Two moles of gas at 1 bar and 298 K are compressed at constant T by use of 5 bar pressure. How much work is done on gas? If the compression is driven by 100 kg mass, how far will it fall in the earth's gravitational filed?

What is given:
n = 2 moles
p_1 = 1 bar
p_2 = 5 bar
T= 298 K
Compression === work is add to the system ==== positive

$$W = -p_2(V_2 - V_1) = -p_2\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right)$$

$$W = -nRT\left(1 - \frac{p_2}{p_1}\right)$$

W = -(2 mole) (8.314 J K-1 mole-1)(298 K) (1-(5/1))
=+19820 J = 19.82 kJ

Work = h m g
H = work/(m g) = 19820 J /[(100kg)(9.8 m s⁻²)] = 20.22 m

Enthalpy

"The heat absorbed in a process at constant pressure is equal to the change in enthalpy if the only work done is reversible pressure-volume work"

$$\Delta H = H_2 - H_1 = q_p$$

This means that any ΔH for a system can be obtained by going from the initial to final state under constant pressure conditions and measuring the heat that develops.

For example, the heat of a reaction ΔH can be obtained by doing a reaction in the open (a constant pressure path) and measuring the resulting heat. This is very convenient because we can get what we want, the heat of a reaction, without having to do anything very special with regard to conditions i.e. establishing the path.

It's for this reason that the constant pressure path is the most special of all and why we have tables of ΔH values and not ΔU values.

$$(dq)_p = dH \quad \text{and} \quad C_p = \frac{(dq)_p}{dT} \qquad \therefore C_p = \frac{dH}{dT} \quad \text{at constant presure}$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \qquad \text{This is analogous to the definition for } C_V$$

The relation between the two heat capacities can be derived easily for IDEAL gases.

$H = U + pV$ and $pV = nRT$

$dH = dU + d(pV)$ and $d(pV) = nRdT$

$\therefore dH = dU + nRdT$

For an ideal gas

$dH = C_p \, dT$ and $dU = C_V \, dT$

$C_p \, dT = C_V \, dT + nR \, dT$

Thus dividing by dT gives

$C_p - C_V = nR$ or

$C_{p,m} - C_{V,m} = R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Since $C_{p,m}$ values for gases are about 30 J K^{-1} mol^{-1} the difference is large.

$$C_{p,m} - C_{V,m} = R$$

$$C_{p,m} = C_{V,m} + R$$

For mono atomic gas

$$C_{V,m} = 3/2 \, R$$

$$\text{and } C_{p,m} = 5/2 \, R$$

10 g of CO_2 (molecular weight 44 g mol^{-1}, $C_{p,m}$ = 46.5 J/K mol) behaving as an ideal gas are heated from 200 K to 430 K reversibly and isobarically at p = 0.75 atm. Analyze the signs and the equations to be used for w, q, ΔU and ΔH. Calculate the values and then comment on the reasonableness of the answers. First write as much information about the initial and final state as possible.

moles of gas   n= 10 g/44 g mol^{-1} = 0.227

initial state

T_1 = 200 K

p_1 = 0.75 atm

$V_1 = nRT_1/p_1$

$= \dfrac{.227 \times .08206 \times 200}{0.75}$

= 4.967 L

final state

T_2 = 430 K

p_2 = 0.75 atm

$V_2 = nRT_2/p$

$= \dfrac{.227 \times .08206 \times 430}{0.75}$

=10.67 L   *expansion so $V_2 > V_1$*

Analysis

(i) isobaric, reversible $\therefore w = -p\Delta V$;   *gas expansion* $\therefore w<0$

(ii) *isobaric* $\therefore$ $q_p = C_p\Delta T = nC_{p,m}\Delta T = \Delta H$; *T increases* $\therefore$ **heat absorbed q>0**

$\Delta U = w + q$; *since heat absorbed and T increases* $\Delta U > 0$

moles of gas   n= 10 g/44 g mol^{-1} = 0.227

initial state   **final state**

T_1 = 200 K T_2 = 430 K
p_1 = 0.75 atm p_2 = 0.75 atm
$V_1 = nRT_1/p_1$ $V_2 = nRT_2/p$
$\quad$ = $\dfrac{.227 \times .08206 \times 200}{0.75}$ $\quad$ = $\dfrac{.227 \times .08206 \times 430}{0.75}$

$\quad$ = 4.967 L   =10.67 L   *expansion so $V_2 > V_1$*

Most work, heat and energy change calculations are less than 5 kJ unless the number of moles is very large or the changes in pressure, temperature or volume are very large

Calculations and *Comments*

(i) work

w = - pΔV = -0.75 atm x(10.67 – 4.967)L = - 3.77 L atm x 101.3 J/L atm   =
-382 J   *sign is as predicted (magnitude < 5 kJ is reasonable)*

(ii) heat

q_p = $nC_{p,m}\Delta T$ = 0.227 mol x 46.5 J K^{-1} mol^{-1} x (430 –200) K
= 2428 J or 2.43 kJ   = ΔH   *sign as predicted magnitude OK*

(iii) energy

ΔU = w + q = -382 + 2428 = 2046 J or 2.05 kJ *sign as predicted*
$\qquad\qquad\qquad\qquad\qquad\qquad$ *magnitude OK*

Adiabatic process with gases

If a gas system expands adiabatically (no heat is gained or lost by the gas) against external pressure p_{ext}

$$dU = dw = -p_{ext}\, dV$$

This apply for any adiabatic process, reversible or irreversible , if PV work kind.

If p_{ext} = zero (adiabatic expand into vacuum) no work is done and there is no change in U. If the expand is opposed by p_{ext}, work is done on the surrounding, and the temperature drops as internal energy converted into work, so

$$\int_{U_1}^{U_2} \delta U = - \int_{V_1}^{V_2} p_{ext}\, dV$$

$$\Delta U = U_2 - U_1 = W$$

For an ideal gas, U is a function of T only so,

$$dU = C_V dt$$

If C_V is independent of temperature,

$$\int_{U_1}^{U_2} dU = C_V \int_{T_1}^{T_2} dT$$

$$\Delta U = U_2 - U_1 = C_V (T_2 - T_1)$$

$$W = \Delta U = C_V \int_{T_1}^{T_2} dT = C_V (T_2 - T_1)$$

For an ideal monatomic gas

$$\Delta U = nC_V \Delta T$$

(all the energy going into heating the gas, no work is being done because $\Delta V = 0$) &

$$\Delta H = \Delta U + \Delta(PV) \text{ or}$$

$$\Delta H = \Delta U + nR\Delta T \text{ or}$$

$$\Delta H = nC_V \Delta T + nR\Delta T = n(C_V + R)\Delta T \text{ or}$$

$$\Delta H = nC_P \Delta T$$

A mole of monoatomic ideal gas at 1 bar and 273.15 K is allowed to expand adiabatically against pressure 0.395 bar until equilibrium is reached (a) what is the final temperature, (b) what is the final volume, (c) how much work is done, (d) what is the change in the internal energy of the gas?

What is given:

n = 1 mole, p_1 = 1 bar = 10^5 Pa (N/m²), T = 273.15 K, p_2 = 0.395 bar = 0.395 x 10^5 Pa (N/m²), C_v = 3/2 R

(a) final temperature

$$V_1 = \frac{nRT}{P_1} = \frac{(1mol)(8.314JK^{-1}mol^{-1})(2273.15K)}{1x10^5 Pa} = 0.0227m^3$$

$$W = -p_{ext}(V_2 - V_1) = C_V(T_2 - T_1)$$

$$W = -0.395x10^5 Pa(V_2 - 0.0227m^3) = \frac{3}{2}R(T_2 - 273.15)$$

$$V_2 = \frac{nRT_2}{P_2} = \frac{(1mol)(8.314JK^{-1}mol^{-1})(T_2)}{0.395x10^5 Pa}$$

T_2 can be calculated = 207.09 K

(b) V_2

$$V_2 = \frac{nRT_2}{P_2} = \frac{(1mol)(8.314JK^{-1}mol^{-1})(207.04K)}{0.395x10^5\,Pa} = 0.04358m^3$$

(c) W = -p$_{ext}$(V$_2$-V$_1$) = -(0.395 x 10^5 Pa)(0.04358m³-0.0227m³)
= -825 J mol^{-1}

(d) ΔU = W =-p$_{ext}$(V$_2$-V$_1$) = C$_v$(T$_2$-T$_1$) =(3/2)R x (207.04 K-273.15 K)
= -825 J mol^{-1}

For adiabatic reversible expansion process:

$$C_{V,m}dT = -PdV_m = -\frac{RT}{V_m}dV_m$$

$$C_{V,m}\frac{dT}{T} = -\frac{R}{V_m}dV_m$$

If the heat capacity is independent of temperature T, then

$$C_{V,m}\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_{1,m}}^{V_{2,m}}\frac{dV_m}{V_m}$$

$$C_{V,m}\ln\frac{T_2}{T_1} = R\ln\frac{V_{1,m}}{V_{2,m}} = (C_{p,m} - C_{V,m})\ln\frac{V_{1,m}}{V_{2,m}}$$

$$\ln\frac{T_2}{T_1} = (\frac{C_{p,m}}{C_{V,m}} - 1)\ln\frac{V_{1,m}}{V_{2,m}}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_{1,m}}{V_{2,m}}\right)^{\left(\frac{C_{p,m}}{C_{V,m}}-1\right)} = \left(\frac{V_{1,m}}{V_{2,m}}\right)^{(\alpha-1)}$$

$$\alpha = \left(\frac{C_{p,m}}{C_{v,m}}\right)$$

From the ideal gas law: $\quad \left(\frac{p_2 V_{2,m}}{p_1 V_{1,m}}\right) = \left(\frac{T_2}{T_1}\right)$

$$\therefore \left(\frac{p_2 V_{2,m}}{p_1 V_{1,m}}\right) = \left(\frac{V_{1,m}}{V_{2,m}}\right)^{\alpha-1}$$

$$\therefore p_2 V_{2,m}^{-\alpha} = p_1 V_{1,m}^{-\alpha}$$

One mole of an ideal mono atomic gas is allowed to expand adiabatically and reversibly from 22.7 L mol^{-1} at 1 bar and 0ºC to a volume of 45.4 L mol^{-1}.
Calculate the final pressure and temperature.
How much work is done? Where α = [(5/2)R/(3/2)R] = 5/3

What is given:
n = 1 mole, $V_{1,m}$ =22.7 L mol^{-1} p_1 = 1 bar , T_1= 0ºC = 273.15 K
$V_{2,m}$ =45.4 L mol^{-1} , α = 5/3
p_2 = ? bar , T_2= ? K

$$p_2 V_{2,m}^{-\alpha} = p_1 V_{1,m}^{-\alpha}$$

$$p_2 = p_1 \left(\frac{V_{1,m}}{V_{2,m}}\right)^{\alpha} = 1bar \left(\frac{22.7 L.mol^{-1}}{45.4 L.mol^{-1}}\right)^{5/3} = 0.315 bar$$

$$T_2 = T_1 \left(\frac{V_{1,m}}{V_{2,m}}\right)^{\alpha-1} = (273.15K)\left(\frac{22.7 L.mol^{-1}}{45.4 L.mol^{-1}}\right)^{\left(\frac{5}{3}-1\right)} = 17207K$$

15

$$W = \int_{T1}^{T2} C_{V,m} dT = C_{V,m} \Delta T =$$

$$= \left(\frac{3}{2}\right) R(172.07K - 273.15K)$$

$$= -1261 J.mol^{-1}$$

Work is negative (expansion) the sign is correct

Thermochemistry

"It deal with heat produced by chemical reactions and solution processes"
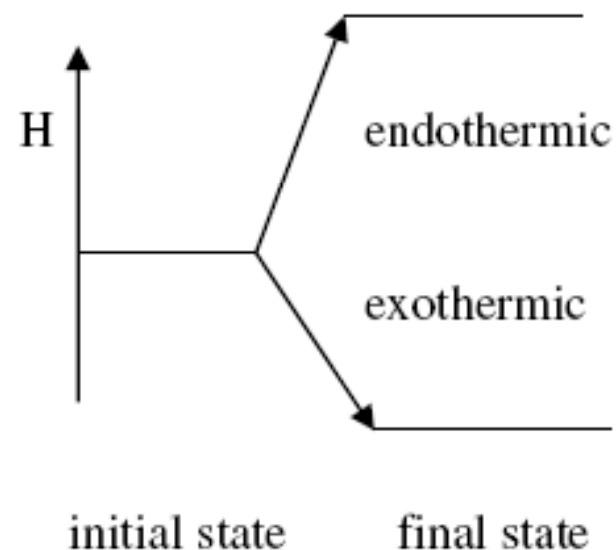
Exothermic Process

enthalpy decreases
$\Delta H < 0$
heat given off
energy decreases
    (usually)
final state more stable

q is negative

Endothermic Process

enthalpy increases
$\Delta H > 0$
heat absorbed
energy increases
    (usually)
final state less stable

q is positive

STANDARD STATE: ΔH values in tables are given for substances in a definite state, called the standard state indicated by superscript θ.

The standard state of a substance at a particular temperature is the most stable state of the substance under 1 atm of pressure [can also use 1 bar = 105 Pa = 0.9869 atm].

Note that the standard state can be for any temperature but for practical purposes we use 25 °C or 298 K. The standard state of some elements at 1 atm and 298 K is given below.

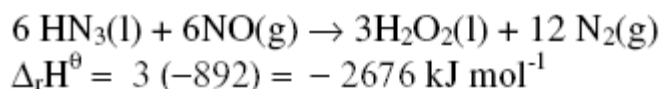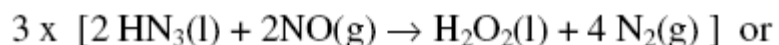| Element	Standard State	Element	Standard State
hydrogen	$H_2(g)$	oxygen	$O_2(g)$
chlorine	$Cl_2(g)$	argon	$Ar(g)$
iodine	$I_2(s)$	bromine	$Br_2(l)$
iron	$Fe(s)$	carbon	$C(s;graphite)$

Standard Heat of Reaction:

The standard heat of a reaction is the sum of the standard heats of formation of products minus the sum of the standard heats of formation of reactants [**Don't forget the stoichiometric coefficients of the balanced reaction**].

$$\Delta_r H^\theta = \sum_{products} \nu \, \Delta_f H^\theta - \sum_{reactants} \nu \, \Delta_f H^\theta$$

$$2\,NH_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4\,N_2(g)$$
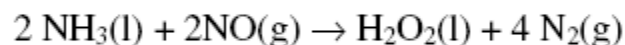
$$\Delta_r H^\theta = \Delta_f H^\theta[H_2O_2(l)] + 4\,\Delta_f H^\theta[N_2(g)] - 2\,\Delta_f H^\theta[HN_3(g)] - 2\,\Delta_f H^\theta[NO(g)]$$

$$= \quad -187.8 \quad + \quad 4\,(0) \quad - 2\,(264.0) \quad - 2\,(90.3)$$

$$= -892 \text{ kJ mol}^{-1}$$

Note that the units of the heat of formation are kJ mol^{-1} and that the stoichiometric coefficient ν has no units. Thus the units of the heat of reaction are kJ mol^{-1}. The mol^{-1} unit is to be understood as "per mol of reaction as written". This ensures that if the reaction is multiplied by any numeric factor then the heat of reaction will increase by the same factor. Thus for the reaction.

$$3 \times [2\,HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4\,N_2(g)\,] \text{ or}$$

$$6\,HN_3(l) + 6NO(g) \rightarrow 3H_2O_2(l) + 12\,N_2(g)$$
$$\Delta_r H^\theta = 3\,(-892) = -2676 \text{ kJ mol}^{-1}$$

DEFINITION of Standard Heat of Formation of Compounds:

This is the heat required to form the compound [in its most stable form] from its constituent elements in their standard states. Thus we need to know the most stable state of the compound and elements in order to be able to write the formation reaction.

For example, the most stable state of water at 1 atm, 298K is the liquid state and its heat of formation is not the same as that of gaseous water (steam).

To write the formation reaction just look at the elements that make up the compound and write the most stable state of these elements.

Formation Reaction	Experimental Heat of Reaction kJ mol^{-1}	
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	-285	is defined as $\Delta_f H^\theta[H_2O(l)]$
$3 H_2(g) + 6 C(s) \rightarrow C_6H_6(l)$	49.0	is defined as $\Delta_f H^\theta[C_6H_6(l)]$
$Na(s) + \frac{1}{2} Br_2(l) \rightarrow NaBr(s)$	-361	is defined as $\Delta_f H^\theta[NaBr(s)]$

NOTE: The heats of formation of ELEMENTS in their standard states is $\equiv$ zero

i.e. $\Delta_f H^\theta[H_2(g)] = \Delta_f H^\theta[Na(s)] = \Delta_f H^\theta[Br_2(l)] = 0$

Reaction Enthalpy [H_r]

Heat production is connected with chemical reaction.

From the first law of thermodynamics:

$$dU = dq - pdV$$

$$dq = dU + pdV$$

and $\qquad$ $H = U + pV$

By differential: $dH = dU + pdV + Vdp$

By substitution: $dH = dq + Vdp$

For a system containing n species and at constant p:

Partial molar enthalpies of species i $\quad \therefore \quad dH = \sum_{i=1}^{N} H_{i,m} \, dn_i$

n_i is the amount of substance i

But $dn_i = \nu_i d\xi$ for a reaction

Where ν_i is the stoichiometric number of reactant i

and ξ is the extent of reaction

$$dH = dq_p = \sum_{i=1}^{N} \nu_i H_{i,m} d\xi$$

The reaction enthalpy will be:

$$\Delta_r H = \left(\frac{dH}{d\xi}\right)_{T,p} = \left(\frac{dq_p}{d\xi}\right) = \sum_{i=1}^{N} \nu_i H_{i,m}$$

It is the derivative of the enthalpy of the system with respect to the extent of reaction.

If one mole of reaction occur=== $\therefore \Delta\xi = 1\text{mol}$

and ΔH =(1mol) Δ$_r$H

What is the meaning of one mole of rxn?

- $H_2 + \dfrac{1}{2}O_2 \rightarrow H_2O$ one mole of rxn

- $2H_2 + O_2 \rightarrow 2H_2O$ two mole of rxn

- ΔH has SI units (Joule) whereas $\Delta_r H$ has SI units Joule mol^{-1}

- If reactants and products are in their standard states:

$$\Delta_r H^{O} = \sum_{i=1}^{N} \nu_i H_{i,m}$$

The standard states are define as follow:

1. A pure gas at a given temperature is ideal gas at one bar pressure.

2. A pure liquid at a given temperature and at one bar pressure.

3. A pure crystalline substance at a given temperature and at one bar pressure.

4. A substance as solution with 1 molality (1mol kg^{-1}) at a given temperature and at one bar pressure.

Thermochemistry LAWs

- **Lavoisier:** The heat absorbed in decomposing a compound must be equal to the heat evolved in its formation under the same conditions.

- **Hess:** The overall heat of a chemical reactions at constant pressure is the same, regardless of the intermediate steps involved.

- Both principles are in good agreement with the First Law of Thermochemistry.

- It is possible to calculate the enthalpy changes for reactions that cannot be studied directly.
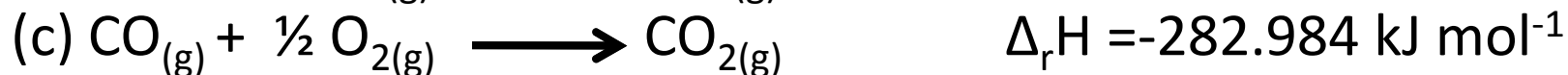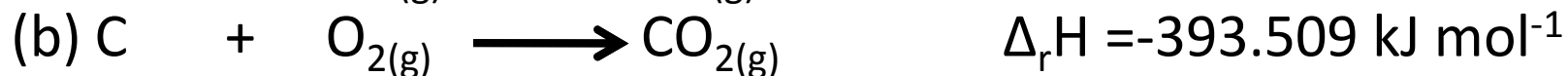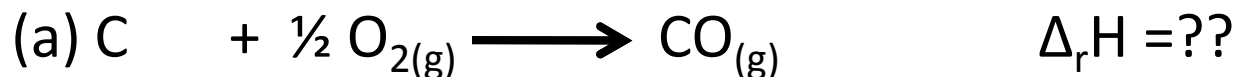
Example:

How to get the $\Delta_f H^\theta$ for the oxidation of glycine(aq) → urea(aq) using known data. This reaction is of interest since urea is the main oxidative metabolic product of amino acids.
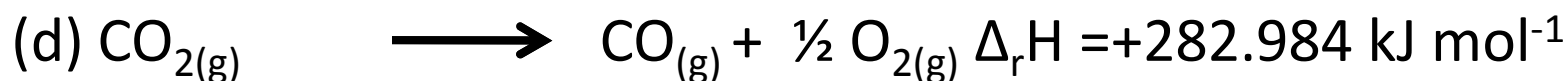
$$3\ O_2(g) + 2\ NH_2CH_2COOH\ (aq) \rightarrow NH_2CONH_2(aq) + 3\ CO_2(g) + 3H_2O(l)$$

glycine　　　　　　　　　　urea
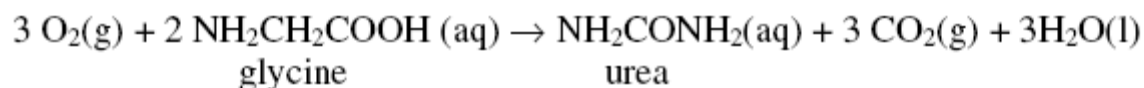
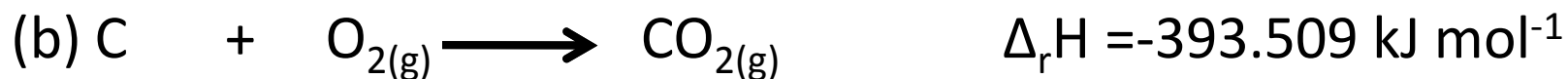|	Reaction	$\Delta_r H^\theta$ /kJ mol^{-1}	
(a)	oxidation of solid glycine to give CO_2, H_2O and NH_3		
	$3O_2(g) + 2\ Gly(s) \rightarrow 4\ CO_2(g) + 2\ H_2O(l) + 2\ NH_3(g)$	-1163	(known)
(b)	hydrolysis of urea(s)		
	$H_2O(l) + urea(s) \rightarrow CO_2(g) + 2NH_3(g)$	131	(known)
(c)	subtract (b) from (a) to give the reaction		
	$3O_2(g) + 2\ Gly(s) \rightarrow urea(s) + 3CO_2(g) + 3\ H_2O(l)$	-1294	(known)

Calculate Δ_rH for a reaction when carbon burns to CO in a limited amount of O2 from these reactions:

(a) $C \quad + \quad \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta_rH =??$

(b) $C \quad + \quad O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta_rH = -393.509 \text{ kJ mol}^{-1}$

(c) $CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta_rH = -282.984 \text{ kJ mol}^{-1}$

- By multiplying eqaution (c) x -1

(d) $CO_{2(g)} \longrightarrow CO_{(g)} + \frac{1}{2} O_{2(g)} \quad \Delta_rH = +282.984 \text{ kJ mol}^{-1}$

Add (b) + (d)

(b) $C \quad + \quad O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta_rH = -393.509 \text{ kJ mol}^{-1}$

==

(a) $C \quad + \quad \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta_rH = (+282.984 - 393.509)$

$= -110.525 \text{ kJ mol}^{-1}$
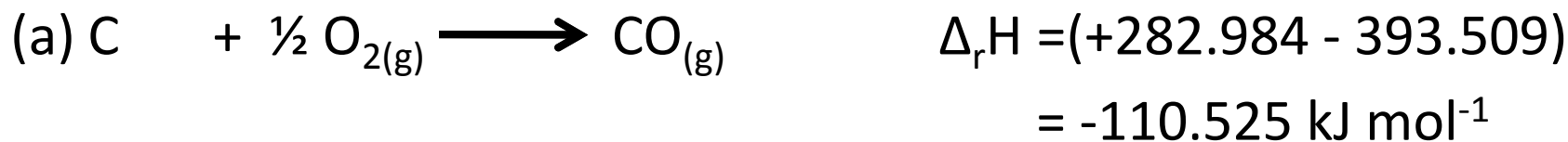
How to calculate the heat of rxn at any temperature:

- We know that at constant pressure $dH = C_p\,dT$

- We can adapt this equation to the heat of a reaction $\Delta_r H$ and introduce a term, $\Delta_r C_p$, which is similar in form to $\Delta_r H$. It is the (constant pressure) heat capacity of the reaction.

For reactants and products in their standard states

$$d\,(\Delta_r H^{\theta}) = \Delta_r C^{\theta}_p\,dT \qquad \text{where} \qquad \Delta_r C_p = \sum_{products}\nu C_{p,m} - \sum_{reactants}\nu C_{p,m}$$

Integrating gives

$$\int_{T_1}^{T_2} d(\Delta_r H^{\theta}) = \Delta_r H^{\theta}\Big|_{T_1}^{T_2} = \int_{T_1}^{T_2}\Delta_r C^{\theta}_p\,dT$$

$$\Delta_r H^{\theta}(T_2) = \Delta_r H^{\theta}(T_1) + \int_{T_1}^{T_2}\Delta_r C^{\theta}_p\,dT \qquad \text{Kirchhoff's Law}$$

$$\boxed{\Delta_r H^{\theta}(T) = \Delta_r H^{\theta}(298) + \Delta_r C^{\theta}_p\,(T - 298)} \qquad \text{Constant Heat Capacity}$$

What is the value of $\Delta_r H°$ at 0K for the reaction:

$$H_{2(g)} \Leftrightarrow 2H_{(g)}$$

where $\Delta_f H°$ at 298 = 217.999 kJ mol^{-1} for H gas

$H_0° - H_{298}°$ = -8.468 kJ mol^{-1} for H_2 gas
$H_0° - H_{298}°$ = -6.197 kJ mol^{-1} for H gas

- $\Delta_r H°$ (298K) = $2\Delta_f H°$ for H gas = 2 x (217.999) = 435.998 kJ mol^{-1}

$$..........................H_{2(g)} \xrightarrow{0K} 2H_{(g)}$$

$$H_{298}^o - H_0^o ..... \downarrow .... \uparrow ....H_0^o - H_{298}^o$$

$$....................H_{2(g)} \xrightarrow{298K} 2H_{(g)}$$
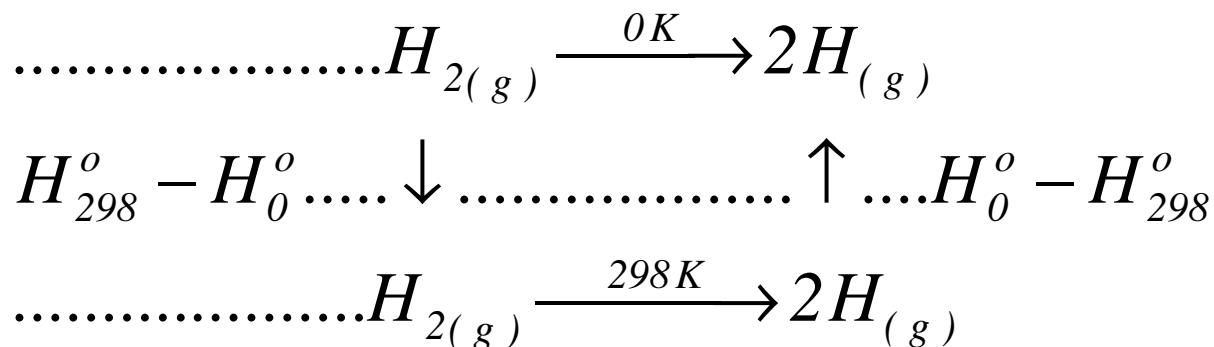
- $\Delta_r H°$ (0K) = (8.467) + (435.998) – 2 x (6.197) = 432.071 kJ mol^{-1}

Calculate the heat of the following reaction at 398 K given values at 298 K

$$2\ NO_2(g) \rightarrow N_2O_4(g)$$

	$2\ NO_2(g)$	$N_2O_4(g)$
$\Delta H^\theta_{f,m}$ kJ mol^{-1}	33.18	9.16
$C^\theta_{p,m}$ J K^{-1} mol^{-1}	37.20	77.28
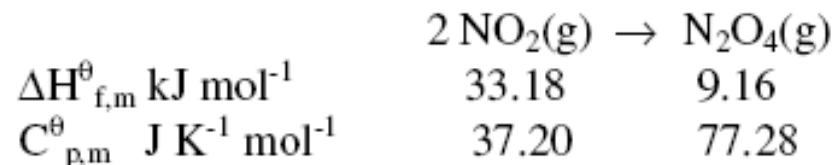
First calculate the heat of reaction at 298 K: $\Delta_r H^\theta = 1 \times 9.16 - 2 \times 33.18 = -57.2$ kJ mol^{-1}

Then the heat capacity of reaction $\Delta_r C^\theta_p = 1 \times 77.28 - 2 \times 37.20 = 2.88$ J K^{-1} mol^{-1}

$$\Delta_r H^\theta(398) = \Delta_r H^\theta(298) + \Delta_r C^\theta_p (398 - 298)$$

$= -57.2$ kJ mol^{-1} $+ .00288$ kJ K^{-1} mol^{-1} $(398 - 298)$K
$= -57.2 + .288 = -56.9$ kJ mol^{-1}

- There are situations where we would like to know the heat of a reaction at other than 298 with high accuracy.

- For example, in industrial large scale reactions heat from an exothermic reaction must be accurately known to design the correct cooling devices so that reactors do not overheat and cause disasters. In these cases, heat capacity of compounds must be known as a function of temperature.

- This will provide an equation for the heat capacity of the reaction as a function of temperature and hence the general Kirchhoff equation can be integrated. Heat Capacity data for a compound have been. fitted empirically to the equation.

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

a, b and c are constants (independent of temperature) for a compound that can be found in tables.
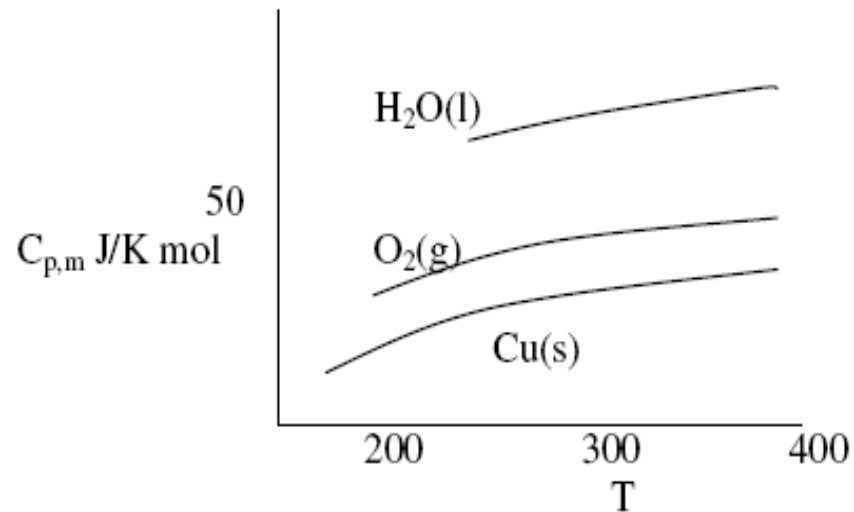
The heat capacity for the reaction can then be written

$$\Delta_r C_p = \Delta a + \Delta b\, T + \frac{\Delta c}{T^2} \quad \text{where} \quad \Delta a,\ \Delta b \text{ and } \Delta c \text{ have the same form as } \Delta_r H$$

$$\Delta a = \sum_{\text{products}} \nu a - \sum_{\text{reactants}} \nu a \quad \text{with similar equations for } \Delta b \text{ and } \Delta c.$$

Since we have an equation for $\Delta_r C_p$ as a function of temperature we can substitute into the integral and do the integration.

$$\Delta_r H^\theta (T_2) = \Delta_r H^\theta (298) + \int_{298}^{T} \Delta_r C_p^\theta \, dT$$

$$= \Delta_r H^\theta (298) + \int_{298}^{T} (\Delta a + \Delta b\, T + \frac{\Delta c}{T^2}) \, dT$$

Integrating gives the temperature dependent Kirchhoff equation.

$$\Delta_r H^\theta (T_2) = \Delta_r H^\theta (298) + \Delta a(T - 298) + \frac{\Delta b}{2}(T^2 - 298^2) - \Delta c\left(\frac{1}{T} - \frac{1}{298}\right)$$

Enthalpy of Solution

- When a solute dissolved in a solvent, heat may be absorbs or evolves.

- Heat of solution: it is the enthalpy change for the solution of 1 mole of solute in n moles of solvent. It is depend on the final concentration of the solution.

- When the solute is dissolved, heat always absorbed to overcome the attraction forces between the molecules or ions of the solid solute (Lattice energy)

- Another process is the strong attraction between the molecules or ions (solvation or hydration in case of water) with solvent which evolves heat.

- The energy required to separate Na^+ from Cl^- in crystalline solid when is dissolved in water is about the same as hydration energy, q, is small positive value at 25 ^{o}C. When Na_2SO_4 is dissolved in water at 25 ^{o}C, there is an evolution of heat because the energy of hydration of ions is greater than the energy required to separate the ions from the crystal.

Calculate the heat of formation of Cl^- ion in water from the reaction

$$HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)} \qquad \Delta_rH° = -75.1 \text{ kJ}$$

- $\Delta_rH° = \sum \Delta_rH° \text{ (product)} - \sum \Delta_rH° \text{ (reactants)}$
  - $= (\Delta_fH° \; H^+_{(aq)} + \Delta_fH° \; Cl^-_{(aq)}) - \Delta_fH° \; HCl_{(g)}$
  - $\Delta_fH° \; H^+_{(aq)} = 0.0$ (agreement)
  - $\Delta_fH° \; HCl_{(g)} = -92.3$ kJ (from the tables)

- $\Delta_rH° = -75.1 \text{ kJ} = (0.0 + \Delta_fH° \; Cl^-_{(aq)}) - (-92.3)$
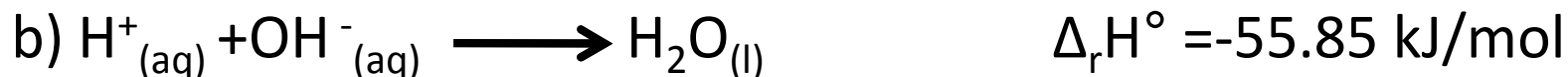- $\Delta_fH° \; Cl^-_{(aq)} = -167.4 \text{ kJ}$

Enthalpy of neutralization

- The heat produced when one mole of H^+ ion (acid) react with one mole of OH^- (base) in dilute solution to form one mole of water.

- $\Delta_r H°$ for strong acid with strong base is constant and equal -55.835 $kJmol^{-1}$. This is due to the complete dissociation of both the strong acid and strong base and the formation of salt.

- When a weak acid or base is neutralized, the heat of neutralization is less, due to the heat absorbed to dissociate the weak acid or base .

Calculate the ionization enthalpy $(\Delta_i H°)$ of HCN from the reaction:

$$HCN_{(aq)} + OH^- \longrightarrow CN^-_{(aq)} + H_2O_{(l)} \qquad \Delta_r H° = -10.3 \text{ kJ/mol}$$

This reaction is consisting of:

a) $HCN_{(aq)} \longrightarrow CN^-_{(aq)} + H^+_{(aq)} \qquad \Delta_i H° = \Delta_r H°$

b) $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \qquad \Delta_r H° = -55.85 \text{ kJ/mol}$

Equation a) + equation b)

- $\Delta_i H° + (-55.85) = -75.1 \text{ kJ} = -10.3$
- $\Delta_i H° \ HCN_{(aq)} = 45.55 \text{ kJ/mol}$