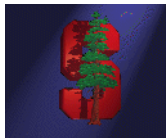# AA 284a
Advanced Rocket Propulsion

Lecture 4
Thermochemistry and Propellants
Part 1

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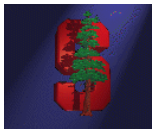**KOÇ UNIVERSITY**

Review of Thermochemistry – Goal and Approach

- Goal:
  - Understand the oxidation reactions
  - Estimate the flame temperature, composition of combustion products -> c* and Isp
  - Inputs: Reactants, stoichiometry (O/F), pressure, temperature of reactants

- Approach:
  - Use equilibrium thermodynamics
  - Combination of First Law/Second Law
  - Remember that equilibrium thermodynamics can**not** answer the questions such as
    - How fast are the reactions ?
    - Are the reactions complete ?
  - These questions can only be answered by chemical kinetics.

Reference on Thermochemistry: Glassman I., "Combustion"
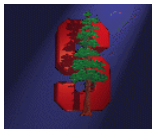
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## Review of Thermochemistry-Definitions and Concepts

- Global Reactions versus Kinetics (elementary reactions)
  - Global Reaction:

  $$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

    - Start with reactants and ask the question: What is the composition and temperature of the end products ?
    - Thermodynamic approach
    - Kinetics is **not** inferred from the reaction equation
  - Kinetics:
    - Represents real chemical reactions
    - Roots in the molecular theory
    - Fairly complex even for very simple systems
      - 100s of equations for Hydrocarbon combustion
      - 10 equations for H2 combustion
    - Reaction steps
      - Initiation (formation of free radicals), chain reactions (propagation of free radicals), termination reactions (elimination of free radicals)

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Review of Thermochemistry-Definitions and Concepts

- Stoichiometry:

  - Accounting of atoms. Generic reaction

  $$\sum_{reactants} v_i A_i \rightarrow \sum_{products} v_i' A_i$$
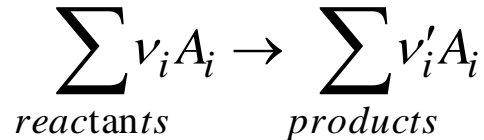
  $$v_i : Moles$$
  $$A_i : Species$$

  - Number atoms are conserved in a chemical reaction

  - The mixture of reactants is "Stoichiometric" if the end products are CO_2 and H_2O only. No excess fuel or oxidizer is present

  - Example: Methane/oxygen reaction

  $$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
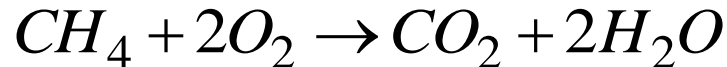
  - Oxidizer to fuel ratio (by mass): *O/F*

  - For methane oxygen reaction $(O/F)_{stoic} = \dfrac{4 \cdot 16}{16} = 4.0$

  - Fuel Rich Mixture: $O/F < (O/F)_{stoic}$
  - Fuel Lean Mixture: $O/F > (O/F)_{stoic}$
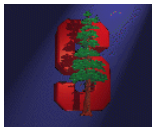
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Review of Thermochemistry-Definitions and Concepts

- Sensible and Chemical Energy
 - It is convenient to define energy in two parts: sensible and chemical

$$\hat{h}_i = \left(\hat{e}_i\right)_{trans} + \left(\hat{e}_i\right)_{rot} + \left(\hat{e}_i\right)_{vib} + \left(\hat{e}_i\right)_{elec} + P_i \hat{v}_i + \left(\hat{\varepsilon}_i\right)_{chem} = \left(\hat{h}_i\right)_{sens} + \left(\hat{\varepsilon}_i\right)_{chem}$$

- Energy Datum:
  - Absolute values of energy are not required
  - Sensible enthalpy is relative to a reference temperature
  - Chemical energy is referenced to a set of reference species
  - JANNAF set of species with zero chemical energy at 25 C
    - O_2, H_2, C(s), Al, Mg, Be …….

- Diatomic molecule (such as O_2)
  - Chemical bond energy at 25 C: $\hat{D}_O$
  - Quantum mechanics can be used to predict the bond energy.

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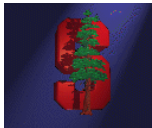
Review of Thermochemistry-Definitions and Concepts

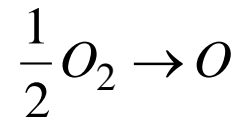- ## Standard Enthalpy of Formation:
  - Chemical energy stored in the bonds of a molecule
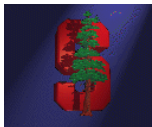 - Defined as (Formation reaction)

$$\sum_{ref\ species} v_i B_i \rightarrow A_j \qquad \Delta \hat{H}_{f\,25C} \equiv \hat{h}_{j25C} - \sum v_i \hat{h}_{i25C}$$
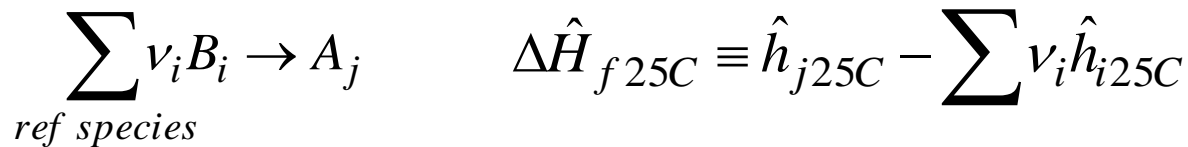
  - Enthalpy at arbitrary temperature can be written as

$$\hat{h}(T) = \Delta \hat{H}_{f\,25C} + \left[\hat{h}(T) - \hat{h}(25\ C) \right]_{sens}$$

  - Example: Formation reaction of atomic oxygen

$$\frac{1}{2} O_2 \rightarrow O$$

$$\Delta \hat{H}_{fO,25C} \equiv \hat{h}_O(25C) - \frac{1}{2} \hat{h}_{O_2}(25C) = \hat{h}_O(25C) = (\hat{\varepsilon}_O)_{chem} = \frac{(\hat{D}_o)_{O_2}}{2}$$

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Review of Thermochemistry-First Law

- First Law of thermodynamics
  - For simple compressible substance
  - For constant volume processes

$$dE = d\left(E_{sens} + E_{chem}\right) = \delta Q$$
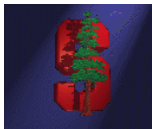
  - If the process is adiabatic

$$dE_{sens} = -dE_{chem}$$

  - Similarly for constant pressure and adiabatic processes

$$dH_{sens} = -dE_{chem}$$
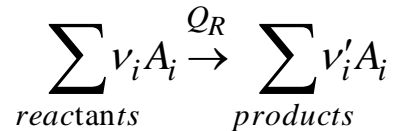
  - In general for an open system

$$\sum_{products} \dot{n}_j \hat{h}_{j,25C} = \sum_{reactants} \dot{n}_i \hat{h}_{i,25C} + \dot{Q} - \dot{W}$$
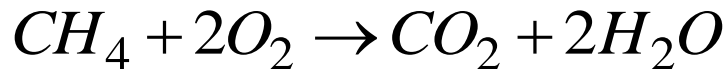
Review of Thermochemistry-First Law

- Heat of Reaction (Combustion)

$$\sum_{reactants} v_i A_i \xrightarrow{Q_R} \sum_{products} v_i' A_i$$
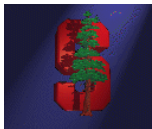
$$Q_R = \Delta H_{R,25C} \equiv H_{prod,25C} - H_{react,25C} = \sum_{prod} v_j \Delta \hat{H}_{fj,25C} - \sum_{react} v_i \Delta \hat{H}_{fi,25C}$$

- Example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$Q_R = \Delta H_{R,25C} = \Delta \hat{H}_{fCO_2,25C} + 2\Delta \hat{H}_{fH_2O,25C} - \Delta \hat{H}_{fCH_4,25C}$$

- Exothermic Reaction: $Q_R < 0$

- Endothermic Reaction: $Q_R > 0$

- Heating Value of a fuel: Heat of rxn with air (or O2) at the stoichiometric ratio. (High and low heating values)

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Review of Thermochemistry-Heat of Formation

- Heat of formation
  - Chemical energy (Energy stored in the bonds of chemical compounds relative to the reference energy state)
  - Critical in estimating the heat release in a chemical reaction.
  - Methods of determining the heat of formation for a compound.
    - Measurement in a bomb calorimeter (from heat of rxns)
    - Quantum mechanical calculations
    - Empirical estimation methods based on bond energies
      - Bond additivity
        - Identify the types and numbers bonds, add the energy for each bond
        - Accurate to 5%
      - Group additivity
        - Identify the types and numbers groups, add the energy for each group
        - Accurate to 2%
  - Bond energy methods are valid for covalent bonds, works for polymers
  - Fairly effective for complex organic compounds
  - Do not try these methods for the ionic compounds such as NaCl
  - Do not use for compounds with highly distorted bonds such as Cubane
  - Can be used to predict other properties such as specific heat and entropy

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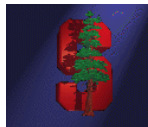KOÇ UNIVERSITY

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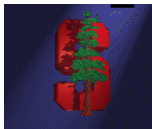
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List of Partial Bond Contributions – Bond Additivity Method

Units of HoF: kcal/mole

Partial Bond Contributions for the Estimation of C_p°, S°, and ΔH_f° of Gas-phase Species at 25°C, 1 atm [1]

Bond	C_p°	S°	ΔH_f°	Bond	C_p°	S°	ΔH_f°
C—H	1.74	12.90	−3.83	S—S	5.4	11.6	−6
C—D	2.06	13.60	−4.73	C_d—C^2	2.6	−14.3	6.7
C—C	1.98	−16.40	2.73	C_d—H	2.6	13.8	3.2
C—F	3.34	16.90	−52.5	C_d—F	4.6	18.6	−39
C—Cl	4.64	19.70	−7.4	C_d—Cl	5.7	21.2	−5.0
C—Br	5.14	22.65	2.2	C_d—Br	6.3	24.1	9.7
C—I	5.54	24.65	14.1	C_d—I	6.7	26.1	21.7
C—O	2.7	−4.0	−12.0	>CO—H [3]	4.2	26.8	−13.9
O—H	2.7	24.0	−27.0	>CO—C	3.7	−0.6	−14.4
O—D	3.1	24.8	−27.9	>CO—O	2.2	9.8	−50.5
O—O	4.9	9.1	21.5	>CO—F	5.7	31.6	−77
O—Cl	5.5	32.5	9.1	>CO—Cl	7.2	35.2	−27.0
C—N	2.1	−12.8	9.3	ϕ-H [4]	3.0	11.7	3.25
N—H	2.3	17.7	−2.6	ϕ-C [4]	4.5	−17.4	7.25
C—S	3.4	−1.5	6.7	(NO_2)—O [4]	—	43.1	−3.0
S—H	3.2	27.0	−0.8	(NO)—O [4]	—	35.5	9.0
C_ϕ—C_ϕ (biphenyl)	—	10.0		C_d—C_d	—	—	7.5

Reference: Benson S. W. "Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters"
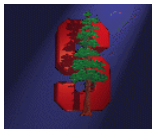
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Bond Additivity Method-Examples

- Note that the values that are listed in the table are for "Ideal Gas" at 25 C.
- For materials in other phases include the following contributions
  - Heat of vaporization at 25 C
  - Heat of melting (if the material is in solid phase)
  - Sensible enthalpy if the material is at a temperature other than 25 C
- Heat of formation for Methane (CH4) at 25 C
  - 4 (C-H): 4 (-3.83) = -15.32 kcal/mol
- Heat of formation for Pentane (C5H12) at 25 C
  - 12 (C-H) + 4 (C-C): 12 (-3.83) + 4 (2.73)= -35.04 kcal/mol
  - MW is approximately: 72 g/mol
  - Heat of formation of ideal gas at 25 C is -487 cal/g
  - Heat of vaporization at 25 C is 58 cal/g
  - Heat of formation at 25 C: -487 - 58= -545 cal/g
- Heat of formation for Ethylene at 25 C
 - 4 (Cd-H): 4 (3.2) = 12.8 kcal/mol

Review of Thermochemistry-First Law

- Adiabatic Flame Temperature (at constant pressure)
    - Introduce reactants into the combustion chamber
        - Oxidizer at *Tox*
        - Fuel at *Tf*
    - Have the reactants burn completely with no heat losses at constant pressure
    - The temperature of the final products (in equilibrium) is referred to as "Adiabatic Flame Temperature"

$$\hat{H}_{prod}(T_c) = \hat{H}_{react}(T_R) \qquad \sum_{prod} v_j \hat{H}_j(T_c) = \sum_{react} v_i \hat{H}_i(T_R)$$

    - Think of this process in two steps (Only accurate to the first order)
        - Reactants converts to the products at constant pressure/temperature. In the process the heat of reaction is released (chemical energy)
        - The heat of reaction is used to heat the products at constant pressure.

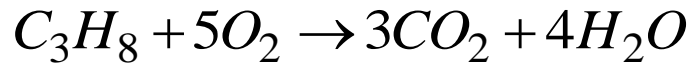$$\sum_{prod} v_j \int_o^{T_c} C_p(T)\, dT = \Delta H_{R,T_R}$$

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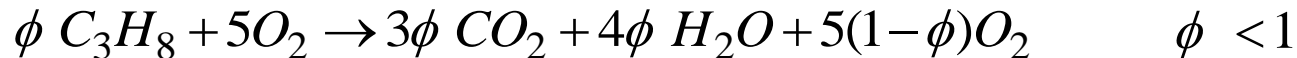
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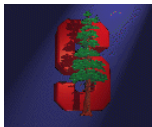
Review of Thermochemistry

- Major Products of Combustion (Hydrocarbon combustion with O2)
  - CO2, CO, H2O, H2, O2
- Secondary products of combustion:
  - OH, O, H, CH2, HO2, C
- Example: Propane/oxygen system
  - Stiochiometric system

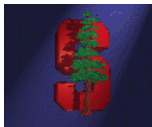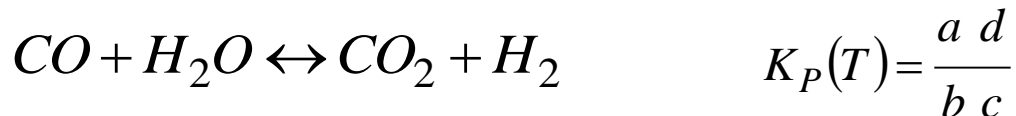 $$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

  - Fuel Lean system:

  $$\phi\, C_3H_8 + 5O_2 \rightarrow 3\phi\, CO_2 + 4\phi\, H_2O + 5(1-\phi)O_2 \qquad \phi < 1$$

  - Fuel Rich system:

  $$\phi\, C_3H_8 + 5O_2 \rightarrow a\, CO_2 + b\, CO + c\, H_2O + d\, H_2 \qquad \phi > 1$$

  - 4 unknowns and 3 equations
  - Need water gas reaction equation to close the set (not a global rxn)

  $$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad K_P(T) = \frac{a\, d}{b\, c}$$

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Review of Thermochemistry-Second Law

- Composition of products cannot be determined from the conservation of atoms alone.

- Second Law:
  - Thermodynamic equilibrium: Entropy is maximized under specified constraints system mass, atom balance, volume, pressure, energy

$$dS_{isolated} \geq 0$$

- Combine first law with the second law for a single component simple compressible substance
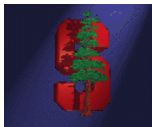
$$TdS - dE - PdV \geq 0$$

- Use the definition of enthalpy to obtain

$$d(TS - H) \geq 0$$

- Or in terms of the Gibbs function $\quad G \equiv H - TS$

$$dG \leq 0$$

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Review of Thermochemistry-Second Law

- For a multi component system the Gibbs function can be written in terms of the pressure and temperature and moles of each component

$$G = G(P, T, n_1, \ldots \ldots n_N)$$

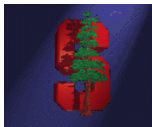- The variation of the Gibbs function with component moles at constant pressure and temperature is

$$dG_{T,P} = \sum \bar{\mu}_i dn_i$$

- Where chemical affinities are defined as

$$\bar{\mu}_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j \neq n_i}$$
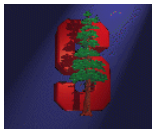
- In equilibrium

$$dG_{T,P} = \sum \bar{\mu}_i dn_i = 0$$

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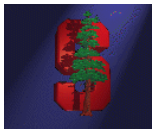
Review of Thermochemistry-Second Law

- Iteration is required to solve for the final composition and temperature of the products
  - Composition determines the energy release and final temperature
  - Final temperature influences the composition
- Same process can be repeated to find the adiabatic flame temperature at constant volume. Gibbs function is replaced by the Helmholtz function.
- Finding the equilibrium product composition and temperature is a cumbersome process
- Use the thermoequilibrium codes
  - STANJAN developed by Bill Reynolds
  - Solves for composition using "Method of Element Potentials"
  - Optimization problem solved by the Lagrange multipliers method
  - Number of equations is related to the number of different atoms in the reactions not the number of compounds involved in the reaction (Number of equations are reduced significantly)
  - STANJAN does **not** directly output the c* and does **not** do nozzle calculations (Isp)
  - The product data files are not complete resulting in high adiabatic flame temperatures.

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Review of Thermochemistry-Results

- Equilibrium Products (for hydrocarbon/oxygen combustion)
  - Fuel Rich Side: H2, H, CO (CO2 and H2O)
  - Fuel Lean Side: O, O2 (CO2 and H2O)
- Must include all possible compounds as products
  - Failure to do so will change the result (overestimate the flame temperature)
- Constant volume adiabatic flame temperature is larger than constant pressure adiabatic flame temperature
  - Pressure work term is eliminated
  - Reduced disassociation due to increased pressure
  - Rocket engine combustion takes place in a "constant pressure" environment
  - Otto cycle uses constant volume combustion
- Maximum heat of reaction takes place at stoic. ratio and on the lean side of the stoic. ratio since the heat of formations for CO (-26.42 kcal/mole), H2 (0 kcal/mole) and H (52.07 kcal/mole) are all larger than the heat of formation of both CO2 (-94.05 kcal/mol) and also H2O (-57.79 kcal/mol)
  - Note that low negative heat of formation values are desirable for the products and high positive values are required for the reactants to obtain the best heat of combustion

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Review of Thermochemistry-Results

- Most hydrocarbons have similar adiabatic flame temperatures since they have similar heating values.

- Adiabatic Flame Temperature (*Tc*) vs O/F
  - Maximum flame temperature is on the rich side of the stiochiometric ratio. The shift from stoic. ratio is induced by the compositional effects. Note that the flame temperature depends on the specific heat of the products

$$Q_R = \sum_{prod} n_i \hat{h}_i (T_c)$$

  - For low O/F (fuel rich): *Tc* is low because of incomplete combustion of the fuel. Heat of combustion is less than the heating value of the fuel.
    - This is the energy deficiency case
  - For high O/F (fuel lean) *Tc* is low because of the dilution effect of the excess oxidizer. The heat of combustion is matched to the heating value of the fuel.
    - This is the dilution case

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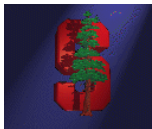
Review of Thermochemistry-Results

- Maximum c* takes place on the fuel rich side of *Tc*

$$c^* \propto \sqrt{\frac{T_c}{MW}}$$

  - MW of the products on the rich side is smaller (H2, CO, other lighter molecules)
- Maximum Isp is on the fuel lean side of the maximum c*

$$Isp \propto c^* C_F(\gamma)$$

- Flame temperature (and c*) increases slightly with increasing pressure
  - Another effect of composition.
  - Recombination direction of the reactions is favored with increasing pressure
  - Reaction is shifting towards the direction to eliminate the effect of increased pressure
- Effect of temperature of reactants
  - As the temperature of reactant increases the flame temperature (and c*) also increases due to the energy balance.
  - The increase in flame is less than the increase in the reactant temperature due to increased disassociation reactions with increased temperature
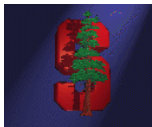 - Example: c* and Isp for LOX is lower than the values for GOX at 25 C

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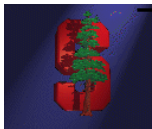
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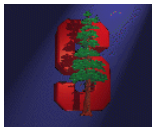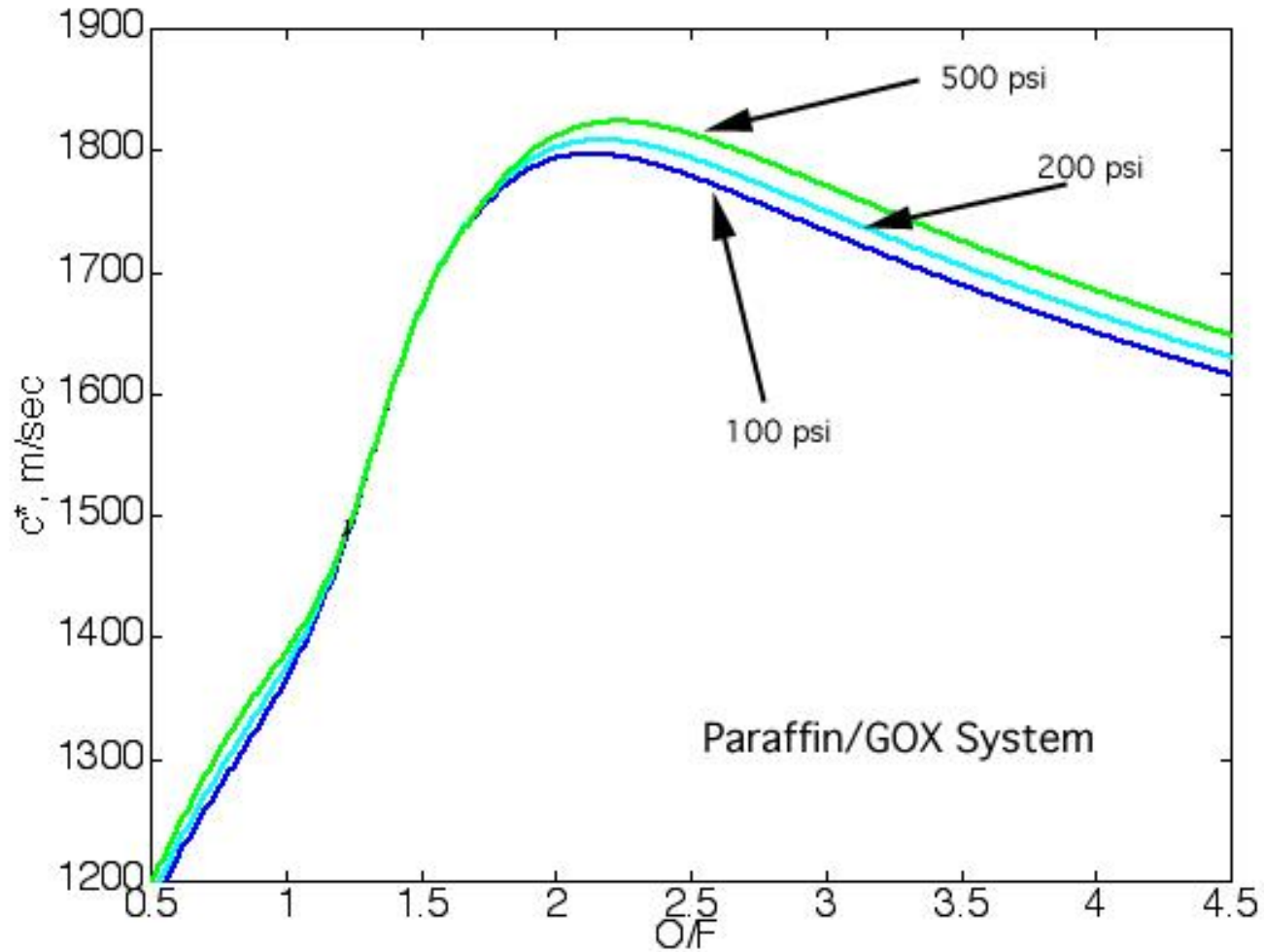## Combustion Characteristics-Paraffin60%-Al40%/N2O System
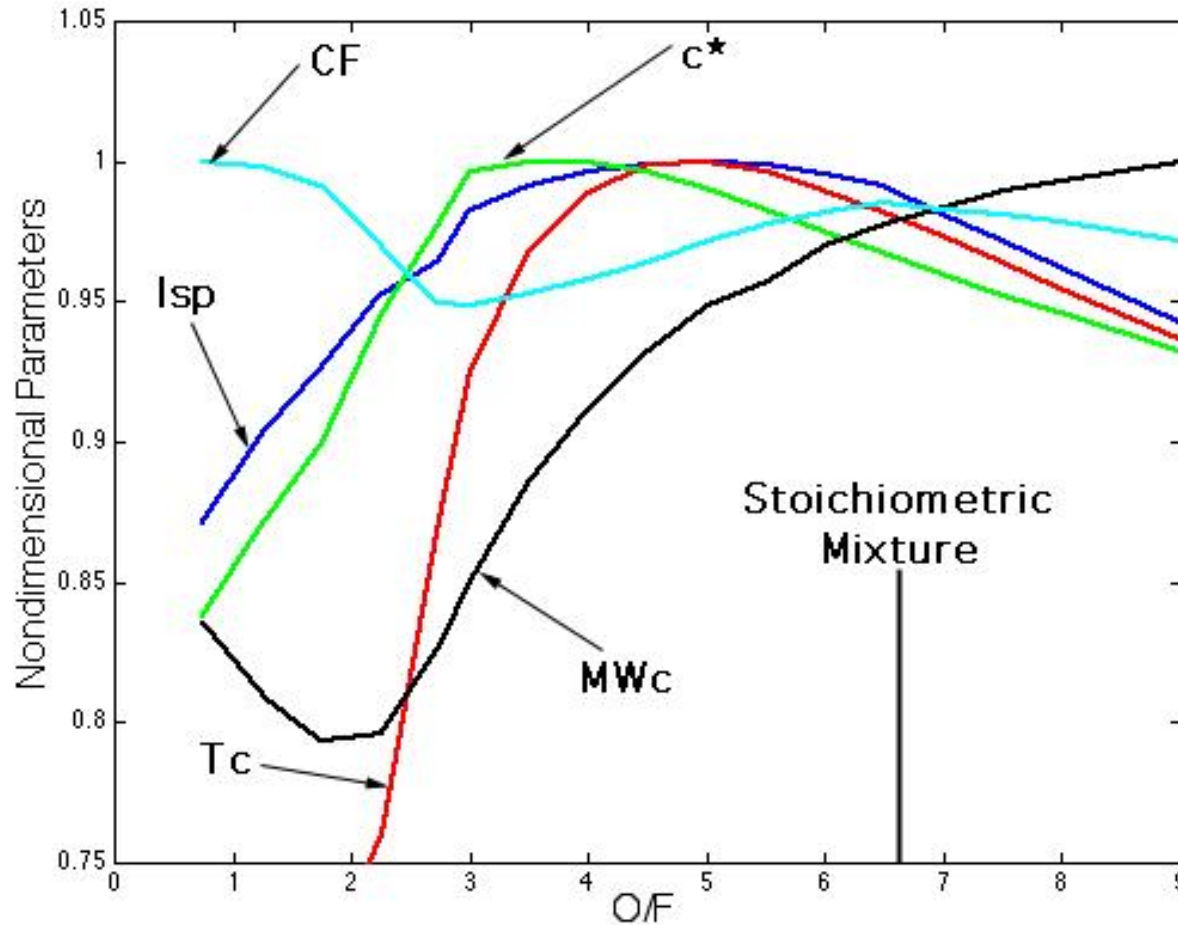
Chamber Pressure: 500 psi

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Effect of Pressure on C*-Paraffin/GOX System

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Review of Thermochemistry-Results

- How does the equilibrium codes calculate Isp values ?
  - The composition, stoichiometry and temperatures of the reactants that enter the combustion chamber are specified (Station 2)
    - Information Needed: O/F and heat of formations of all the components at the temperature and state of interest.
  - Calculate the composition and temperature of the products in the combustion chamber (Station 2)
  - Select the type of chemistry "Shifting Equilibrium" vs "Frozen Equilibrium"
  - Iterations 1: Station 2 (Nozzle entrance) to nozzle throat
    - Isentropic expansion (H and S are kept constant)
    - Expand until the velocity is matched to the speed of sound at the throat
  - Iterations 2: Nozzle throat to nozzle exit
    - Isentropic expansion (H and S are kept constant)
    - Given area ratio
      - Expand until the following equation (based on mass flow balance) satisfied

$$\frac{A_e}{A_t} = \frac{\rho^* u^*}{\rho_e u_e}$$

    - Given exit pressure
      - Expand until the exit pressure is matched to the ambient pressure

$$P_e = P_a$$

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