

<Thermochemistry.> OH<sub>2</sub> in Turnus. Book.

- New chemical species produced at an elevated temperature in combustion processes.
- Heat release from the reactions.

i) Chemical Reaction + ii) Thermal Energy Production.

i) Chemical reaction : effective collision between molecules,  
 → need for understanding molecular motion (e.g. speed distribution  
 collision frequency).

- Maxwellian Speed Distribution.

$$X(C) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} C^2 \exp\left(-\frac{mc^2}{2kT}\right)$$

derivation: Physical Gas Dynamics (V. Kruger)

- most probable C.m.p. =  $\sqrt{\frac{2kT}{m}}$

- average  $\bar{C} = \int_0^\infty C X(C) dC = \frac{2}{\sqrt{\pi}} \cdot \sqrt{\frac{2kT}{m}}$

- RMS  $\bar{C}^2 = \int_0^\infty C^2 X(C) dC = \sqrt{\frac{3kT}{m}}$ . (proportional to kinetic (trans.) energy)

- Collision Frequency (Rate)

$$Z_{AB} = \frac{n_A n_B}{\sigma} d_{AB}^2 \left( \frac{8\pi kT}{m_{AB}} \right)^{1/2}, \quad d_{AB} = \frac{d_A + d_B}{2}$$

$$\begin{aligned} &= 1 \quad A \neq B \\ &= 2 \quad B \equiv A. \end{aligned}$$

- Mean Free Path. (no collision  $\Rightarrow$  no reaction)

$$\lambda_A = \frac{1}{\pi \int_0^\infty n_F d_A^2 \sqrt{1 + (m_A/m_F)}}$$

$\Rightarrow T \uparrow \Rightarrow$  kinetic energy  $\uparrow$ , Collision rate  $\uparrow \Rightarrow$  fast reaction  
 $P \uparrow \Rightarrow n$  (# density)  $\uparrow \Rightarrow$  Collision rate  $\uparrow$ , mean free path  $\downarrow \Rightarrow$  Fast. React.

ii) Thermal Energy Production: conversion of chemical energy to thermal or heat energy.

→ In other words: chemical energ  $\rightarrow$  sensible energy.

Internal Energy  $U =$  chemical energy + sensible energy.

◦ Sensible energy.

$$= \text{Translational } (E_{\text{tr}}) + \text{Electronic } (E_{\text{elec}}) + \text{Vibrational } (E_{\text{vib}}) \\ + \text{Rotational } (E_{\text{rot}})$$

Measured as  $T_{\text{tr}}$  (or  $T$ ),  $T_{\text{elec}}$ ,  $T_{\text{vib}}$ ,  $T_{\text{rot}}$ .

◦ Chemical energy.

= Energy stored in the bonds of molecules.

$$\tilde{U}_i = [(U_i)_{\text{trans}} + (U_i)_{\text{elec}} + (U_i)_{\text{vib}} + (U_i)_{\text{rot}}] + (U_i)_{\text{chem.}}$$

Internal E of species i  $= (U_i)_{\text{sensible}}$

$$\circ \text{ Total enthalpy } h_i = U_i + P_i V_i = \underbrace{(U_i)_{\text{sensible}} + P_i V_i}_{= (h_i)_{\text{sensible}}} + (U_i)_{\text{chem}}$$

$$(U_i)_{\text{sensible}} = \int_{T_{\text{ref}}}^T C_V \, dT.$$

const. vol. specific heat. of species i

$$(h_i)_{\text{sensible}} = \int_{T_{\text{ref}}}^T C_P \, dT$$

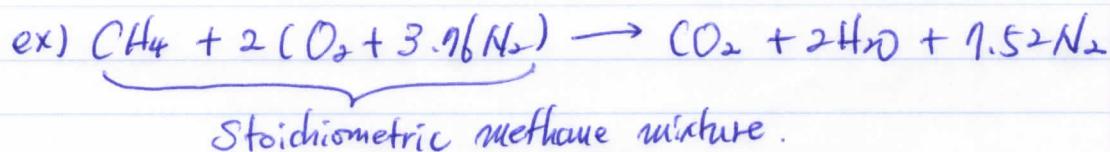
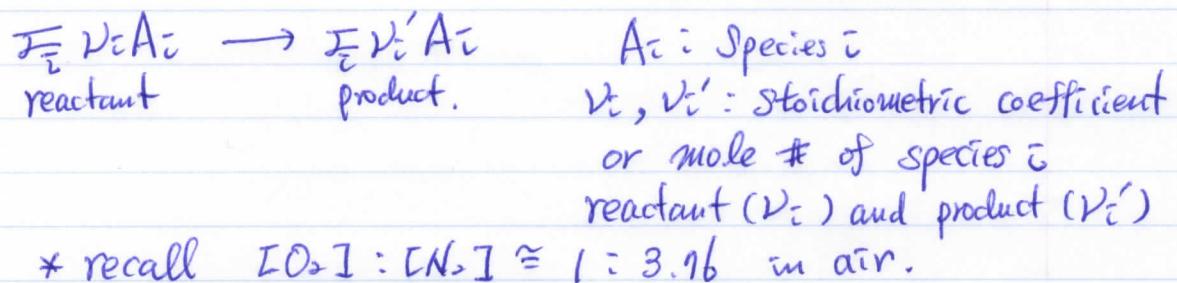
Const. pressure specific heat.

⇒ Thermal E. production  $\Rightarrow$   $(U_i)_{\text{chem}} \downarrow$  and  $(U_i)_{\text{sensible}} \uparrow$

Now, we know that combustion (chemical reaction) produces thermal energy. This enables self-sustainable combustion process!

- Definitions & Concepts.

i) Stoichiometry.  
conservation of mass & atom.



→ Neither fuel nor oxygen is present in excess in the reactant.

No fuel ( $CH_4$ ) & No  $O_2$  in product gas.

	$v_i$	$v'_i$	
$i=1$	$A_1 = CH_4$	1	$\Rightarrow$ stoichiometric mixture.
$i=2$	$A_2 = O_2$	2	$v_i > v'_i$ consumption
$i=3$	$A_3 = N_2$	1.52	$v_i = v'_i$ not participating in reaction
$i=4$	$A_4 = CO_2$	0	$v_i < v'_i$ production
$i=5$	$A_5 = H_2O$	0	

Think Point!

What if  $H_2O$  is produced? Species production depends on P.T.

What is the role of  $N_2$ ? • Thermal energy absorption  
 $\rightarrow$  diffusion effect will be discussed later.

• Participate in three body reaction.

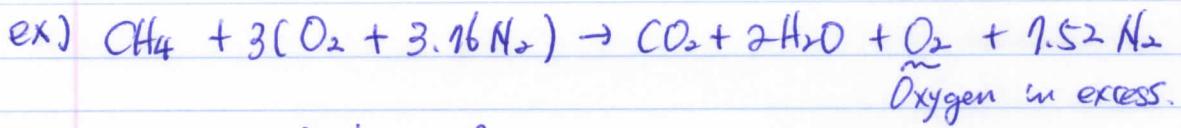
\*\* Equivalence Ratio,  $\phi$ .

$$\phi = \frac{\text{fuel}/O_2 \text{ or Air}}{(\text{fuel}/O_2 \text{ or Air})_{\text{stoic}}}$$

$\phi = 1$  : stoichiometric mixture

$\phi > 1$  : fuel rich

$\phi < 1$  : fuel lean



$\Rightarrow$  Lean Burn.

$$\phi = \frac{1/3}{(1/2)_{\text{stic}}} = \frac{2}{3} < 1$$

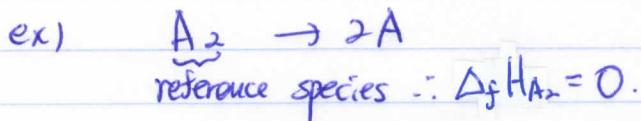
Lean & Rich Flammability Limit

$\phi_{\text{LFL}}$  &  $\phi_{\text{RFL}}$  defines flammable mixture.

ii) Standard Enthalpy (Heat) of Formation:  $\Delta_f H$

\*  $(\Delta_f H)_{\text{chem}}$  is expressed in terms of an Enthalpy of formation.

$\Rightarrow \Delta_f H =$  "the difference between the enthalpy of the species at the reference temperature and the enthalpy of the reference species from which it is formed."



$$\therefore \Delta_f H_{\text{A}_2} = 0.$$

$$2\Delta_f H_A = 2\underbrace{h_A(0\text{K})}_{\text{* known.}} - \underbrace{h_{\text{A}_2}(0\text{K})}_{\text{standard if Tref = 0K}} = 2\Delta_f H_A(0\text{K})$$

\* What if  $T_{\text{ref}} = 298\text{K}$ ?

$$\Delta_f H_A(298\text{K}) \equiv h_A(298\text{K}) - \frac{1}{2}h_{\text{A}_2}(298\text{K})$$

$$= \left\{ [h_A(298\text{K}) - h_A(0\text{K})]_{\text{sensible}} + \underbrace{(\Delta_f H_A)_{\text{chem}}}_{\substack{\uparrow \\ \text{not a func. of } T.}} \right\} - \frac{1}{2} \left\{ [h_{\text{A}_2}(298\text{K}) - h_{\text{A}_2}(0\text{K})]_{\text{sensible}} + (\Delta_f H_{\text{A}_2})_{\text{chem}} \right\}$$

$$= \underbrace{\int_{0\text{K}}^{298\text{K}} C_{p,A} dT - \frac{1}{2} \int_{0\text{K}}^{298\text{K}} C_{p,\text{A}_2} dT}_{\parallel} + \Delta_f H_A(0\text{K})$$

Heat of Reaction  $\Delta H_R(T)$

$$= H_{\text{prod}}(T) - H_{\text{react}}(T) = Q_p$$

$Q_p$  = heat generated by the reaction.

when  $T = T_{\text{ref.}}$ ,  $\Delta H_R(T_{\text{ref.}})$  is standard heat of reaction.

In practice  $T_{\text{react}} \neq T_{\text{product.}}$ ,  $T_R < T_p$

$\therefore$  Actual thermal energy available is  $< \Delta H_R(T)$

### \* Thermodynamics.

- First law.

energy production + energy inflow = energy outflow + energy storage  
from exothermic reactions. independent of amount.

\* Simple Compressible Substance (S.C.S.) to express state  
a pure substance for which  $PdV$  work is the only reversible work mode.

- Control mass (no mass transfer)

$$\underbrace{\delta Q}_{\text{heat trans.}} - \underbrace{PdV}_{\text{change in internal energy (storage)}} = dU$$

across sys. boundary.

$$dU = d(U_{\text{seus}} + E_{\text{chem}}) = fQ$$

- adiabatic ( $\delta Q = 0$ ), constant volume ( $dV = 0$ )

$$dU = 0 \Rightarrow [d(U_{\text{seus}}) = -d(E_{\text{chem}})] \text{ Ad., C.V.}$$

- \* constant pressure (typical process in open system)

$$H = U + PV \text{ (control mass)}$$

$$\therefore dH = dU + PdV + Vdp \xrightarrow{P \text{ const.}} = \delta Q + Vdp$$

$$dH = d(H_{\text{sens}} + \bar{E}_{\text{chem}}) = fQ = 0 \text{ (adiabatic)}$$

$$\therefore \boxed{d(H_{\text{sens}}) = -d(\bar{E}_{\text{chem}})} \quad \text{Ad., C.P.}$$

- Time derivative of First law.

$$\text{energy production rate} + \text{energy inflow rate} = \text{energy outflow rate} \\ + \text{energy storage rate}$$

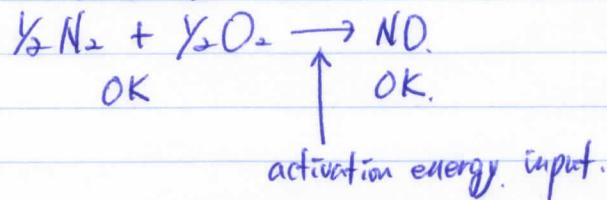
\* Steady process  $\rightarrow$  storage rate = 0

\* Control Volume  $\rightarrow$  mass transfer  $\neq 0$

$$\frac{dH_{\text{out}}}{dt} = \frac{dH_{\text{in}}}{dt} + \frac{dQ}{dt} + \frac{dW}{dt}$$

\* Application of the first law. to reactive systems

ex) NO formation reaction



$$Q_{\text{in}} = \frac{1}{2}(f_{\text{o}})_{N_2} + \frac{1}{2}(f_{\text{o}})_{O_2}$$

$\underbrace{\quad}_{\text{dissociation energy.}}$



First law.

$$\frac{1}{2}h_{N_2}(0K) + \frac{1}{2}h_{O_2}(0K) + Q_{\text{in}} = h_{NO}(0K) + Q_{\text{out}}$$

$$Q_{\text{in}} - Q_{\text{out}} = \frac{1}{2}((f_{\text{o}})_{N_2} + (f_{\text{o}})_{O_2}) - (f_{\text{o}})_{NO}$$

$$= h_{NO}(0K) - \frac{1}{2}(h_{N_2}(0K) + h_{O_2}(0K)) \equiv \Delta_f H_{NO}(0K)$$