

# UNIT-1

1

COMBUSTION

# OVERVIEW

2

- In our development of model for Thermal Rocket Thrust Chambers, we considered two primary components:
  1. Combustion (or Heating) Chamber
  2. Nozzle
- Developed a 1-D model that allowed us to predict important parameters
  - $U_e$ , Isp, Thrust (and associated derived characterization coefficients:  $C_F$ ,  $C^*$ )
  - Model simplified with many assumptions
- Next step was to examine nozzle
  - Types of nozzles, performance, impact of altitude, etc.
  - Connect performance to shape and design of optimum and realistic shapes
- **Now examine Combustion Chamber – but must know something about Combustion first**

# SUMMARY OF KEY EXIT VELOCITY EQUATIONS

$$U_e = \sqrt{2C_p T_{o2} \left[ 1 - \left( \frac{p_e}{p_{02}} \right)^{(\gamma-1)/\gamma} \right]} \stackrel{\textcircled{3}}{=} \sqrt{\frac{2\gamma\bar{R}}{(\gamma-1)\bar{M}} T_{o2} \left[ 1 - \left( \frac{p_e}{p_{02}} \right)^{(\gamma-1)/\gamma} \right]}$$

$$U_e \approx \sqrt{2 \frac{\bar{Q}_R}{\bar{M}} \left[ 1 - \left( \frac{p_e}{p_{02}} \right)^{(\gamma-1)/\gamma} \right]}$$

How does this quantity help to dictate whether to operate rocket fuel rich or lean?  
(answer on next slide)

## Key Assumptions

- Quantity of heat added at constant pressure
- Constant specific heats

For high  $U_e$  (for all thermal rockets), desire:

- Propellants with low molecular weight,  $M$
- Propellant mixtures with large  $Q_R/M$  (not at  $T_{\max}$ )**
- High combustion chamber pressure,  $P_{02}$

# WHY DO LH<sub>2</sub>-LOX ROCKETS RUN FUEL RICH?

4

- **Desire high heating value,  $Q_R$ , and low molecular weight,  $M$** 
  - Running rocket fuel rich (or lean) will reduce  $Q_R$
  - However, if fuel is lighter in molecular weight than oxidizer, fuel rich will reduce average molecular weight
  - **The overall ratio  $Q_R/M$  is increased**
  - **As fuel-rich mixtures are burned, as it is found that resultant reduction in  $M$  more than offsets accompanying reduction in  $Q_R$**
  - Also note that when dissociation is present, O/F ratio, much less than stoichiometric for maximum specific impulse
- **Explains why SSME run fuel-rich (H<sub>2</sub>-O<sub>2</sub>) – fuel has lower molecular weight**
- **Also explains why rockets use oxidizer-rich case when oxidizer has lower molecular weight (V-2 rocket for example, alcohol-oxygen rocket)**

# OVERVIEW: GENERAL COMMENTS

5

- Recall: Rocket performance strongly dependent on T/W and Isp
- Design of combustion chamber is critical to both of these metrics
  - Isp depends strongly on **composition** and **T** of combustion products
  - Intensity of combustion (energy transferred per unit time per unit volume) determines size (mass) of combustion chamber
- Combustion products of a well designed combustion chamber are very nearly in ***thermodynamic equilibrium***

Q: What does ***thermodynamic equilibrium*** mean?

A: At combustion chamber T & P, time required for mixing of fuel and oxidizer and for chemical reactions to take place is small compared to average residence time in combustion chamber

# OVERVIEW: GENERAL COMMENTS

- Time-scale ratios are so important: Non-dimensional number

- Known as Damköhler Number
- Ratio of flow to chemical time scales

6

$$Da = \frac{\tau_{flow}}{\tau_{chem}}$$

- **If  $Da \gg 1$**

- Flow 'change' time is much longer than chemical time
- There are many units of time for reactions to take place during flow traverse
- System is in chemical equilibrium in combustion chamber

- **If  $Da \ll 1$**

- Flow time is much shorter than chemical time
- Flow changing at rate much faster than which chemical reactions may occur
- May occur in rocket nozzles (frozen flow)

- Typical numbers for rocket (and gas turbine engines) combustors

- Flow time 1 ms, chemical time scale 1  $\mu$ s
- $Da \sim O(10^{-3}/10^{-6}) \sim O(1000)$

# OVERVIEW: GENERAL COMMENTS

7

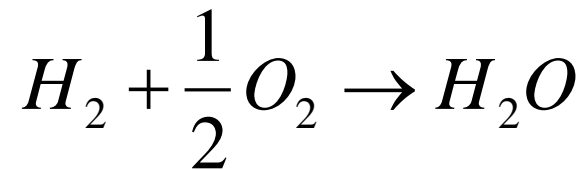
- Combustion chamber properties are calculated using method of equilibrium combustion thermochemistry
  - Review of equilibrium combustion thermodynamics and chemical reactions
  - Goal is to understand basic concepts and set up governing equations
  - Perform simplified calculations (examples to come)
  - Detailed description and realistic results – need computer solver (NASA CEA)
- **Rocket combustion chamber temperatures are so high that typically substantial portion of combustion products are dissociated**
- During expansion in nozzle,  $T$  falls so rapidly there may be insufficient time for dissociated products to recombine
- Gas composition at each stage of expansion may not be in equilibrium ( $Da \ll 1$ )
- When gas expands in such a manner it is called frozen flow

# OVERVIEW: GENERAL COMMENTS

Q: What does stoichiometric ratio mean and how is it calculated?

8

A: Stoichiometric ratio of oxidizer to fuel for a balanced equation where all fuel and all oxidizer is consumed. Consider again:



Stoichiometric ratio for this reaction (relevant to liquid rocket propulsion) given by:

$$r = \frac{\frac{1}{2} O_2}{H_2} = \frac{\frac{1}{2} (2 \times 16)}{2 \times 1} = \frac{16}{2} = 8$$

If  $r < 8$ , there is more fuel than oxidizer

izer (relative to stoichiometric ratio) and mixture is called fuel-rich

If  $r > 8$ , there is more oxidizer than fuel (relative to stoichiometric ratio) and mixture is called oxidizer-rich or fuel-lean

# COMBUSTION THERMOCHEMISTRY

GOAL: Represent what happens in combustor, to convert liquid propellants to hot gases at  $T_c$  and  $P_c$ .

Qualitatively:

- Difference between chemical energies of **reactants** (chemicals injected into combustion chamber) and that of reaction **products** (hot gases we seek to describe) shows up as thermal energy of **products**

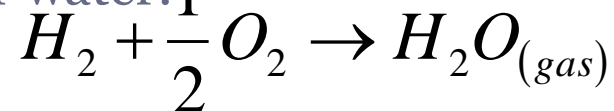
Think of it as sequence of 2 steady flow process:

1. Formation by chemical reactions of products from reactants at standard T & P
  - Such a process cannot happen in practice
  - Think of it as a process in which the reactions occur at standard T & P while heat is added in the amount necessary to keep T constant
  - Heat added in such an ideal process is defined as the Standard Heat of Formation  $\Delta H_f^\circ$  of the products if the reactants are elements in their standard states
2. Use heat added in step 1 to change T of products
  - T change is given by Steady-Flow Energy Equation

# COMBUSTION THERMOCHEMISTRY

- Every chemical substance has a Standard Heat of Formation defined this way. (10)

- For example for water:1



$$\Delta H_{f, H_2O_{(gas)}}^0 = -241.827 \text{ KJ/mol}$$

- Cumbersome notation necessary to indicate reaction product is liquid water
- Heat of formation of liquid water would differ from this by the heat of vaporization

## **NOTE: Heat of formation of water is negative**

- Heat is released in its formation
- Heat of formation is negative for all exothermic reactions
  - System must give off heat to maintain (or return to) reference temperature

TABLE 6-1. Chemical Thermodynamic Properties of Selected Substances at 298.15 K (25°C) and 0.1 MPa (1 bar)

Substance	Phase*	Molar Mass (g/mol)	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	$\log K_f$	$S^\circ$ (J/mol-K)	$C_p$ (J/mol-K)
Al (crystal)	s	29.9815	0	0	0	28.275	24.204
Al <sub>2</sub> O <sub>3</sub>	l	101.9612	-1620.567	-1532.025	268.404	67.298	79.015
C (graphite)	s	12.011	0	0	0	5.740	8.517
CH <sub>4</sub>	g	16.0476	-74.873	-50.768	8.894	186.251	35.639
CO	g	28.0106	-110.527	-137.163	24.030	197.653	29.142
CO <sub>2</sub>	g	44.010	-393.522	-394.389	69.095	213.795	37.129
H <sub>2</sub>	g	2.01583	0	0	0	130.680	28.836
HCl	g	36.4610	-92.312	-95.300	16.696	186.901	29.136
HF	g	20.0063	-272.546	-274.646	48.117	172.780	29.138
H <sub>2</sub> O	l	18.01528	-285.830	-237.141	41.546	69.950	75.351
H <sub>2</sub> O	g	18.01528	-241.826	-228.582	40.047	188.834	33.590
N <sub>2</sub> H <sub>4</sub>	l	32.0451	+50.626	149.440	-28.181	121.544	98.840
N <sub>2</sub> H <sub>4</sub>	g	32.0451	+95.353	+159.232	-27.897	238.719	50.813
NH <sub>4</sub> ClO <sub>4</sub>	s	117.485	-295.767	-88.607	15.524	184.180	128.072
ClF <sub>3</sub>	g	130.4450	-238.488	-146.725	25.706	310.739	97.165
ClF <sub>3</sub>	g	92.442	-158.866	-118.877	20.827	281.600	63.845
N <sub>2</sub> O <sub>4</sub>	l	92.011	-19.564	+97.521	-17.085	209.198	142.509
N <sub>2</sub> O <sub>4</sub>	g	92.011	9.079	97.787	-17.132	304.376	77.256
NO <sub>2</sub>	g	46.0055	33.095	51.258	-8.980	240.034	36.974
HNO <sub>3</sub>	g	63.0128	-134.306	-73.941	12.954	266.400	53.326
N <sub>2</sub>	g	28.0134	0	0	0	191.609	29.125
O <sub>2</sub>	g	31.9988	0	0	0	205.147	29.376
NH <sub>3</sub>	g	17.0305	-45.898	-16.367	2.867	192.774	35.652

\* s = solid, l = liquid, g = gas

Source: References 6-11 and 6-12

# COMBUSTION THERMOCHEMISTRY

12

- **NOTE 1**

- Heat of formation may be negative, positive or zero (KJ/mole)
- Heat is released in its formation
- Heat of formation is negative for all exothermic reactions
  - ✦ This is because the system must give off heat to maintain (or return to) reference temperature
- Convention that heat added is positive is purely arbitrary

- **NOTE 2**

- Heat of formation for elements in their standard states is ZERO

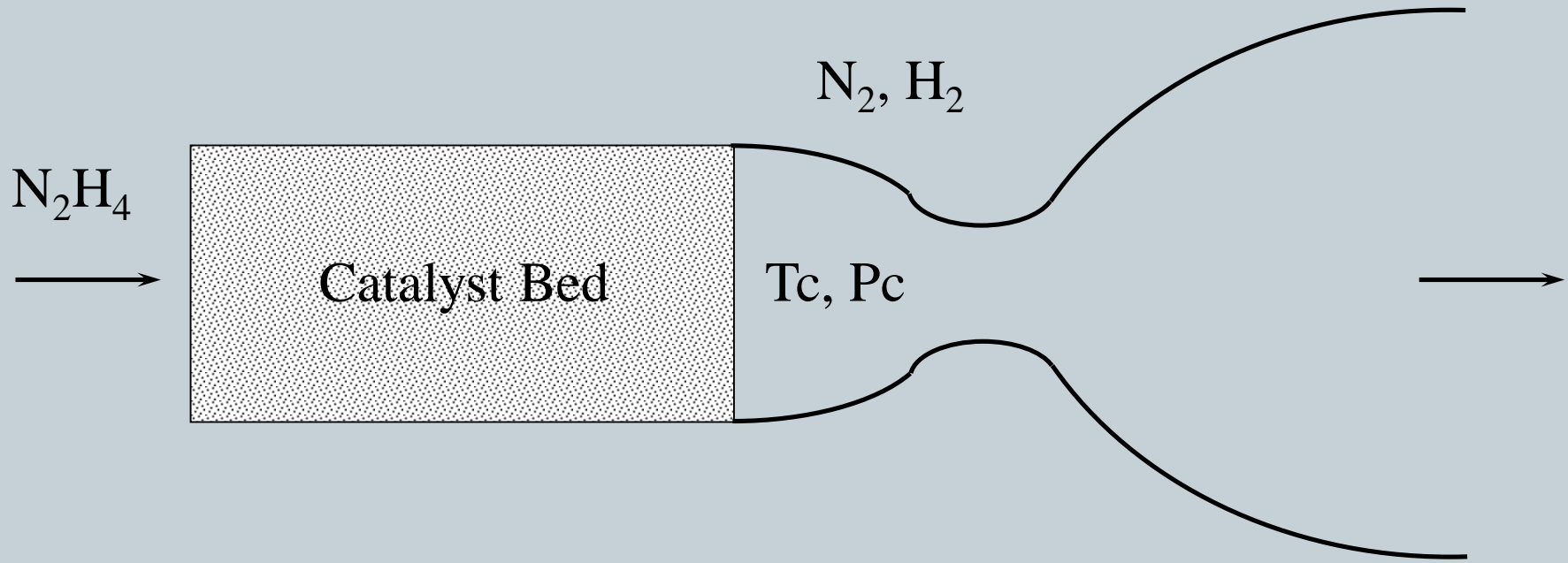
- **NOTE 3**

- Substances that are **stable** at normal room T & P have **negative** heats of formation
- Substances that are **unstable** (explosives) have **positive** heats of formation

# EXAMPLE: APPLICATION TO ROCKETS

Consider a monopropellant rocket engine using Hydrazine fuel,  $\text{N}_2\text{H}_4$

- Substance has physical properties much like those of water
- However has a positive Standard Heat of Formation of 50.2 kJ/mole
- Assume it decomposes to produce only  $\text{N}_2$  and  $\text{H}_2$



# EXAMPLE: APPLICATION TO ROCKETS

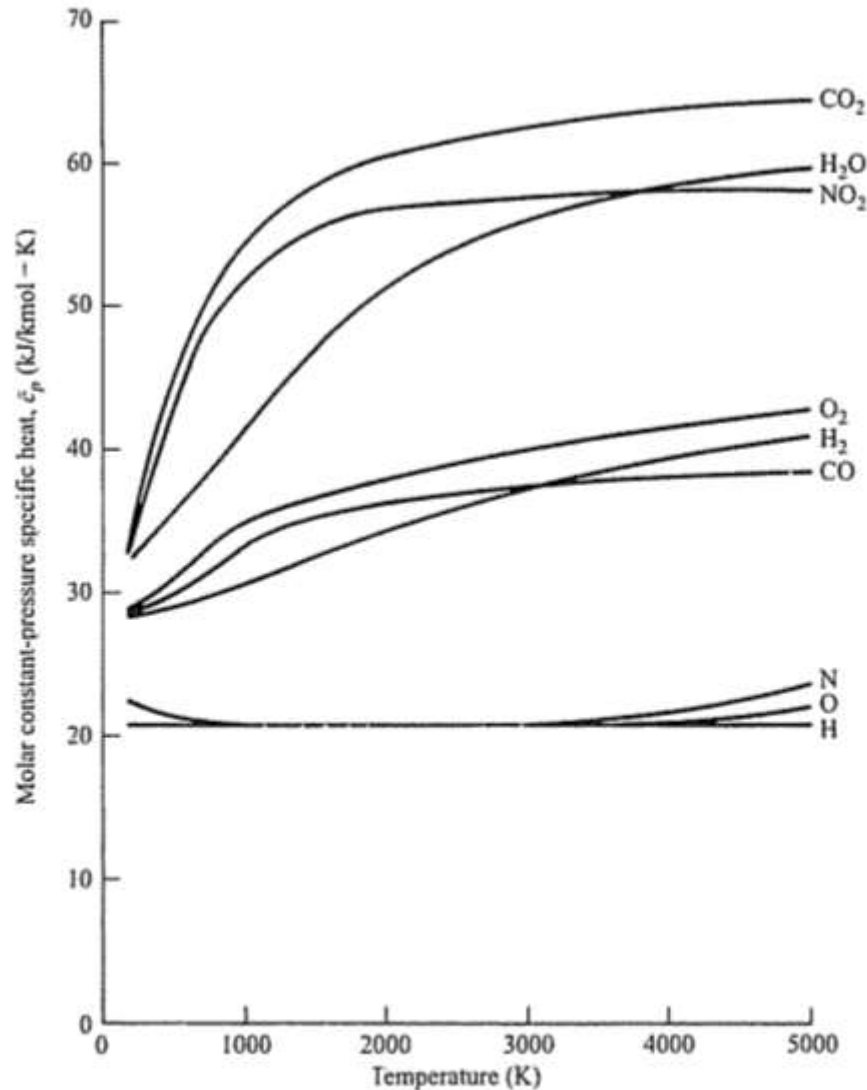
- Enthalpy of each product can be approximated by  $C_p T$
- Chamber temperature is given by:

14

- Specific heats are per mole if heat of formation is per mole
- Constant pressure process
- $C_p = C_p(T)$
- Assumed products of combustion are nitrogen and hydrogen
- In general there might be some ammonia ( $NH_3$ ) and perhaps other compounds in the decomposition products of hydrazine

$$\left[ C_{p,N_2} + 2C_{p,H_2} \right] (T_c - T_0) = \Delta H_{f,N_2H_4}^0$$

# TEMPERATURE DEPENDENCE OF SPECIFIC HEATS



**Figure 2.2** Molar constant-pressure specific heats as functions of temperature for monatomic (H, N, and O), diatomic (CO, H<sub>2</sub>, and O<sub>2</sub>), and triatomic (CO<sub>2</sub>, H<sub>2</sub>O, and NO<sub>2</sub>) species. Values are from Appendix A.

Example:

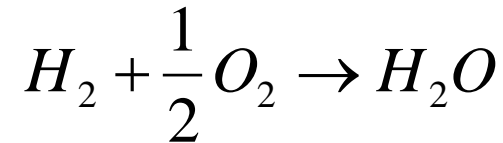
- Enthalpy often approximated as  $h(T) = C_p T$
- In combustion chemistry, enthalpy must take into account variable specific heats,  $h(T) = C_p(T)T$
- If  $C_p(T)$  can be fit with quadratic, solution for flame temperature for certain classes of problems  $\phi < 1$  and  $T < 1250$  K leads to closed form solutions
- For higher order fits or  $\phi > 1$  and/or  $T > 1250$  K, iterative closure schemes are required for solution of flame temperature
- Also will discuss a definition of enthalpy that accounts for chemical bonds
- 1<sup>st</sup> law concepts defining heat of reaction, heating values, etc.

# DISSOCIATION: GENERAL COMMENTS

Q: What does combustion products are dissociated mean?

16

A: Consider burning (combustion) of a hydrogen and oxygen mixture



○ In complete combustion we have:

○ All reactants go into forming products

✦ In this case hydrogen and oxygen form water

○ At high enough temperature products may further breakdown

○ Reaction may proceed in reverse,  $H_2O$  breaking down into  $H_2$  and  $O_2$

$$H_2O \rightarrow \alpha H_2 + \beta O_2 + \gamma H + \delta OH + \epsilon O + \eta O_3$$

# DISSOCIATION: GENERAL COMMENTS



- Think about terms  $\beta$ ,  $\delta$ ,  $\nu$ ,  $\varepsilon$ ,  $\eta$  as a ‘wasted energy opportunity’
- Instead of liberating all chemical energy of reaction into just water, some of it is subsequently ‘wasted’ by using high T energy to form other products
- Highest  $U_e$  and  $I_{sp}$  will always be achieved with **no** dissociation
  - Never occurs at operating T of actual rockets
  - Must deal with dissociation of products
- Also note, left side of equation still has stoichiometric ratio of O/F
  - Ratio is not best one to use when dissociation occurs (lower side)

# IN-CLASS EXAMPLE: SUMMARY

Governing equation: 7 unknowns ( $T_c, \alpha, \beta, \delta, \nu, \sigma, \eta$ ) and  $P_c$  set



$$2 = 2\alpha + 2\beta + \delta + \nu$$

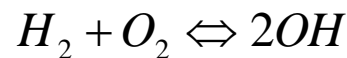
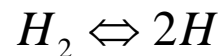
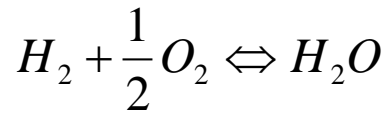
$$2m = \alpha + \delta + 2\varepsilon + \eta$$

2 equations from H and O atom balance

$$K_{P,OH}(T) = \frac{\delta^2}{\beta\varepsilon}$$

$$K_{P,O}(T) = \frac{\eta^2 P_c}{\sigma\varepsilon}$$

4 linearly independent relations  
from equilibrium approximation



Equilibrium constant expressions  
written in terms of partial pressures

$$K_{P,H_2O}(T) = \frac{P_{H_2O}}{P_{H_2} (P_{O_2})^{1/2}}$$

$$K_{P,H}(T) = \frac{(P_H)^2}{P_{H_2}}$$

$$K_{P,OH}(T) = \frac{(P_{OH})^2}{P_{H_2} (P_{O_2})}$$

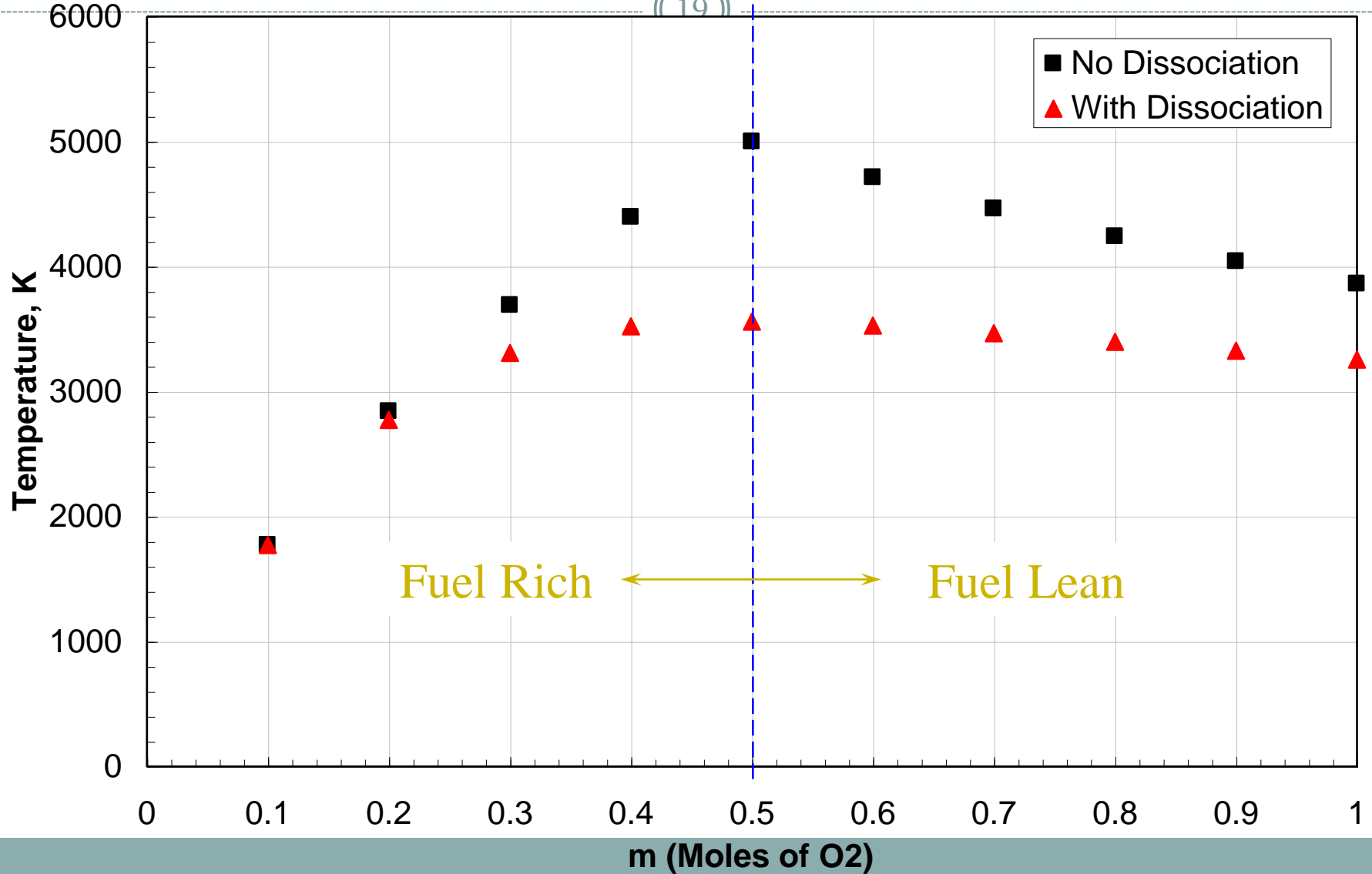
$$K_{P,O}(T) = \frac{(P_O)^2}{P_{O_2}}$$

Equilibrium constant expressions  
Written in terms of unknowns

6 equations, 7 unknowns  $\rightarrow T_c$

# EXAMPLE CEA CALCULATION: H<sub>2</sub>-O<sub>2</sub> COMBUSTION

Chamber Pressure = 30 atm, Inlet Temperature for H<sub>2</sub>, O<sub>2</sub> = 300 K



# EXAMPLE CEA CALCULATION: H<sub>2</sub>-O<sub>2</sub> COMBUSTION

Chamber Pressure = 30 atm., Inlet Temperature H<sub>2</sub>, O<sub>2</sub> = 300 K

20

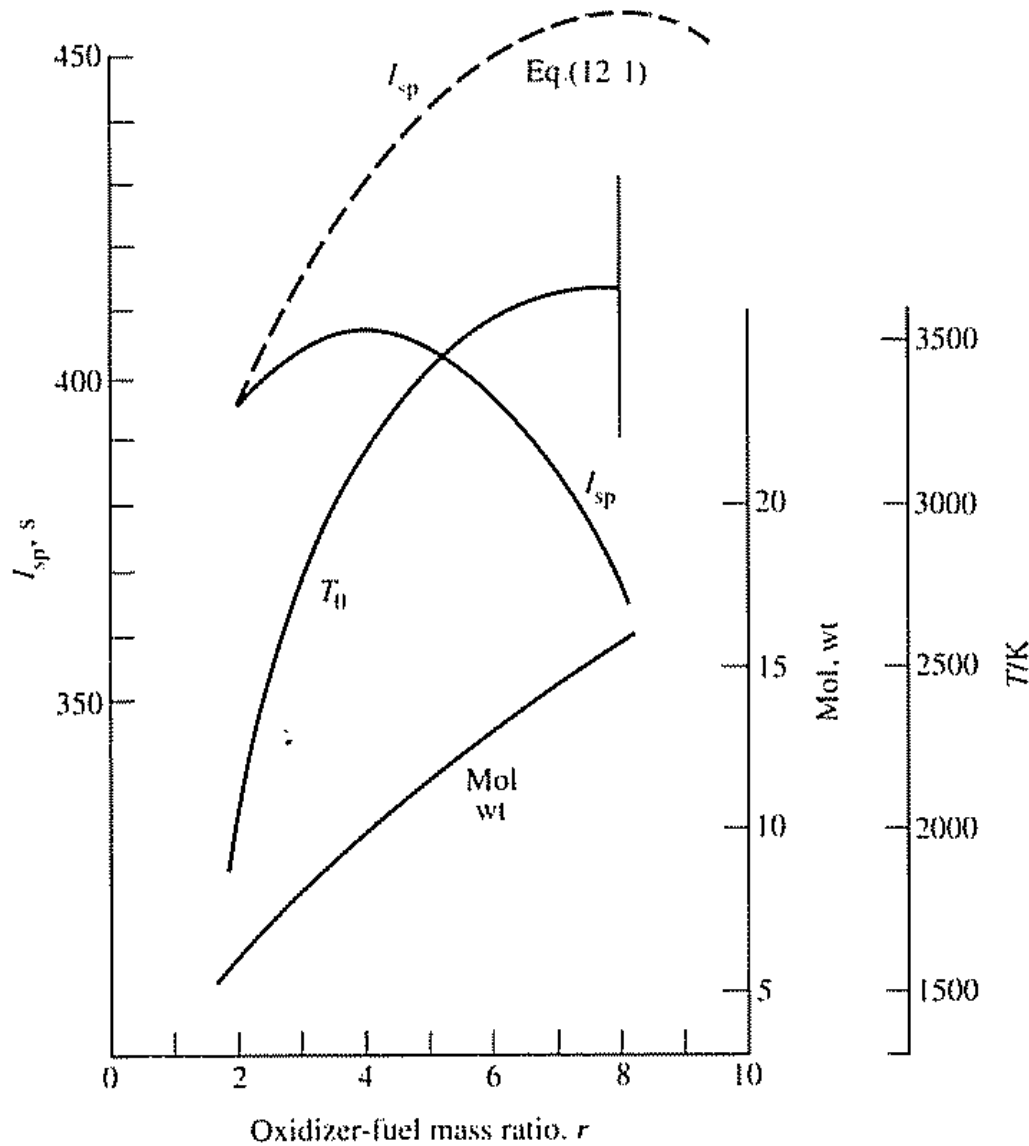
m	T	Product	Mole Fraction	Mass Fraction	m	T	Product	Mole Fraction	Mass Fraction
0.1	1772.31	H2O	0.2	0.6908	0.1	1772.02	H2O	0.1999	0.6108
		H2	0.8	0.3092			H2	0.79996	0.30919
		O2	0	0			O2	3.53E-12	2.17E-11
0.2	2840.63	H2O	0.4	0.85627	0.2	2772.76	H2O	0.39558	0.85209
		H2	0.6	0.14373			H2	0.59206	0.14271
		O2	0	0			O2	5.74E-06	2.20E-05
0.3	3689.95	H2O	0.6	0.93058	0.3	3307.6	H2O	0.54965	0.88438
		H2	0.4	0.069421			H2	0.38081	6.86E-02
		O2	0	0			O2	9.47E-04	2.71E-03
0.4	4395.34	H2O	0.8	0.97279	0.4	3520.31	H2O	0.63081	0.83643
		H2	0.2	0.02721			H2	0.22414	3.33E-02
		O2	0	0			O2	1.10E-02	2.59E-02
0.5	4999.19	H2O	1	1	0.5	3559.4	H2O	0.65403	0.75804
		H2	0	0			H2	0.13308	1.73E-02
		O2	0	0			O2	4.06E-02	8.36E-02
0.6	4713.77	H2O	0.90909	0.84918	0.6	3526.13	H2O	0.6479	0.68055
		H2	0	0			H2	8.33E-02	9.79E-03
		O2	0.090909	0.15082			O2	8.63E-02	1.61E-01
0.7	4462.78	H2O	0.83333	0.73788	0.7	3465.91	H2O	0.62974	0.61333
		H2	0	0			H2	5.49E-02	5.99E-03
		O2	0.16667	0.26212			O2	1.39E-01	2.40E-01
0.8	4240.2	H2O	0.76923	0.65238	0.8	3396.99	H2O	0.6072	0.5569
		H2	0	0			H2	3.76E-02	3.86E-03
		O2	0.23077	0.3476			O2	1.92E-01	3.13E-01
0.9	4041.34	H2O	0.71429	0.58464	0.9	3325.8	H2O	0.58363	0.50961
		H2	0	0			H2	2.65E-02	2.59E-03
		O2	0.28571	0.41536			O2	2.43E-01	3.77E-01
1	3862.53	H2O	0.6667	0.52964	1	3254.78	H2O	0.56036	0.46971
		H2	0	0			H2	1.91E-02	1.79E-03
		O2	0.3333	0.47036			O2	2.91E-01	4.33E-01

# CEA PRACTICE PROBLEMS

21

- Determine impact of chamber pressure
  - Repeat calculation for  $P_c = 10$  atm.
    - ✦ No dissociation,  $m = 0.2, 0.5, 0.7$
    - ✦ With dissociation,  $m = 0.2, 0.5, 0.7$
  - Repeat calculation for  $P_c = 80$  atm.
    - ✦ No dissociation,  $m = 0.2, 0.5, 0.7$
    - ✦ With dissociation,  $m = 0.2, 0.5, 0.7$

# SUMMARY



- Note location of maximum  $I_{sp}$  when dissociation included
- What are trade-offs?
  - Thrust
  - Carry more  $H_2$ , how is tank size affected?

# CHEMICAL REACTIONS OCCURRING WITHIN ROCKET NOZZLES

23

# NOZZLE FLOW OF REACTING GASES

Suppose that we have determined composition of gases in combustion chamber

24

Now compute flow through nozzle taking into account chemical reactions

- 3 major deviations from simple model based on ideal gas behavior
  1. Composition of gas is not necessarily constant in flow
    - ✦ Properties that are composition dependent must be treated as variables along flow direction
    - ✦ Specific heats, gas constant and ratio of specific heats
  2. Sum of thermal energy and kinetic energy is no longer constant
    - ✦ Exchange of chemical energy and thermal energy
  3. Non-isentropic
    - ✦ We can neglect this entropy change for 2 special cases

# NOZZLE FLOW OF REACTING GASES

- To deal with the flow, we first note that energy conservation for the gas flow is:

$$H_c = H(T, P) + \frac{u^2}{2}$$

- This replaced the ideal gas energy equation:

$$C_p T_c = C_p T + \frac{u^2}{2}$$

- Need statement about variation of entropy
  - Transfer from chemical to thermal energy takes place at finite rate, therefore entropy increase
- There are 2 limiting cases for which entropy change is very small
  1. **Chemical Equilibrium**
  2. **Frozen Flow**

# NOZZLE FLOW OF REACTING GASES

## • Chemical Equilibrium

- Approached if the reactions occur fast enough to keep up with T & P change caused by expansion
- Flow time  $\gg$  Reaction time
- Chemical energy is transferred through an infinitesimal  $\Delta T$

$$S = \sum x_i(P, T) S_i(P, T) = S_c$$

- $x_i$  determined by equilibrium at local T & P

## • Frozen Flow

- Reactions occur slowly,  $x_i$  are fixed at their chamber values
- Flow time  $\ll$  reaction time
- No chemical energy release

$$S = \sum x_i(P_c, T_c) S_i(P, T) = S_c$$

# NOZZLE FLOW OF REACTING GASES

27

- Chemical Equilibrium and Frozen Flow are 2 limiting cases
  - Provide an upper and lower limit for the velocity at a given pressure
- **Chemical Equilibrium** gives **maximum** thermal energy availability for conversion for kinetic energy
- **Frozen Flow** gives **minimum**

Phenomenological explanation of why this is so:

- Gases leaving combustion chamber are so hot products of combustion are highly dissociated
- Dissociated compounds will tend to recombine because of large drop in  $T$  during nozzle expansion process
- Recombination is exothermic and acts as heat source in flow (changes in  $C_p$  and  $\gamma$ )
- **However,  $I_{sp}$  always lower with dissociation than with no dissociation at all**