

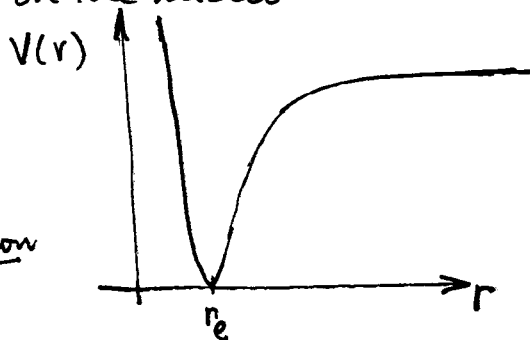
Thermochemistry.

When species conversion occurs in a chemical reaction the process is invariably inelastic (at the microscopic/molecular level).

From the molecular point of view the "chemical bond" is an electrical force resulting from the complex interaction of two (or more) nuclei and several electrons. Because nuclei are positively charged they would repel each other strongly. The molecule hangs together because many electrons are between the nuclei (on the average) and the nuclei are attracted to the electrons; other electrons "screen" the nuclei. Details are complex and require quantum chemistry.



We can construct a simplified picture by looking at the interaction potential for a given molecule. For simplicity consider a diatomic molecule eg. N_2 , O_2 , NO . $V(r)$ is the potential energy of the system as a function of internuclear separation assuming electrons "equilibrate" with this separation. The force acting on the nuclei is $F(r) = -\frac{dV}{dr}$



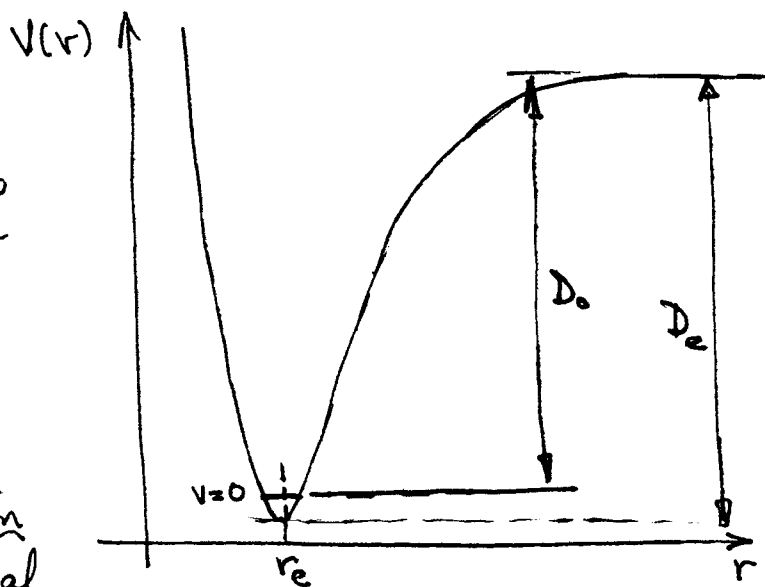
As $r \rightarrow \infty$ we have free atoms.
($F \rightarrow 0$)
For r very small \rightarrow strong repulsion

In between there is an attractive region. Note that at the minimum of $V(r)$, $F = -\frac{dV}{dr} = 0$ so there is a classical equilibrium at r_e - the "equilibrium" nuclear separation.

Quantum mechanics requires that the molecules can never be perfectly at rest at the bottom of the potential "well".

Instead they vibrate with at zero-point vibration in the lowest vibrational

quantum state characterized by vibrational quantum number $v=0$. Excited vibrational states have $v > 0$



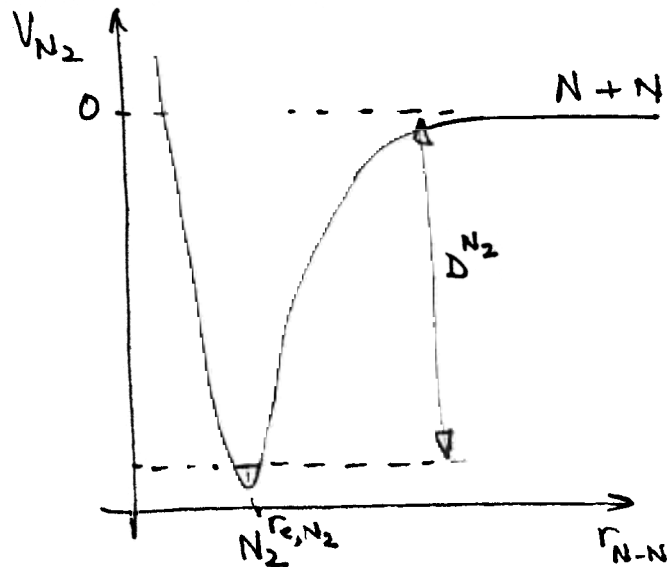
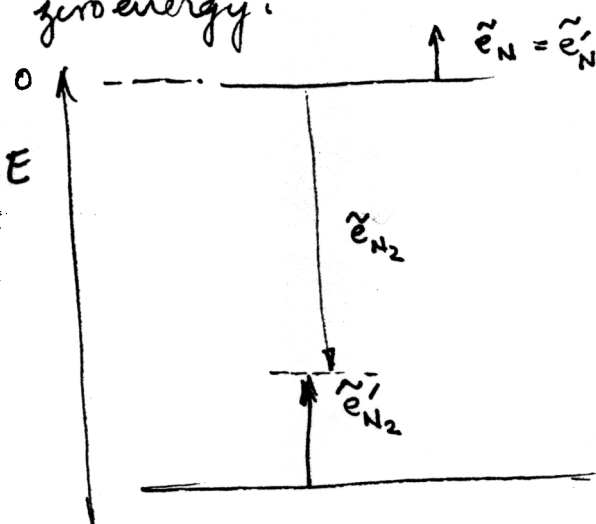
Now the energy scale is relative - only energy differences are important when dealing with conversions of species in chemical reactions. In order to deal with many reactions in a multispecies "soup" it is convenient to define a system zero so that N atoms have the same energy whether they come from the dissociation of N_2 via $N_2 \longrightarrow N+N$ or NO via $NO \longrightarrow N+O$ and similarly for other species.

For a consistent energy assignment one requires a definition of reference ^{chemical} species in a reference

state and specify their energy is zero at this state. Any other state and/or species is measured relative to this state. For ideal gases life is simplified because only temperature is required in the state-specification.

choose free atoms (& electrons) at 0K to have

zero energy.



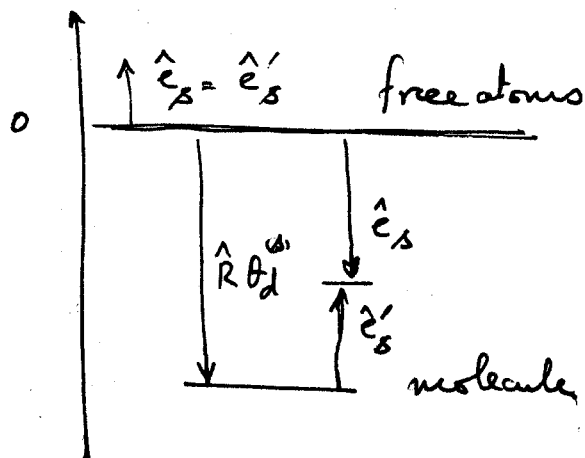
Energies can be written on a per molecule, per mole, or ~ unit mass basis.

per molecule \tilde{e}
 per mole \hat{e}
 per unit mass e

} ← convenient for chemistry

In general $\hat{e}_s = \hat{e}'_s - \hat{R}\theta_d$

In our system (arbitrary but convenient choice), $\theta_d \equiv 0$ for atoms.



$$E = \sum_s N_s \hat{e}_s$$

$$\hat{e}_s = \hat{e}_{\text{trans}}^{(s)} + \hat{e}_{\text{elec}}^{(s)} + \hat{e}_{\text{rot}}^{(s)} + \hat{e}_{\text{vib}}^{(s)} - \hat{R}\theta_d^{(s)}$$

only for diatomic & polyatomic molecules.

$$= \frac{3}{2} \hat{R}T + \hat{e}_{\text{elec}}^{(s)} + \hat{R}T + \hat{e}_{\text{vib}}^{(s)} - \hat{R}\theta_d^{(s)}$$

usually negligible diatomics small at low $\frac{1}{T}$ large

$$= \frac{5}{2} \hat{R}T + \hat{e}_{\text{elec}}^{(s)} + \hat{e}_{\text{vib}}^{(s)} - \hat{R}\theta_d^{(s)}$$

$$H = \sum_s N_s \hat{h}_s \quad \hat{h}_s = \hat{e}_s + \hat{R}T \quad \text{for ideal gases}$$

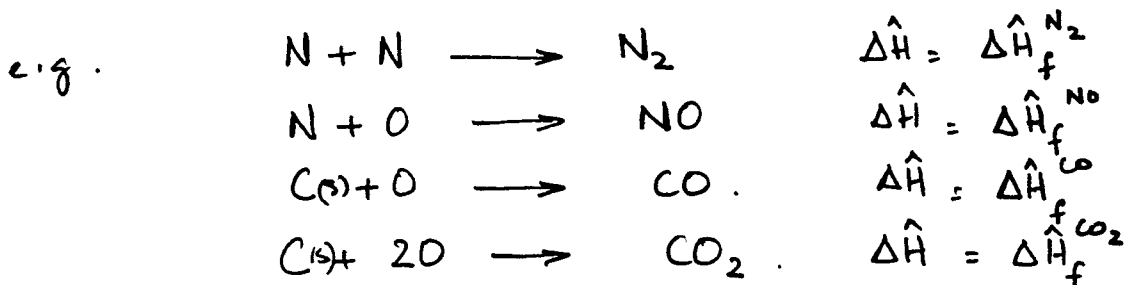
$$\text{so } \hat{h}_s = \frac{7}{2} \hat{R}T + \hat{e}_{\text{vib}}^{(s)} + \hat{e}_{\text{elec}}^{(s)} - \hat{R}\theta_d^{(s)}$$

In general $-\hat{R}\theta_d^{(s)}$ is called $\hat{h}_f^{(s)}$ or $\Delta \hat{H}_f^{(s)}$
the (reference) enthalpy of formation

Enthalpy of reaction $\Delta \hat{H}_{(R)} \equiv \left(\frac{\partial H}{\partial \xi} \right)_{P, T}$

sometimes called the "heat of reaction".

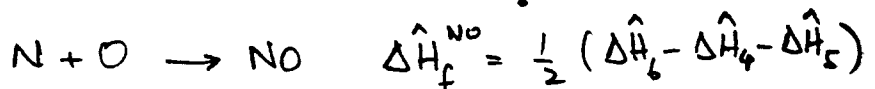
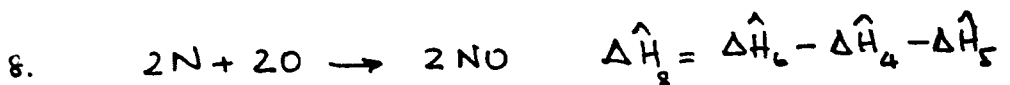
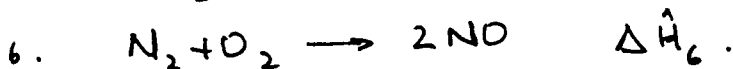
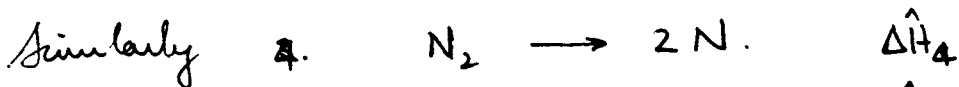
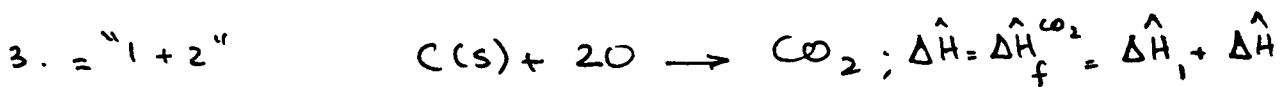
The enthalpy of formation is the enthalpy of reaction for the reaction that produces one mole of the substance from the chosen reference species.



etc. s - stands for "solid", g - gas. - usually omitted.

Note that $C + O_2 \longrightarrow CO_2$ $\Delta \hat{H} \neq \Delta \hat{H}_f^{CO_2}$.

because O_2 (molecular) is not a reference species.



$\Delta \hat{H}$ \equiv enthalpy change of reacting mixture for unit change in progress of reaction at constant p, T . $\left(\frac{\partial H}{\partial \xi}\right)_{p, T}$.

$$dQ = dH - V dp.$$

$$dQ_{p, T} = (dH)_{p, T}$$

$$H = \sum_{\Delta} \nu_{\Delta} \hat{h}_{\Delta} \quad \hat{h}_{\Delta} = f(T) \text{ only.}$$

$$\text{so } dH_{p, T} = \sum_{\Delta} \hat{h}_{\Delta}(T) (d\nu_{\Delta})_{p, T}$$

$$d\nu_{\Delta} = \nu_{\Delta} d\xi.$$

$$\text{so } (d\nu_{\Delta})_{p, T} = \nu_{\Delta} (d\xi)_{p, T}.$$

$$\text{Finally } \left[\left(\frac{\partial H}{\partial \xi}\right)_{p, T} = \sum_{\Delta} \nu_{\Delta} \hat{h}_{\Delta} = \Delta \hat{H} \right]$$

Chemical Thermodynamic derivation of Law of Mass Action.

$$\prod_{\Delta} (p_{\Delta}^*)^{\nu_{\Delta}} = K_p(T)$$

Want to show this, and obtain $K_p(T)$ in terms of other thermodynamic variables.

One can show.
$$\prod_{\Delta} (p_{\Delta}^*)^{\nu_{\Delta}} = \exp\left[-\frac{1}{RT} \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ}\right]$$

where
$$\hat{g}_{\Delta}^{\circ} = \hat{h}_{\Delta} - T \left[\int_{T_0}^T \frac{\hat{c}_{p,\Delta}}{T} dT + \hat{s}_{\Delta,0} + \hat{R} \ln p_0 \right]$$

Thus
$$\exp\left[-\frac{1}{RT} \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ}\right] = K_p(T)$$

Outline of idea.

Equilibrium is attained (for an isolated system) when entropy is maximized \leftarrow follows from 2nd Law of thermodynamics.

Consider a system where $E, V, \{N_s\}$

i.e. energy, volume, & set of mole numbers (composition) are the variables.

$S = S(E, V, N_s)$. - some functional dependence

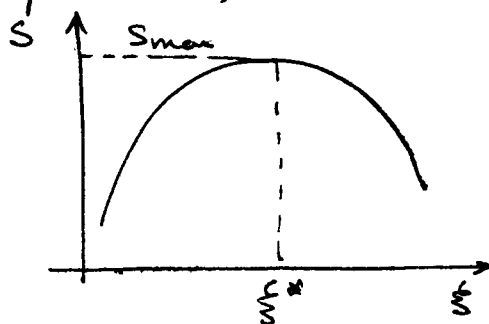
then
$$dS = \left(\frac{\partial S}{\partial E}\right)_{V, N_s} dE + \left(\frac{\partial S}{\partial V}\right)_{E, N_s} dV + \sum_s \left(\frac{\partial S}{\partial N_s}\right)_{E, V, N_s'} dN_s$$

Entropy change as a function of change in independent variables describing state of the system.

Entropy production due to irreversible processes is guaranteed ≥ 0 .

For an isolated system - no entropy transfer ($\dot{Q}=0$)
 so if system is in mechanical & thermal equilibrium only irreversible chemical reactions can change entropy. If we could plot $S(\xi)$

The equilibrium value of ξ would be at S_{\max} .



In general

$$\begin{aligned}
 TdS &= Td_e S + Td_i S \\
 &\quad \text{external} \quad \text{internal} \\
 &\quad \text{transfer} \quad \text{production} \\
 &= dQ + Td_i S \\
 &= dE + pdV + Td_i S.
 \end{aligned}$$

$$Td_i S = - \sum_{\Delta} \hat{\mu}_{\Delta} d\hat{N}_{\Delta} \geq 0 \quad \text{from 2nd Law.}$$

$$\Rightarrow \sum_{\Delta} \hat{\mu}_{\Delta} d\hat{N}_{\Delta} \leq 0.$$

$$\text{but } d\hat{N}_{\Delta} = \nu_{\Delta} d\xi \quad \text{so } \left(\sum_{\Delta} \hat{\mu}_{\Delta} \nu_{\Delta} \right) d\xi \leq 0.$$

$$\text{At eq'b'm we have an equality. } \boxed{\sum_{\Delta} \hat{\mu}_{\Delta}^* \nu_{\Delta} = 0.}$$

This is the condition of equilibrium & hence is a form of law of mass action. If we could express chemical potential $\hat{\mu}_{\Delta}$ in terms of other variables (more familiar ones) we are finished.

Thermodynamic definitions of other variables

$$\left(\frac{\partial S}{\partial E}\right)_{V, N_s} \equiv \frac{1}{T} \quad \left(\text{equivalently } T \equiv \left(\frac{\partial E}{\partial S}\right)_{V, N_s}\right).$$

$$\left(\frac{\partial S}{\partial V}\right)_{E, N_s} \equiv \frac{P}{T} \quad \left(\text{equivalently } P \equiv \left(\frac{\partial E}{\partial V}\right)_{S, N_s}\right)$$

&

$$\left(\frac{\partial S}{\partial N_s}\right)_{E, V, N_{s'}} \equiv -\frac{\hat{\mu}_s}{T} \quad \hat{\mu}_s \text{ - "chemical potential" (molar specific)}$$

Substituting these definitions

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \sum_s \frac{\hat{\mu}_s}{T} dN_s$$

$$\text{or } TdS = dE + PdV - \sum_s \hat{\mu}_s dN_s.$$

Now 1st Law of thermo gives $dE + PdV = dQ$.

and we know that heat transfer results in an entropy transfer.

However for an isolated system $dQ=0$, $dW = -PdV = 0$
 $dE=0$

entropy can still change if chemical reactions are occurring

$$TdS = -\sum_s \hat{\mu}_s dN_s$$

We think of entropy transfer (external effect)

and entropy production (internal effect).

entropy transfer may be positive or negative depending on whether Q is to or from system.

Recap.

At eq'b'm for a system

$$\sum_i \hat{\mu}_i^* \nu_i = 0.$$

One can show that

$$\hat{\mu}_s = \hat{g}_s \quad \text{where} \quad \hat{g}_s = \hat{g}_s(T, p)$$

$$\hat{g}_s = \hat{h}_s - T \hat{S}_s$$

Natural variables
to describe \hat{g}

$$\hat{h}_s = \hat{h}_s(T) \quad \text{for an ideal gas}$$

$$= \hat{h}_s(T_0) + \int_{T_0}^T \hat{c}_{p,s}(T) dT$$

$$= \hat{h}_s^\circ + \int_{T_0}^T \hat{c}_{p,s}(T) dT$$

$$d\hat{S}_s = \hat{c}_{p,s} \frac{dT}{T} - \hat{R} \frac{d\hat{p}_s}{\hat{p}_s} \quad \text{for an ideal gas}$$

Integrating $\hat{S}_s(T, p) = \hat{S}_s(T_0, p_0) + \int_{T_0}^T \hat{c}_{p,s} \frac{dT}{T} - \hat{R} \ln \frac{p_s}{p_0}$

$$= \hat{S}_s^\circ + \int_{T_0}^T \hat{c}_{p,s} \frac{dT}{T} - \hat{R} \ln \frac{p_s}{p_0}$$

Substituting in \hat{g}_s

$$\hat{g}_s = \hat{h}_s^\circ + \int_{T_0}^T \hat{c}_{p,s}(T) dT - T \left\{ \hat{S}_s^\circ + \int_{T_0}^T \hat{c}_{p,s} \frac{dT}{T} - \hat{R} \ln \frac{p_s}{p_0} \right\}$$

Define $\hat{g}_s^\circ = \left(\hat{h}_s^\circ + \int_{T_0}^T \hat{c}_{p,s} dT \right) - T \left\{ \hat{S}_s^\circ + \int_{T_0}^T \hat{c}_{p,s} \frac{dT}{T} + \hat{R} \ln p_0 \right\}$

Then $\hat{g}_s = \hat{g}_s^\circ + \hat{R} T \ln p_s$ but units of p
must be known

Convention - choose atmospheres
and $p_0 = 1 \text{ atm}$ so $\hat{R} \ln p_0 = 0$

Substituting in law of mass action $\sum_{\Delta} \hat{\mu}_{\Delta}^* \nu_{\Delta} = 0$

and using $\hat{\mu}_{\Delta}^* = \hat{g}_{\Delta}^* = \hat{g}_{\Delta}^{\circ} + \hat{R}T \ln p_{\Delta}^*$

$$\sum_{\Delta} (\hat{g}_{\Delta}^{\circ} + \hat{R}T \ln p_{\Delta}^*) \nu_{\Delta} = 0.$$

$$\hat{R}T \sum_{\Delta} \nu_{\Delta} \ln p_{\Delta}^* = - \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ}$$

$$\hat{R}T \sum_{\Delta} \ln p_{\Delta}^{*\nu_{\Delta}} = - \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ}$$

$$\ln x_1 + \ln x_2 + \dots \left\{ \begin{array}{l} \ln x_1 + \ln x_2 + \ln x_3 + \dots = \ln x_1 x_2 x_3 \dots \\ \sum \ln x_i = \ln \prod x_i \end{array} \right\}$$

$$\hat{R}T \ln \prod_{\Delta} p_{\Delta}^{*\nu_{\Delta}} = - \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ}.$$

$$\ln \prod_{\Delta} p_{\Delta}^{*\nu_{\Delta}} = - \frac{1}{\hat{R}T} \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ}.$$

$$\prod_{\Delta} p_{\Delta}^{*\nu_{\Delta}} = \exp \left[- \frac{1}{\hat{R}T} \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ} \right].$$

But LHS $\equiv K_p(T)$

$$\text{So } K_p(T) = \exp \left[- \frac{1}{\hat{R}T} \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ} \right]$$

$$\text{where } \hat{g}_{\Delta}^{\circ} = \hat{h}_{\Delta}^{\circ}(T) - T \left\{ \hat{S}_{\Delta}^{\circ} + \int_{T_0}^T \frac{\hat{C}_{p,\Delta}}{T} dT + \hat{R} \ln \frac{p_{\Delta}^{\circ}}{p_0} \right\}$$

dropped for
 $p_0 = 1 \text{ atm.}$

Specific heat of reacting mixtures.

Two well defined limiting values

- (1) "Frozen" specific heat - no chemical reaction as temperature is changed -
- (2) "Equilibrium" specific heat - system is always at equilibrium composition as temperature changes.

- (1) corresponds to rapid heating ^(or cooling) or slow reactions
- (2) slow heating/cooling or fast reactions.

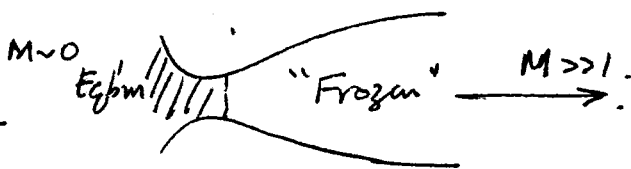
The general case of "finite rate kinetics" is computationally expensive. Sometimes convenient to divide flow into two zones either equilibrium or frozen.

Ex. Rocket nozzle

Combustion chamber \rightarrow high p, T

\Rightarrow fast reactions, slow flows

\Rightarrow slow T variation \Rightarrow equilibrium zone.



In supersonic nozzle - low p , low T - slow reactions

\Rightarrow high speed \Rightarrow rapid T variation \Rightarrow frozen zone.

Often assume that flow "freezes" at or near throat.

$$H = \sum_{\Delta} \mathcal{N}_{\Delta} \hat{h}_{\Delta} \equiv \mathcal{N}_{\text{tot}} \hat{h}_{\text{mix}} \begin{array}{l} \leftarrow \text{molar specific enthalpy} \\ \text{of mixture} \end{array}$$

$$= m h_{\text{mix}} \begin{array}{l} \leftarrow \text{mean enthalpy per} \\ \text{unit mass of mixture.} \end{array}$$

latter is more convenient since m is const, whereas \mathcal{N}_{tot} varies (in general) when reactions occur.

$$h_{\text{mix}} = \frac{1}{m} H = \frac{1}{m} \sum_{\Delta} \mathcal{N}_{\Delta} \hat{h}_{\Delta}$$

$$c_{p, \text{mix}} \equiv \left(\frac{\partial h_{\text{mix}}}{\partial T} \right)_p = \frac{1}{m} \left[\frac{\partial}{\partial T} \left(\sum_{\Delta} \mathcal{N}_{\Delta} \hat{h}_{\Delta} \right) \right]_p$$

(1) Frozen $c_p \Rightarrow \mathcal{N}_{\Delta} = \text{const} \quad (d\xi = 0)$

$$c_{p, \text{mix}}^{\text{frozen}} = \frac{1}{m} \sum_{\Delta} \mathcal{N}_{\Delta} \left(\frac{\partial \hat{h}_{\Delta}}{\partial T} \right)_p$$

$$\hat{h}_{\Delta} = \hat{h}'_{\Delta} + \Delta \hat{H}_f^{\Delta} \quad \text{or} \quad \hat{h}_{\Delta} = \hat{h}_{\Delta} - R \hat{\theta}_{\Delta}^{\Delta}$$

$$\left(\frac{\partial \hat{h}_{\Delta}}{\partial T} \right)_p = \left(\frac{\partial \hat{h}'_{\Delta}}{\partial T} \right)_p = \hat{c}_{p, \Delta}$$

specific heat of species is independent of ref. state since it is a derivative (change).

$$c_{p, \text{mix}}^{\text{frozen}} = \frac{1}{m} \sum_{\Delta} \mathcal{N}_{\Delta} \hat{c}_{p, \Delta}$$

(2) Equilibrium. $c_{p, \text{mix}}^* = \frac{1}{m} \sum_{\Delta} \left\{ \mathcal{N}_{\Delta} \left(\frac{\partial \hat{h}_{\Delta}}{\partial T} \right)_p + \hat{h}_{\Delta} \left(\frac{\partial \mathcal{N}_{\Delta}}{\partial T} \right)_p \right\}$

$$= \frac{1}{m} \sum_{\Delta} \left\{ \mathcal{N}_{\Delta} \hat{c}_{p, \Delta} + \hat{h}_{\Delta} \nu_{\Delta} \left(\frac{\partial \xi^*}{\partial T} \right)_p \right\}$$

$$= c_{p, \text{mix}}^{\text{frozen}} + \frac{1}{m} \left(\frac{\partial \xi^*}{\partial T} \right)_p \sum_{\Delta} \nu_{\Delta} \hat{h}_{\Delta}$$

$$C_{P, \text{mix}}^* = C_{P, \text{mix}}^{\text{frozen}} + \frac{1}{m} \left(\frac{\partial \xi^*}{\partial T} \right)_P \Delta \hat{H}_R$$

$$= \frac{1}{m} \left[\sum_A \nu_A^2 C_{P, A} + \underbrace{\left(\frac{\partial \xi^*}{\partial T} \right)_P \Delta \hat{H}_R} \right].$$

This term can be very large.
 contribution of enthalpy of reaction.

van't Hoff's Equation - variation of K_p with T .

$$\ln K_p = -\frac{1}{RT} \sum_{\Delta} \nu_{\Delta} \hat{g}_{\Delta}^{\circ} \quad \text{Note } K_p = K_p(T) \text{ only}$$

$$\frac{d \ln K_p}{dT} = -\frac{d}{dT} \left\{ \sum_{\Delta} \frac{\nu_{\Delta} \hat{g}_{\Delta}^{\circ}}{RT} \right\} = \sum_{\Delta} \nu_{\Delta} \hat{h}_{\Delta} / RT^2$$

(finally)

$$= \frac{\Delta \hat{H}_R}{RT^2}$$

Result follows from $\frac{\hat{g}_{\Delta}^{\circ}}{RT} = \frac{\hat{h}_{\Delta}}{RT} - \frac{1}{R} \left[\int_{T_0}^T \frac{\hat{C}_{p\Delta}}{T} dT + \hat{S}_{\Delta}^{\circ} + R \ln p_{\Delta} \right]$.

$$\frac{d \hat{h}_{\Delta}}{dT} = \hat{C}_{p\Delta}$$

$$\frac{d}{dT} \left(\frac{\hat{g}_{\Delta}^{\circ}}{RT} \right) = \frac{1}{RT} \hat{C}_{p\Delta}' - \frac{\hat{h}_{\Delta}}{RT^2} - \frac{1}{RT} \hat{C}_{p\Delta}'$$

$$\Delta \text{ So } -\frac{d}{dT} \sum_{\Delta} \frac{\nu_{\Delta} \hat{g}_{\Delta}^{\circ}}{RT} = \sum_{\Delta} \frac{\nu_{\Delta} \hat{h}_{\Delta}}{RT^2} = \frac{1}{RT^2} \sum_{\Delta} \nu_{\Delta} \hat{h}_{\Delta}$$

$$= \frac{1}{RT^2} \Delta \hat{H}_R$$

↑ enthalpy of reaction

Note: for endothermic reactions $\Delta \hat{H}_R > 0 \Rightarrow \frac{d \ln K_p}{dT} > 0$
 exothermic reactions $\Delta \hat{H}_R < 0 \Rightarrow \frac{d \ln K_p}{dT} < 0$

Hence for endothermic reactions K_p increases with T
 conversely exothermic reactions have K_p decreasing
 with (increasing) T .