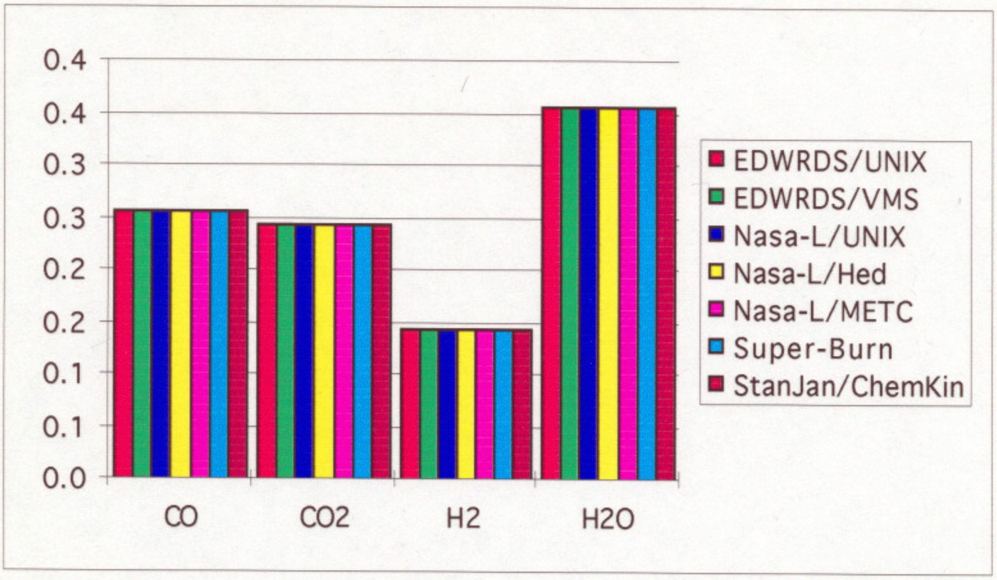
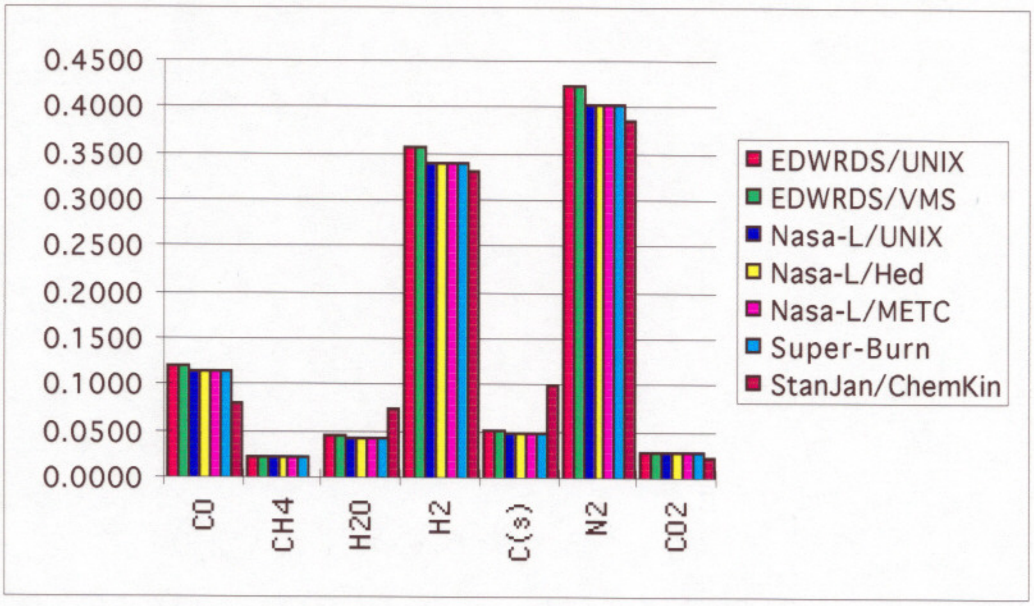
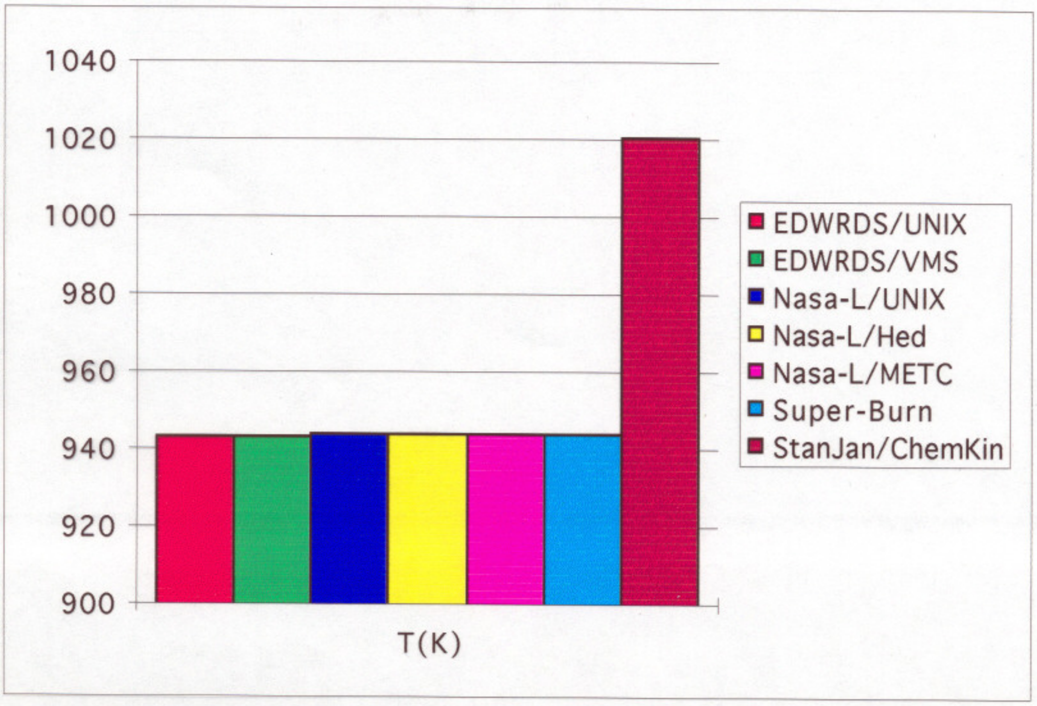
Case 1
CO/H2O(g)/O2 in ratio 1/1/0.1
1 atm, 1500 K (TP case)

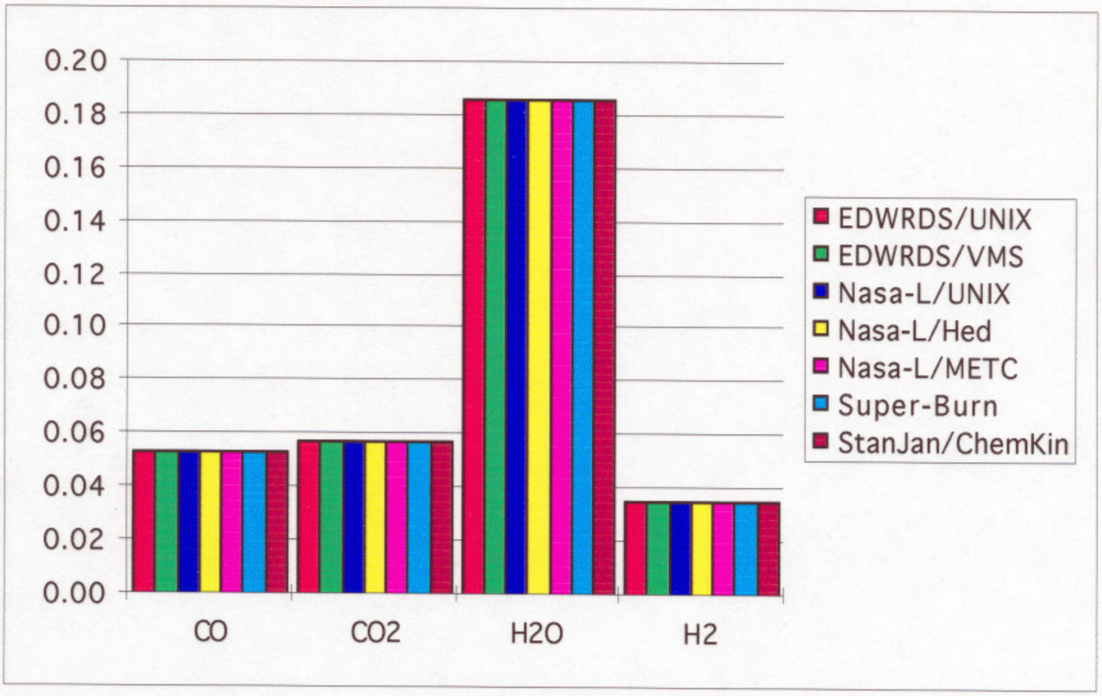


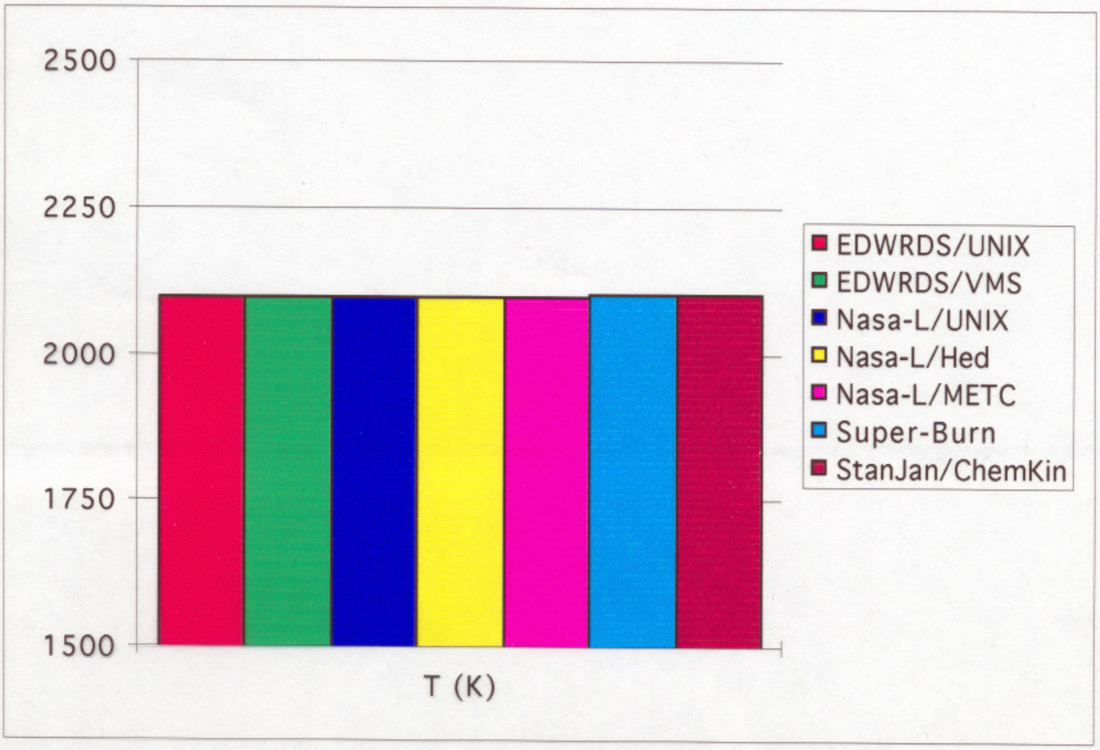
Case 3
CH4/Air, Equiv. Ratio = 4.0
1 atm (HP Case)





Case 2
CH4/Air, Equiv. Ratio = 1.25
1 atm (HP Case)





1. Hand back/reports

2. Discuss class
   - partners
   - workload
   - Weighting for 1st project
   - schedule

3. What is Chemkin & Why was it writen?

   - organized set of library subroutines to use with driver programs that use thermo & multiple elementary reactions
   - written so you only had to do it once, & not reinvent the wheel for every new code
   - develped at Sandia CRF, but widely used!

4. Basic Chemkin package:

   A. Interpreter
      1. reads the reaction mechanism, elements, species
      2. reads in additional thermo data (if needed)
      3. writes the linking file

   B. Thermodynamic Data Base

      - minor modification to Nasa-Lewis data base

$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_P$

same

$\left(\frac{\partial S}{\partial T}\right)_P = C_p/T$

$$\frac{C_p^\circ}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{H^\circ}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T}$$

$$\frac{S^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7$$

→ 2 temperature ranges

   C Linking file

      - assembles the FORTRAN code

   D. Gas-Phase Subroutine Library

      subroutines that get values of C_p, ρ, h, r_i, etc.

      given values of Y_i, P, T, etc.

      Actually, $Y(1) = T$, $Y(2)$ = Mass fraction of species 1

Chemkin History

- Developed at Sandia (Livermore, CA)
- Gained worldwide acceptance
- BYU got a copy
- Company formed to market the code

  Reaction Design

  www.reactiondesign.com

5. Convenient packages for "routine" analysis

we do not have this! → *A. Plug flow (1-D, no axial diffusion) (laminar)

B. Perfectly-stirred reactor (PSR)

C. Premixed 1-D laminar flame

*D. Surface reaction

E. Senkin

*F. Opposed jet

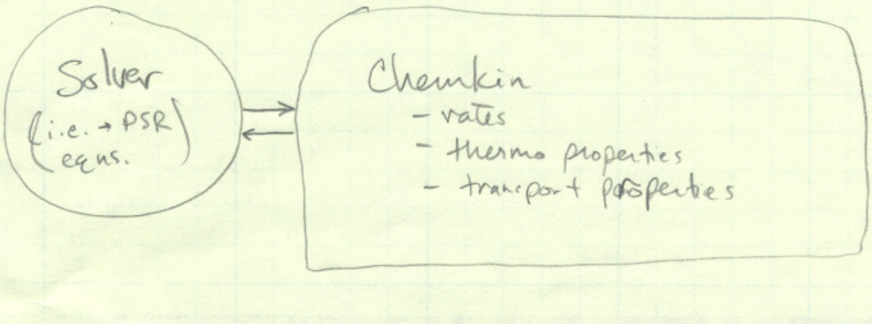
*G. Partially-stirred reactor (PaSR)

H. Equilibrium

I. Transport property look-up

*J. Plasmas

* Not to be studied in this class



6. Example:

A. Figure 2 (program schematic)

→ put in the reaction mechanism and inlet conditions

→ use the code that describes the right reactor (PSR, etc.)

B. Sample reaction set (overhead)

C. Sample problem: Batch reactor, constant P
(like a CSTR)

Overall continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho v = 0 \qquad (= r_{solid \to gas})$$

Species continuity

$$\underbrace{\frac{\partial \rho_i}{\partial t}} + \nabla \cdot (\rho_i v + j_i) = r_i \qquad (\text{mass basis})$$

$$\frac{\partial y_i \rho}{\partial t} = y_i \frac{\partial \rho}{\partial t} + \rho \frac{\partial y_i}{\partial t} \qquad \nabla \cdot y_i \rho v = y_i \nabla \cdot \rho v + \rho v \cdot \nabla y_i$$

$$y_i \frac{\partial \rho}{\partial t} + \rho \frac{\partial y_i}{\partial t} + y_i \nabla \cdot \rho v + \rho v \cdot \nabla y_i + \nabla \cdot j_i = r_i$$

OR

$$y_i \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot \rho v \right)}_{\text{overall continuity}} + \rho \left(\frac{\partial y_i}{\partial t} + v \cdot \nabla y_i \right) + \nabla \cdot j_i = r_i$$

$$\rho \left(\frac{\partial y_i}{\partial t} + v \cdot \nabla y_i \right) + \nabla \cdot j_i = r_i$$

no spatial derivatives in batch reactor

$$\boxed{\rho \frac{\partial y_i}{\partial t} = r_i}$$

Chemkin example: $\overset{\text{mass fraction}}{\frac{\partial y_k}{\partial t}} = \frac{\dot{\omega}_k W_k}{\rho}$

$\dot{\omega}_k$ ← molar production rate of k

W_k ← MW

ρ ← mass density

Energy

$$\rho C_p \frac{DT}{Dt} = -\nabla\cdot q - \tau:\nabla v + \Sigma j_i g_i + \left(\frac{\partial \ln V}{\partial T}\right)_{p, x_i} \frac{Dp}{Dt}$$

$$+ \Sigma H_i\left[\nabla\cdot J_i - \dot{r}_i\right]$$

$$\rho C_p\left(\frac{\partial T}{\partial t} + v\cdot\nabla T\right) =$$

no spatial derivatives, adiabatic, ideal, no viscous or body forces

$$\boxed{\rho C_p \frac{\partial T}{\partial t} = -\Sigma H_i \dot{r}_i}$$

Chemkin example:

molar production rate of species k

$$\frac{\partial T}{\partial t} = -\frac{1}{\rho C_p} \Sigma h_k \dot{\omega}_k W_k \leftarrow MW$$

mass heat capacity

enthalpy of species k per unit mass

D. Show sample program

F_1 = energy eqn.

$F_2 \rightarrow F_{K+1}$ = species cont. eqns.

F = RHS of eqn. to be used in a solver!
(with a time step)

<u>Advantage:</u> "simple" to program if you know the system.

E. Show Igor plots

F. Note units:

P = dynes/cm^2
m = g
d = cm
E = cal
t = s

$$k = AT^{\beta}e^{-E/RT}$$

A β E

```
ELEMENTS
O H N
END
SPECIES
  O  O2  H  H2  OH  HO2  H2O  H2O2
  N2
END
REACTIONS
  H+O2 = O+OH                (MILLER 81)              5.1E16   -0.82  16510
  H2+O = H+OH                (MILLER 77)              1.8E10    1.0    8830
  H2+OH = H2O+H              (DIXON-LEWIS 77)         1.2E09    1.3    3630
  OH+OH = H2O+O              (COHEN 79)               6.0E08    1.3    0.0
  H+OH+M = H2O+M             (MILLER 77)              7.5E23   -2.6    0.0
    H2O /20.0/
  O2+M = O+O+M               (MILLER 81)              1.9E11    0.5   95560
  H2+M = H+H+M               (MILLER 77)              2.2E12    0.5   92600
    H2O/6.0/  H/2.0/  H2/3.0/
  H2+O2 = OH+OH               (MILLER 77)             1.7E13    0.0   47780
  H+O2+M = HO2+M              (SLACK 77)              2.1E18   -1.0    0.0
    H2O/21.0/  H2/3.3/  O2/0.0/  N2/0.0/
  H+O2+O2 = HO2+O2           (SLACK 77)               6.7E19   -1.42    0.0
  H+O2+N2 = HO2+N2           (SLACK 77)               6.7E19   -1.42    0.0
  HO2+H = H2+O2              (LLOYD 74)               2.5E13    0.0     700
  HO2+H = OH+OH              (LLOYD 74)               2.5E14    0.0    1900
  HO2+O = OH+O2              (LLOYD 74)               4.8E13    0.0    1000
  HO2+OH = H2O+O2            (LLOYD 74)               5.0E13    0.0    1000
  HO2+HO2 = H2O2+O2          (TROE 69)                2.0E12    0.0    0.0
  H2O2+M = OH+OH+M           (BAULCH 72)              1.2E17    0.0   45500
  H2O2+H = HO2 + H2          (BAULCH 72)              1.7E12    0.0    3750
  H2O2+OH = H2O+HO2          (BAULCH 72)              1.0E13    0.0    1800
END
```

Figure 3. Example input file for the Chemkin Interpreter.

The Interpreter

Input of the reaction description to the Interpreter is designed to be essentially format-free and in familiar chemical notation. Nevertheless, there is still a certain syntax that must be followed. Some of the capabilities of the Interpreter are evident from the simple example input file shown in Fig. 3.

The first information that must be supplied to the Interpreter is about the chemical elements (or isotopes) that combine to form the species appearing in the reaction mechanism. The purpose of identifying the elements explicitly is to fix the order in which arrays of element information in the Gas-Phase Subroutine Library are referenced. For example, if a Chemkin subroutine were called to return an array of atomic weights for the elements they would be in exactly the same order in which they were presented to the Interpreter (e.g. if the atomic weights were stored in an array AWT, then in this example AWT(3) would be the atomic weight of the nitrogen). For the elements that appear on the periodic

```
      SUBROUTINE FUN( NEQ, TIME, Y, F)
      DIMENSION Y(NEQ), F(NEQ)
C
C  INPUT -
C    NEQ   - the number of dependent variables.
C    TIME  - the independent variable, time.
C    Y     - the dependent variable vector (length NEQ), structured as:
C            y(1)   = T, the temperature in Kelvins,
C            y(k+1) = Yk, the mass fraction of the kth species.
C  OUTPUT -
C    F     - The righthand sides of the governing equations.
C----------------------------------------------------------------------
C
      DIMENSION WT(10), H(10), WDOT(10)
C
C          These arrays are required to store output of some Chemkin
C        Subroutine calls.  They allow for up to 10 species.
C          WT(*)  - The mocelecular weights of the species (g/mole).
C          H(*)   - The species enthalpies (erg/mole*K)
C          WDOT(*)- The species molar production rates (moles/cc*sec).
C----------------------------------------------------------------------
C
      COMMON /CHEMKIN/ KK, P, IWORK(200), WORK(200)
C
C        This common block contains parameters and data that are needed,
C      but not available through the FUN call list.
C        KK     - the number of species.
C        P      - the pressure in dynes/cm**2
C        IWORK - the Chemkin integer work space.
C        WORK  - the Chemkin real work space.
C
      CALL CKRHOY( P, Y(1), Y(2), IWORK, WORK, RHO)
      CALL CKCPBY(    Y(1), Y(2), IWORK, WORK, CPB)
      CALL CKHMS (    Y(1),       IWORK, WORK, H)
      CALL CKWYP ( P, Y(1), Y(2), IWORK, WORK, WDOT)
      CALL CKWT  (                IWORK, WORK, WT)
C
C         form the summation in eq. (6)
      SUM=0.
      DO 100 K=1,KK
         SUM = SUM + H(K)*WDOT(K)*WT(K)
 100  CONTINUE
C
C         form the righthand sides of eqs. (6) and (7)
      F(1) = - SUM / (RHO*CPB)
      DO 200 K=1,KK
        F(K+1) = WDOT(K) * WT(K) / RHO
 200  CONTINUE
C
      RETURN
      END
```

ρ

c_p

h

$\dot{\omega}_k$

W_k (MW's)

$= \Sigma h_k \dot{\omega}_k W_k$

$= \frac{\Sigma h_k \dot{\omega}_k W_k}{\rho c_p}$

$= \frac{\dot{\omega}_k W_k}{\rho}$

Figure 4. Subroutine for defining governing equations for solution by LSODE.