = 117\text{ bar}}$$

Q6 In class, the differential for the heat dq_{rev} for an ideal gas

$$dq = C_V\,dT + p\,dV$$ "failed" the test for an exact differential

(reversible: $p_{ext} = p$)

significance: the state function $q(T,V)$ does not exist

$\Longrightarrow$ q is path-dependent

What about $$\frac{dq_{rev}}{T} = dS = \frac{C_v}{T}\,dT + \frac{p}{T}\,dV\ ?$$

The Test:

If dS is an exact differential, then

$$\left(\frac{\partial \frac{C_v}{T}}{\partial V}\right)_T \overset{?}{\underset{?}{=}} \left(\frac{\partial \frac{p}{T}}{\partial T}\right)_V$$

Left Side

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

(switch order of differentiation)

$$= T\left[\frac{\partial}{\partial T}\overset{0\text{ (ideal gas)}}{\cancel{\left(\frac{\partial U}{\partial V}\right)_T}}\right]_V = 0$$

Right Side

$$\left(\frac{\partial \frac{p}{T}}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\overset{\text{constant at fixed V}}{\frac{nR}{V}}\right)_V = 0$$

So what?

Significance:

Right Side = Left Side $\Longrightarrow$ dS is an exact differential

$\therefore$ The State function $S(T,V)$ exists

Later, we'll see S is the entropy