

Topics / Chapters

Chapter 1 : No exclusions

2 : No exclusions

3 : No exclusions

4 : 4, 6

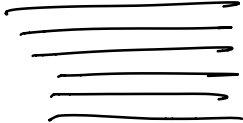
5 : No exclusions

6 : 6, 14 (Exam 2 will cover sections associated with class lectures)

Grading Points : Exam 2 and onward.

Things to

Examples :



$$\Delta S = \frac{dq}{T}$$

$$dS = \frac{q}{T}$$

$$\int_{V_1}^{V_2} d(\ln V) = \ln(V_2 - V_1)$$

No units

Improper use
of mathematical symbols

Avoid

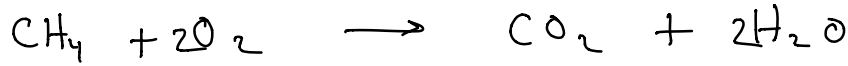
Δq

ΔW

Not stating
Assumptions

Use of Incorrect
Equation

Thermochemistry



$$T = 298.15 \text{ K} \leftarrow \text{constant}$$

$$P = 1 \text{ bar} \leftarrow \text{constant}$$

$$\Delta H_{\text{rxn}} = q_p$$

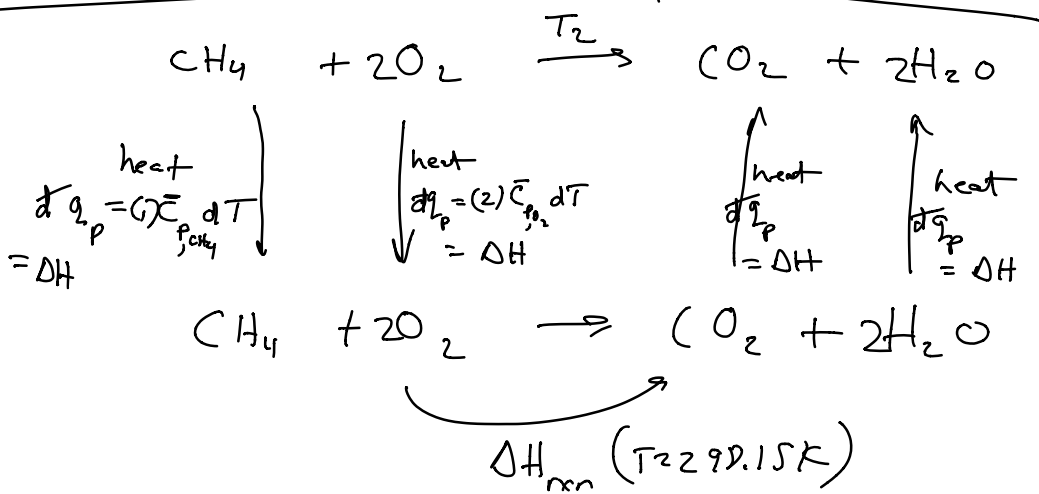
Standard States $\rightarrow P = 1 \text{ bar}$

$$\rightarrow \Delta H_{\text{rxn}} = \sum_{i=1}^{\text{all species}} \nu_i \Delta H_{f,i}^{\circ} \quad \text{at a particular } T$$

What is ΔH_{rxn} at T_2 , given

ΔH_{rxn} at T_1 ?

$$T_1 = 298.15 \text{ K}$$



$$\Delta H = \int_{T_2}^{T_1} (1) \bar{c}_{p, \text{CH}_4} dT + \int_{T_2}^{T_1} (2) \bar{c}_{p, \text{O}_2} dT + \Delta H_{\text{rxn}}(T_1 = 298.15 \text{ K})$$

$$+ \int_{T_1}^{T_2} (1) \bar{c}_{p, \text{CO}_2} dT + \int_{T_1}^{T_2} (2) \bar{c}_{p, \text{H}_2\text{O}} dT$$

$$\Delta H = \int_{T_1}^{T_2} (-1) \bar{c}_{p, \text{CH}_4} dT + \int_{T_1}^{T_2} (-2) \bar{c}_{p, \text{O}_2} dT + \Delta H_{\text{rxn}}(T_1 = 298.15 \text{ K})$$

$$+ \int_{T_1}^{T_2} (1) \bar{c}_{p, \text{CO}_2} dT + \int_{T_1}^{T_2} (2) \bar{c}_{p, \text{H}_2\text{O}} dT$$

$$\Delta H = \Delta H_{\text{rxn}}(T_1 = 298.15 \text{ K}) + \int_{T_1}^{T_2} \left[(1) \bar{c}_{p, \text{CO}_2} + (2) \bar{c}_{p, \text{H}_2\text{O}} - (1) \bar{c}_{p, \text{CH}_4} - (2) \bar{c}_{p, \text{O}_2} \right] dT$$

$$= \Delta H_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} (\Delta \bar{c}_p) dT = \Delta H_{\text{rxn}}(T_2)$$

$$\Delta \bar{c}_p = (1) \bar{c}_{p, \text{CO}_2} + (2) \bar{c}_{p, \text{H}_2\text{O}} - (1) \bar{c}_{p, \text{CH}_4} - (2) \bar{c}_{p, \text{O}_2}$$

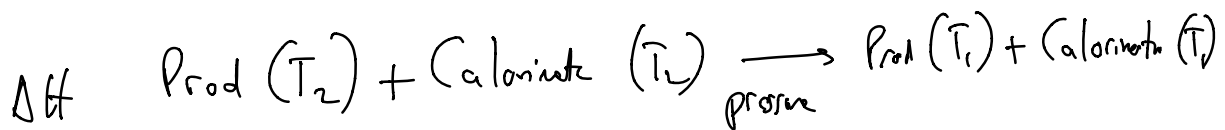
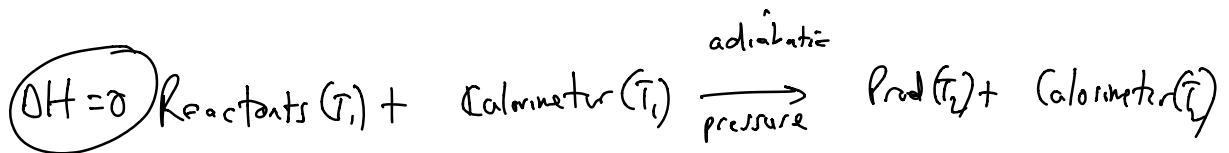
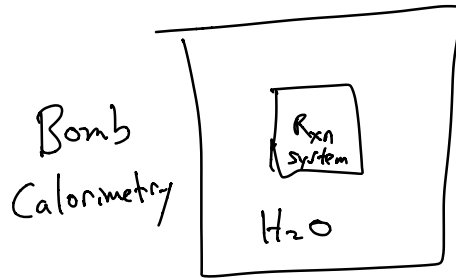
$$= \sum_{\text{species}} \nu_i \bar{c}_{p, i}$$

$\nu_i < 0$ Reactant

$\nu_i > 0$ Product

Calorimetry

constant pressure
Chemical Rxn.



$$\Delta H = \int_{T_2}^{T_1} n_{\text{prod}} \bar{C}_{p, \text{Products}} dT + \int_{T_2}^{T_1} n_{\text{calorimeter}} \bar{C}_{p, \text{Calorimeter}} dT$$

$$\Delta H_{\text{rxn}} = \int_{T_2}^{T_1} (n_{\text{products}} \bar{C}_{p, \text{prod}} + n_{\text{calorimeter}} \bar{C}_{p, \text{calorimeter}}) dT$$

before experiment,
need to calibrate

$$\rightarrow \underline{\bar{C}_{p, \text{calorimeter}}}$$

Open Systems

→ n changes (amount, moles, particles)

G very important!

at T, P constant $(dG)_{T,P} \leq 0$

G is a minimum at
Equilibrium!

(when $T \& P$ constant)

if n change, $G(T, P, n)$

$G(T, P, n_1, n_2, n_3, \dots)$

$$dG(T, P, n_1, n_2, \dots) = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 \\ + \mu_3 dn_3 + \dots$$

$$dG = Vdp - SdT + \sum_{i=1}^m \mu_i dn_i$$

m species, m components in system

μ_i = chemical potential of
species " i "

$$\mu_i \equiv \left(\frac{\partial G(T, P, n_1, n_2, \dots)}{\partial n_i} \right)_{T, P, \{n_j, j \neq i\}}$$

$$V \equiv \left(\frac{\partial G}{\partial P} \right)_{T, \{n_j\}}$$

$$dA(T, V, n_1, n_2, \dots) = -pdV - SdT + \sum_{i=1}^m \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, \{n_j \neq i\}}$$

$$\left(\frac{\partial A}{\partial n_i} \right)_{T, V, \{n_j \neq i\}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, \{n_j \neq i\}}$$

G : extensive property

V, G, A, U, H depends on amount

intensive = independent of amount
 T, P, ρ , viscosity

μ_i intensive or extensive?

intensive property $\approx \frac{\text{extensive}}{\text{extensive}}$

$$\lambda G(T, P, n_1, n_2, \dots) = G(T, P, \lambda n_1, \lambda n_2, \dots)$$

Additional Material

Proof of μ_i based on Gibbs Free Energy =

μ_i based on Helmholtz Free Energy

We know:

$$G = H - TS$$

and $H = U + PV$

So: $G = U + PV - TS$

But: $A = U - TS$

So: $G = A + PV$

Gibbs Free Energy

Helmholtz Free Energy

Let's consider a 2-species system
species 1 & species 2

Consider the TOTAL Differential of G and A .

$$\textcircled{A} \quad dG(T, p, n_1, n_2) = Vdp - SdT + \left(\frac{\partial G}{\partial n_1} \right)_{T, p, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, p, n_1} dn_2$$

$$\textcircled{B} \quad dA(T, V, n_1, n_2) = -pdV - SdT + \left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2} dn_1 + \left(\frac{\partial A}{\partial n_2} \right)_{T, V, n_1} dn_2$$

Recall! $G = A + pV$

So, $dG = dA + d(pV)$

$$dG = dA + Vdp + p dV$$

use \textcircled{A} and \textcircled{B} for dG and dA

$$Vdp - SdT + \left(\frac{\partial G}{\partial n_1} \right)_{T, p, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, p, n_1} dn_2 = -pdV - SdT + \left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2} dn_1 + \left(\frac{\partial A}{\partial n_2} \right)_{T, V, n_1} dn_2 + pdV + Vdp$$

Several terms cancel, leaving:

$$\left(\frac{\partial G}{\partial n_1} \right)_{T, p, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, p, n_1} dn_2 = \left(\frac{\partial A}{\partial n_1} \right)_{T, V, n_2} dn_1 + \left(\frac{\partial A}{\partial n_2} \right)_{T, V, n_1} dn_2$$

Now, there are $d\eta_1$ and $d\eta_2$ terms
that we can combine as:

$$d\eta_1 \left[\left(\frac{\partial G}{\partial \eta_1} \right)_{T, P, \eta_2} - \left(\frac{\partial A}{\partial \eta_1} \right)_{T, V, \eta_2} \right] + d\eta_2 \left[\left(\frac{\partial G}{\partial \eta_2} \right)_{T, P, \eta_1} - \left(\frac{\partial A}{\partial \eta_2} \right)_{T, V, \eta_1} \right] = 0$$

To Guarantee this equality for all $d\eta_1$ & $d\eta_2$
the following conclusions arise:

$$\left[\left(\frac{\partial G}{\partial \eta_1} \right)_{T, P, \eta_2} - \left(\frac{\partial A}{\partial \eta_1} \right)_{T, V, \eta_2} \right] = 0$$

$$\left[\left(\frac{\partial G}{\partial \eta_2} \right)_{T, P, \eta_1} - \left(\frac{\partial A}{\partial \eta_2} \right)_{T, V, \eta_1} \right] = 0$$

This leads to:

$$\left(\frac{\partial G}{\partial \eta_1} \right)_{T, P, \eta_2} = \left(\frac{\partial A}{\partial \eta_1} \right)_{T, V, \eta_2}$$

$$\left(\frac{\partial G}{\partial \eta_2} \right)_{T, P, \eta_1} = \left(\frac{\partial A}{\partial \eta_2} \right)_{T, V, \eta_1}$$

As I presented in class without proof (page 7)