Chemistry 231 **Assignment #3** (due Tuesday, 02 October, in class)

1. **a)** The following equations for dH are both correct.

[4]

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \qquad (1)$$

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \qquad (2)$$

Which equation ((1) or (2)) is more convenient for calculating enthalpy changes? Explain.

b) Use $(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p$ to show $(\partial H/\partial p)_T = 0$ for an ideal gas.

2. Use $df = (2x/y^2)dx - (2x^2/y^3)dy$ to prove the function $f(x,y)$ exists. [2]

3. **a)** 75.0 L of helium (assumed to be an ideal gas with $C_{V\mathrm{m}} = 3R/2$) initially at 300 K and 1.00 bar is heated reversibly to 350 K at constant volume. Calculate ΔU, ΔH, q and w.

[6]

b) 75.0 L of helium (assumed to be an ideal gas with $C_{V\mathrm{m}} = 3R/2$) initially at 300 K and 1.00 bar is heated reversibly to 350 K at constant pressure. Calculate ΔU, ΔH, q and w.

c) More heat is required to heat the helium from 300 K to 350 K at constant pressure than at constant volume. Why?

4. Suspose a hatch on the International Space Station is accidentally opened, causing the air inside the Station to expand very rapidly and therefore adiabatically (no time for heat transfer) into the
[3] vacuum of outer space ($p_{\mathrm{external}} = 0$). For this expansion, show $\Delta T = \Delta U = \Delta H = q = w = 0$!

5. Air (assumed to be an ideal gas with $C_{V\mathrm{m}} = 5R/2$) initially at 0 °C and 0.800 bar is reversibly compressed to 1.00 bar under adiabatic conditions. Calculate ΔT and ΔU, ΔH, q, w for one mole
[4] of air.

6. A "Chinook" is a wind that blows eastward over the Rocky Mountains, warming significantly as the air flows downward onto the foothills and the prairie. Why is a Chinook a warm wind? Give
[1] a brief thermodynamic explanation. *Hint*: Refer to Question 5.

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Q1 a) $dH = C_p\,dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp$

is more convenient for enthalpy calculations because is expressed in terms of measurable quantities: C_p, V, T, $(\partial V/\partial T)_p$

$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$ is correct, but not useful for practical calculations unless $(\partial H/\partial T)_p$ and $(\partial H/\partial p)_T$ can be evaluated

b) $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$

for an ideal gas $\left(V = \frac{nRT}{p}\right)$:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left[\frac{\partial\left(\frac{nRT}{p}\right)}{\partial T}\right]_p$$

$$= V - T\frac{nR}{p}\left(\frac{\partial T}{\partial T}\right)_p$$

$$= V - \frac{TnR}{p}$$

$$= \frac{nRT}{p} - \frac{nRT}{p}$$

$$= 0$$

Q2 $\quad df = \frac{2x}{y^2}\,dx - \frac{2x^2}{y^3}\,dy$

$$df = g(x,y)\,dx + h(x,y)\,dy$$

$$g(x,y) = \frac{2x}{y^2} \qquad h(x,y) = -\frac{2x^2}{y^2}$$

the function $f(x,y)$ exists if:

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y \qquad \text{"The Test"}$$

$$\left(\frac{\partial g}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{2x}{y^2}\right)\right]_x = 2x\left(\frac{\partial \frac{1}{y^2}}{\partial y}\right)_x = (2x)\left(\frac{-2}{y^3}\right)$$

$$= -\frac{4x}{y^3} \qquad \left(\frac{dy^n}{dn} = ny^{n-1}\right)$$

$$\left(\frac{\partial h}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(\frac{-2x^2}{y^2}\right)\right]_y = -\frac{2}{y^2}\left(\frac{\partial x^2}{\partial x}\right)_y = \left(\frac{-2}{y^2}\right)2x$$

$$= -\frac{4x}{y^2}$$

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y = -\frac{4x}{y^3} \Rightarrow \text{the function } f(x,y) \text{ exists}$$

(Q3) 75.0 L of He at 300 K, 1.00 bar

number of moles $n = \frac{PV}{RT} = \frac{(1.00\,bar)(75.0\,L)}{(0.08314\,L\,bar\,K^{-1}mol^{-1})(300\,K)}$

$n = 3.007$ mol

a) 75.0 L of He at 300 K, 1.00 bar initially is heated at constant volume to 350 K

$w = -\int P_{external}\,\cancel{dV}^{\,0}$ constant volume : $dV = 0$

$w = 0$

$\left(\begin{array}{l} \text{note: } C_V = nC_{V,m} = n(3/2)R \\ C_p = nC_{p,m} = n(C_{V,m} + R) = n(5/2)R \end{array}\right)$

for an ideal gas, the internal energy depends only on the temperature and $dU = C_V dT$

$$\Delta U = \int_{U_i}^{U_f} dU = \int_{T_i}^{T_f} C_V\,dT = \int_{T_i}^{T_f} nC_{V,m}\,dT = \int_{T_i}^{T_f} n\frac{3}{2}R\,dT$$

$$\Delta U = n\frac{3}{2}R\int_{T_i}^{T_f} dT = n\frac{3}{2}R(T_f - T_i)$$

$$\Delta U = (3.007\text{ mol})\frac{3}{2}(8.314\text{ J K}^{-1}\text{mol}^{-1})(350-300)\text{ K}$$

$\Delta U = 1875$ J $\qquad \Delta U = q + \cancel{w}^{\,0} = q = 1875$ J

for an ideal gas, the enthalpy depends only on T and

$$\Delta H = \int dH = \int C_p\,dT = \int nC_{p,m}\,dT = n\frac{5}{2}R\int dT$$

$$\Delta H = (3.007\text{ mol})\frac{5}{2}(8.314\text{ J K}^{-1}\text{mol}^{-1})(350-300)\text{K} = 3125\text{ J}$$

(Q3 cont.)

b) 75.0 L of He at 300 K, 1.00 bar initially is heated to 350 K at constant pressure

$$\Delta U = n \frac{3}{2} R \int_{300K}^{350K} dT = 1875\ J$$

$$\Delta H = n \frac{5}{2} R \int_{300K}^{350K} dT = 3125\ J$$

same ΔU, ΔH whether the gas is heated from 300 K to 350 K at const. V or const. p

U, H depend on T only

$$q = \Delta H = 3125\ J \quad (q = \Delta H \text{ at const. } p)$$

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

(pressure constant $p = p_{ext} = 1.00$ bar)

$$w = -p(V_f - V_i)$$

$$w = -pV_f + pV_i = -nRT_f + nRT_i = -nR(T_f - T_i)$$

$$w = -(3.007\ \text{mol})(8.314\ J\ K^{-1}\ \text{mol}^{-1})(350-300)\ K$$

$$w = -1250\ J$$

(or, ~~use~~ $w = \Delta U - q = 1875J - 3125J =$)

c) More heat is required for heating the gas at constant pressure because work is also being done by the gas to push back the surroundings

$$\Delta U_{const.V} = \Delta U_{const\ p}$$

$$q_v + \underbrace{w_v}_{0} = q_p + w_p$$

$$q_p = q_v - w_p = 1875J - (-1250)J = 3125J$$

Q4 adiabatic expansion into a vacuum ($P_{ext} = 0$)

$$dU = dq + dw$$

$$dU = \underbrace{dq}_{0\,(\text{adiabatic})} - \underbrace{P_{ext}}_{0}\, dV$$

$dU = 0$ $\quad dq = 0 \quad dw = 0$

the internal energy of an ideal gas depends only on T

if $dU = 0$ then $dT = 0$

H also depends only on T $\quad$ so $dH = 0$

Q5 reversible adiabatic compression of 1.00 mol of air from 0°C, 0.800 bar (on a mountain top) to 1.00 bar (on the prairie)

assume ideal gas behavior, and $C_{Vm} = \frac{5}{2}R$ (constant)

from class notes (or the equation sheet):

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \qquad \gamma = \frac{C_{pm}}{C_{Vm}} = \frac{C_{Vm}+R}{C_{Vm}} = \frac{(7/2)R}{(5/2)R} = \frac{7}{5}$$

$$\frac{P_i}{P_f} = \frac{V_f^{\gamma}}{V_i^{\gamma}} = \left(\frac{V_f}{V_i}\right)^{\gamma} = \left(\frac{nRT_f/P_f}{nRT_i/P_i}\right)^{\gamma} = \left(\frac{T_f}{T_i}\right)^{\gamma}\left(\frac{P_i}{P_f}\right)^{\gamma}$$

$$\left(\frac{T_f}{T_i}\right)^{\gamma} = \frac{P_i}{P_f} \Big/ \left(\frac{P_i}{P_f}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma} \qquad \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}} = \left(\frac{P_i}{P_f}\right)^{-2/7}$$

$$\frac{T_f}{T_i} = \left(\frac{0.80\text{ bar}}{1.00\text{ bar}}\right)^{-2/7} = 1.066 \qquad T_f = 1.066(273.15\text{ K})$$

$$T_f = 291\text{ K} \quad (18\,°\text{C})$$

(Q5 cont.)

per mole of air:

$$\Delta U_m = \int C_{V,m}\, dT = \int \tfrac{5}{2} R\, dT = \tfrac{5}{2} R (T_f - T_i)$$

$$\Delta U_m = \tfrac{5}{2} (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) (291-273)\ \mathrm{K} = 374\ \tfrac{\mathrm{J}}{\mathrm{mol}}$$

$$\Delta H_m = \int C_{p,m}\, dT = \int \tfrac{7}{2} R\, dT = \tfrac{7}{2} R (T_f - T_i)$$

$$\Delta H_m = \tfrac{7}{2} (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) (291-273)\ \mathrm{K} = 524\ \mathrm{J}$$

$q_m = 0$ (adiabatic)

$$\Delta H_m = w_m + q_m = w_m = 374\ \mathrm{J\,mol^{-1}}$$

(Q6) cool air on the mountains is at higher altitude and lower pressure than the air on the lower-altitude foothills and prairie

elevation $\approx$ 1000 m
$p \approx 0.8$ bar

as the air decends, the pressure rises and the air is compressed adiabatically

warms up (T increases) as the wind blows to lower altitudes (e.g. see Q5)

$\Rightarrow$ Chinooks are warm winds