Chemistry 231 **Tutorial #2**

1. Prove $$T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p = \frac{\beta^2 VT}{\kappa}$$

2. Use the general relation $C_p - C_V = \dfrac{\beta^2 VT}{\kappa}$ to calculate $C_{pm} - C_{Vm}$ at 25 °C and 1.00 bar for

   a) an ideal gas

   b) liquid water ($\beta = 0.000204\ \mathrm{K}^{-1}$, $\kappa = 0.0000459\ \mathrm{bar}^{-1}$, $\rho = 0.997\ \mathrm{g\ cm}^{-3}$).

3. Calculate $(\partial p/\partial T)_V$ at 25 °C and 1.00 bar for **a)** an ideal gas

   b) liquid water

4. **a)** Give a brief definition of a "Joule-Thomson (JT) expansion"

   b) Give two important practical applications of JT expansions.

   c) What is the significance of the "inversion temperature" in JT expansions?

   d) Why would you expect ammonia to show a larger JT effect than methane?

5. Use the expression $\mu_{JT} = -V_m(1 - \beta T)/C_{pm}$ derived in class to calculate the JT coefficient for

   a) helium (assumed to be an ideal gas)

   b) liquid water at 25 °C and 1.00 bar ($C_{pm} = 75.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$)

6. Calculate q, w, ΔU and ΔH for the combustion reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

   a) at 25 °C and a constant pressure 1.00 bar

   b) at 25 °C and constant volume (reactants initially at 1.00 bar).

Data at 25 °C:

$\Delta H_f^\circ(CH_4, g) = -74.6\ \mathrm{kJ\ mol^{-1}}$
$\Delta H_f^\circ(O_2, g) = 0$ (*why?*)
$\Delta H_f^\circ(CO_2, g) = -110.5\ \mathrm{kJ\ mol^{-1}}$

$$\Delta H_f^\circ(\mathrm{H_2O}, l) = -285.8 \text{ kJ mol}^{-1}$$

7. Calculate ΔH° for the reaction

$$\mathrm{H_2(g)} + \mathrm{F_2(g)} \rightarrow \mathrm{2HF(g)}$$

a) at 25 °C

b) at 1000 °C (state any approximations you make)

Data at 25 °C: $\Delta H_f^\circ(\mathrm{H_2}, \mathrm{g}) = 0$ $\quad C_{pm}^\circ(\mathrm{H_2}, \mathrm{g}) = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H_f^\circ(\mathrm{F_2}, \mathrm{g}) = 0$ $\quad C_{pm}^\circ(\mathrm{F_2}, \mathrm{g}) = 31.3 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H_f^\circ(\mathrm{HF}, \mathrm{g}) = -273.3 \text{ kJ mol}^{-1}$ $\quad C_{pm}^\circ(\mathrm{HF}, \mathrm{g}) = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$

8. Estimate the adiabatic flame temperature for the reaction of equimolar amounts of $\mathrm{H_2(g)}$ and $\mathrm{F_2(g)}$ initially at 25 °C. Use data from the previous question.

9. Why are combustion reactions in an oxygen atmosphere generally much hotter (and much more dangerous) than combustion reactions in air?

10. Why are ΔU and ΔH nearly identical for many chemical reactions involving liquids and solids?

11. Partial differential equations can be useful for calculating experimental errors.

To demonstrate this application, suppose the number of moles of ideal gas in a tank is to be determined by measuring the temperature and pressure of the gas and the volume of the tank and using

$$n = pV/RT$$

to calculate the number of moles of gas. If T, p, V and their errors are

310.5 (± 0.5) K $\qquad$ 11.7 (± 0.2) bar $\qquad$ 50.00 (± 0.05) L

estimate the resulting error in the calculated value of n. *Suggestion*: Start with

$$\mathrm{d}n = \left(\frac{\partial n}{\partial T}\right)_{p,V} \mathrm{d}T + \left(\frac{\partial n}{\partial p}\right)_{T,V} \mathrm{d}p + \left(\frac{\partial n}{\partial V}\right)_{T,p} \mathrm{d}V$$

12. To illustrate current research in thermochemistry, with important industrial and biochemical applications, visit the website of Prof. Peter Tremaine at the University of Guelph.

http://tremaine.cs.uoguelph.ca/peter-tremaine

Chem 231 $\boxed{\text{Tutorial \#2}}$

①
$$LS = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

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

cyclic rule on $\left(\frac{\partial p}{\partial T}\right)_V$

$$= \frac{T\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2}{-\left(\frac{\partial V}{\partial p}\right)_T}$$

inverse rule on $\left(\frac{\partial p}{\partial V}\right)_T$

$$= \frac{TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$

$\times \frac{1}{V}$ top and bottom

why? To get β and κ!

$$= \frac{TV\beta^2}{\kappa}$$

(used the definitions:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$
)

② a) for an ideal gas:

$\alpha = \frac{1}{T}$ $\qquad \kappa = \frac{1}{p}$ (from equation sheet)

recall

$$C_p - C_V = \frac{\alpha^2 V T}{\kappa} = \frac{\frac{1}{T^2} V T}{\frac{1}{p}} = \frac{pV}{T} = nR$$
$$= n(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$\therefore C_{pm} - C_{Vm} = R$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{nRT}{p}\right)\right]_p = \frac{1}{V}\frac{nR}{p}\frac{\partial T}{\partial T}$$
$$= \frac{nR}{pV} = \frac{nR}{nRT} = \frac{1}{T}$$ (if needed)

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left[\frac{\partial}{\partial p}\left(\frac{nRT}{p}\right)\right]_T = \left(-\frac{1}{V}\right) nRT \left(\frac{\partial \frac{1}{p}}{\partial p}\right)_T$$
$$= -\left(\frac{nRT}{V}\right)\left(\frac{-1}{p^2}\right) = \frac{nRT}{pV}\frac{1}{p} = \frac{1}{p}$$ (if needed)

b) $$C_p - C_V = \frac{\alpha^2 V T}{\kappa} = \frac{\alpha^2 n V_m T}{\kappa}$$

$$V_m = \frac{\text{molar mass}}{\text{density}} = \frac{18.01\,\mathrm{g\,mol^{-1}}}{0.997\,\mathrm{g\,cm^{-3}}} = 18.06\,\frac{\mathrm{cm^3}}{\mathrm{mol}} = 0.01806\,\frac{\mathrm{L}}{\mathrm{mol}}$$

$$C_p - C_V = \frac{(0.000204\,\mathrm{K^{-1}})^2\, n\,(0.01806\,\mathrm{L})(298\,\mathrm{K})}{(0.0000459\,\mathrm{bar^{-1}})}$$

$$= n(0.00488\,\mathrm{L\,bar\,K^{-1}\,mol^{-1}})$$

1 L bar = 100 J

$$= n(0.488\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$C_{pm} - C_{Vm} = 0.488\,\frac{\mathrm{J}}{\mathrm{K\,mol}}$

3. a) for an ideal gas:

$$\left(\frac{\partial p}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)\right]_V = \frac{nR}{V}\left(\frac{\partial T}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T}$$

$$= \frac{1.00\text{ bar}}{298\text{ K}} = 0.00336\text{ bar K}^{-1}$$

or// use $\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p = \dfrac{\left(\frac{\partial V}{\partial T}\right)_p}{-\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa}$

recall (see Q2) $\alpha = \frac{1}{T}$ and $\kappa = \frac{1}{p}$ (ideal gas)

so $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa} = \dfrac{\frac{1}{T}}{\frac{1}{p}} = \frac{p}{T} = 0.00336\text{ bar K}^{-1}$

b) for liquid water (can't use $pV = nRT$!)

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

(from equation sheet, and proved above)

$$= \frac{0.000204\text{ K}^{-1}}{0.0000459\text{ bar}^{-1}}$$

data from Q2.

$$= 4.44\text{ bar K}^{-1}$$

④ a) expansion of a fluid (usually a gas) at constant enthalpy under adiabatic conditions
$(\Delta H = 0)$ $(q = 0)$

can produce cooling, heating, or no temperature change

b) refrigeration / air conditioning

gas liquefaction

c) at the inversion temperature, $\mu_{JT} = 0 = \left(\frac{\partial T}{\partial P}\right)_H$

<u>no temperature change</u> for expansion or compression

d) NH_3 and CH_4 have similar molecular sizes and numbers of electrons, but NH_3 molecules can "hydrogen bond", leading to stronger $NH_3 \cdots NH_3$ attractions relative to $CH_4 \cdots CH_4$ attractions

increasing the attractive intermolecular forces increases μ_{JT}

in fact, NH_3 is an important refrigerant used in chillers and ice makers for industrial applications

⑤ a) for helium, treated as an ideal gas: use $\beta = \frac{1}{T}$

proof:

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{nRT}{p}\right)\right]_p = \frac{nR}{pV}\left(\frac{\partial T}{\partial T}\right)_p$$

$$= \frac{nR}{pV} = \frac{nR}{nRT} = \frac{1}{T} \quad \text{(ideal gas)}$$

$$\mu_{JT} = -\frac{V_m(1-\beta T)}{C_{pm}} = \frac{V_m\left(1-\frac{1}{T}T\right)}{C_{pm}} = \frac{V_m(1-1)}{C_{pm}}$$

$$\mu_{JT} = 0 \quad \text{(ideal gas)}$$

b) for liquid water at 25 °C and 1 bar:

$$\beta = 0.000204\ \text{K}^{-1} \qquad C_{pm} = 75.3\ \text{J K}^{-1}\,\text{mol}^{-1}$$

$$V_m = \frac{\text{molar mass}}{\text{density}} = \frac{M}{\rho} = \frac{18.015\ \text{g mol}^{-1}}{0.997\ \text{g cm}^{-3}}$$

$$V_m = 18.07\ \text{cm}^3\,\text{mol}^{-1} = 18.07\times10^{-6}\ \text{m}^3\,\text{mol}^{-1}$$

(SI units)

$$\mu_{JT} = -V_m\frac{1-\beta T}{C_{pm}} = \left(\frac{\partial p}{\partial T}\right)_H$$

$$= -\left(18.07\times10^{-6}\ \frac{\text{m}^3}{\text{mol}}\right)\frac{1-(0.000204\ \text{K}^{-1})(298\ \text{K})}{75.3\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

$$= -2.25\times10^{-7}\ \frac{\text{Pa}}{\text{K}} = -0.0225\ \frac{\text{bar}}{\text{K}}$$

$(\Delta n_{gas} = 1 - 3 = -2 \text{ mol})$

⑥ a) $CH_4(g) + 2O_2(g) \xrightarrow[1\text{ bar}]{25°C} CO_2(g) + 2H_2O(l)$

at 1 bar: $\Delta H = \Delta H^\circ = q$ (pressure constant)

(constant pressure) : $\Delta H = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$

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

$$= [-110.5 + 2(-285.8) - (-74.6) - 2(0)] \text{ kJ}$$

$$\Delta H_p = -607.5 \text{ kJ} = q_p = \Delta H^\circ$$

$p = 1 \text{ bar} = p^\circ$ (fixed)

$$w_p = -\int p_{ext}\, dV = -p^\circ \int dV$$

$$w_p = -p^\circ(V_{prod.} - V_{reactants})$$

negligible!

$$= -p^\circ[V_m(CO_2,g) + \cancel{2V_m(H_2O,l)} - V_m(CH_4,g) - 2V_m(O_2,g)]$$

$$= -p^\circ[-2V_m(\text{ideal gas})]$$

$$= -p^\circ \Delta V_{gas} = -RT\Delta n_{gas} = -RT(-2 \text{ mol})$$

$$= +(8.314 \text{ J K}^{-1} \text{mol})(298 \text{ K})(2 \text{ mol})$$

$w_p = 4.95$ kJ (work is positive, system compressed) $\Delta n_{gas} = -2$ mol

$$\Delta U_p^\circ = q_p + w_p = \Delta H^\circ - RT\Delta n_{gas} = -607.5 + 4.95$$

$$\Delta U_p^\circ = -602.6 \text{ kJ}$$

(6. cont)

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

at constant volume

$$w = -\int p_{ext}\,dV = 0 \qquad (dV = 0)$$

easy!

to calculate ΔU at constant volume, take ΔU_p at constant pressure from part a, then subtract w_p, to bring the gas back to constant volume

$$\Delta U_v = \Delta U_p - w_p = \Delta H_p + RT\Delta n_g$$

$$= -602.6\ \text{kJ} - 4.95\ \text{kJ}$$

$$= -607.5\ \text{kJ}$$

$$\Delta U_v = q_v + \cancelto{0}{w_v} \qquad \text{so } q_v = -607.5\ \text{kJ}$$

$$\Delta H_v = \Delta(U + PV)_v = \Delta U_v + \Delta(PV)$$

only important for gases

$$= \Delta U_v + \Delta(n_{gas}RT) = \Delta U_v + RT\Delta n_{gas}$$

$$= -607.5\ \text{kJ} + (8.314\ \text{J K}^{-1}\text{mol}^{-1})(298\ \text{K})(-2\ \text{mol})$$

$$= -607.5 - 4.95 = -612.4\ \text{kJ}$$

⑦ a) $H_2(g) + F_2(g) \xrightarrow[1\ \text{bar}]{25\,°C} 2HF(g)$

$$\Delta H° = 2\Delta H^°_{fm}(HF,g) - \Delta H^°_{fm}(H_2,g) - \Delta H^°_{fm}(F_2,g)$$

$$= 2(-273.3) - 0 - 0$$

$$= -546.6\ \text{kJ}$$

b) $T_1 = 298\,K$ $T_2 = (1000 + 273) = 1273\,K$

$$\Delta H°(T_2) = \Delta H°(T_1) + \int_{T_1}^{T_2} \Delta C_p°\, dT$$

$$\approx \Delta H°(T_1) + \Delta C_p°(T_2 - T_1)$$

(assume $\Delta C_p°$ is constant)

$$\Delta C_p° = 2C^°_{pm}(HF,g) - C^°_{pm}(H_2,g) - C^°_{pm}(F_2,g)$$

$$= 2(29.1) - 28.8 - 31.3 = -1.9\ \text{J K}^{-1}$$

$$\Delta H°(1273\,K) = \Delta H°(298\,K) + \Delta C_p°(1273\,K - 298\,K)$$

$$= -546.6\ \text{kJ} + (-1.9\ \text{J K}^{-1})(975\,K)$$

$$= -546.6\ \text{kJ} - 1852\ \text{J}$$

$$\Delta H°(1273\,K) = -548.4\ \text{kJ}$$

(8.) adiabatic flame temperature for

$$H_2(g) + F_2(g) \rightarrow 2HF(g)$$

$T_i = 298\ K$ $\Delta H^\circ(T_i) = -546.6\ kJ$
(from previous question)

$$C_p(\text{products}) = 2\,C_{pm}(HF, g)$$

$$= 2(29.1\ J\ K^{-1})$$

$$= 58.2\ J\ K^{-1}$$

$$T_f \approx T_i - \frac{\Delta H^\circ(T_i)}{C_p(\text{products})}$$

$$= 298K - \frac{-546{,}600\ J}{58.2\ J\ K^{-1}}$$

$$= 298K + 9392\ K$$

$$= 9690\ K$$

assumed constant C_p (products)

actual flame temperature is lower

because vibrations increase C_p (products)

at high temperatures

⑨ If fuel is burned in pure oxygen (no inert N_2), all of the heat released is used to heat the reaction products.

If fuel is burned in air, some of the heat released is used to heat the inert nitrogen present in air, so the heat capacity is larger, and a lower flame temperature is reached

The higher temperatures reached by burning fuel in oxygen increases the rate constants for combustion reactions, igniting materials (e.g., metals) that would not normally burn at lower temperatures, generating even higher temperatures.

⑩

$$H \equiv U + pV$$

$$\Delta H = \Delta U + \overbrace{\Delta(pV)}^{\text{important only for gases (large volumes)}}$$

the internal energy change and the enthalpy change differ by $\Delta(pV)$. The molar volumes of solids and liquids are typically 1000's of times smaller than gas volumes
Also, The volumetric thermal expansion coefficients and isothermal compressibilities of solids and liquids are very low compared to the corresponding values for gases (Tables 3.1, 3.2), so volume changes for liquids and solids are small

$$n = \frac{pV}{RT}$$

method: error δx in x produces error $\frac{\partial f}{\partial x}\delta x$ in f

⑪ The changes dT, dp, dV in T, p, V produce the following change in n

$$dn = \left(\frac{\partial n}{\partial T}\right)_{p,V} dT + \left(\frac{\partial n}{\partial p}\right)_{T,V} dp + \left(\frac{\partial n}{\partial V}\right)_{T,p} dV$$

$$\left(\frac{\partial n}{\partial T}\right)_{p,V} = \left[\frac{\partial}{\partial T}\left(\frac{pV}{RT}\right)\right]_{p,V} = \frac{pV}{R}\frac{\partial \frac{1}{T}}{\partial T} = \frac{pV}{R}\left(\frac{-1}{T^2}\right) = -\frac{n}{T}$$

$$\left(\frac{\partial n}{\partial p}\right)_{T,V} = \left[\frac{\partial}{\partial p}\left(\frac{pV}{RT}\right)\right]_{T,V} = \frac{V}{RT}\frac{\partial p}{\partial p} = \frac{V}{RT} = \frac{n}{p}$$

$$\left(\frac{\partial n}{\partial V}\right)_{T,p} = \left[\frac{\partial}{\partial V}\left(\frac{pV}{RT}\right)\right]_{T,p} = \frac{p}{RT}\frac{\partial V}{\partial V} = \frac{p}{RT} = \frac{n}{V}$$

$$n = \frac{pV}{RT} = \frac{11.7 \text{ bar}\,(50.00 \text{ L})}{(0.08314 \text{ L bar K}^{-1}\text{ mol}^{-1})(310.5 \text{ K})}$$

$$n = 22.66 \text{ mol}$$

error in n due to error in T

$$= \left(\frac{\partial n}{\partial T}\right)_{p,V}(\text{error in } T) = \left(-\frac{n}{T}\right)(\pm 0.5\text{K})$$

$$= \frac{22.66 \text{ mol}}{310.5 \text{ K}}(\pm 0.5\text{K}) = \pm 0.036 \text{ mol}$$

(11 cont.)

error in n due to error in p

$$= \left(\frac{\partial n}{\partial p}\right)_{T,V} (\text{error in } p) = \frac{n}{p}(\pm 0.2 \text{ bar})$$

$$= \frac{22.66 \text{ mol}}{11.7 \text{ bar}}(\pm 0.2 \text{ bar}) = \pm 0.39 \text{ mol}$$

error in n due to error in V

$$= \left(\frac{\partial n}{\partial V}\right)_{T,p} (\text{error in } V) = \frac{n}{V}(\pm 0.05 \text{ L})$$

$$= \frac{22.66 \text{ mol}}{50.00 \text{ L}}(\pm 0.05 \text{ L}) = \pm 0.022 \text{ mol}$$

$$\text{total error in } n = \overset{\text{from } T}{(\pm 0.036 \text{ mol})} + \overset{\text{from } p}{(\pm 0.39 \text{ mol})} + \overset{\text{from } V}{(\pm 0.022 \text{ mol})}$$

$$= \pm 0.45 \text{ mol}$$

important: notice that most of the error in n is from the error in p

used:

$$\pm \Delta n = \left(\pm \frac{\partial n}{\partial T}\Delta T\right) + \left(\pm \frac{\partial n}{\partial p}\Delta p\right) + \left(\pm \frac{\partial n}{\partial V}\Delta V\right)$$

another solution: (easier!)

notice $$dn = \left(\frac{\partial n}{\partial T}\right)_{p,V} dT + \left(\frac{\partial n}{\partial p}\right)_{T,V} dp + \left(\frac{\partial n}{\partial V}\right)_{T,p} dV$$

$$dn = \frac{-n}{T}\,dT + \frac{n}{p}\,dp + \frac{n}{V}\,dV$$

simplifies to (in terms of relative changes)

$$\frac{dn}{n} = -\frac{dT}{T} + \frac{dp}{p} + \frac{dV}{V}$$

fractional (relative) error in n is the sum of the fractional errors in T, p, V

$\pm\dfrac{0.5\text{ K}}{310.5\text{ K}} = \pm 0.16\,\%$ error in T

$\pm\dfrac{0.2\text{ bar}}{11.7\text{ bar}} = 1.7\,\%$ error in p ← largest source of error

$\pm\dfrac{0.05\text{ L}}{50.00\text{ L}} = 0.10\,\%$ error V

$(0.16 + 1.7 + 0.10) = 1.96\,\%$

total:

$1.96 \sim 2.0\,\%$ error in n:

2.0% of $n = 22.66$ mol

$= \pm\, 0.45$ mol