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Implementation of PLOG function in Chemkin II and III

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1. PLOG formulation

A number of fitting methods have been proposed to fit the broadened pressure fall-off effect. For example, Troe [1] introduced a broaden factor, *F*, to fit the pressure fall-off rate constant,

$$\frac{k_u}{k_\infty}=\frac{k_0/k_\infty}{1+k_0/k_\infty}F(k_0/k_\infty),\ \log F(k_0/k_\infty)\approx\frac{\log F_{cent}}{1+(\log k_0/k_\infty)^2}\ \text{at low temperature} \qquad (1)$$

Where F_{cent} is a function of reduced temperature and decreases from unity at 0 K with the increase of temperature.

Since many pressure fall-off reaction cannot be fitted using a single Arrhenius expression, recently, a generalized polynomial fitting for the temperature and pressure dependent polynomial is proposed by James Miller (2010) [2] and programmed in Chemkin Pro by using given rate constants

$$k_u(T,p_i)=\sum_{j=1}^{M}A_{ij}T^{nij}\exp(-E_0^{ij}/RT),\qquad i=1,...,N,\qquad M\geq 1 \qquad (2)$$

at a set of pressures, $p=p_1, p_2,\ldots p_N$. M and N are user specified numbers. The extrapolation is bounded by the two pressure limits, p_1 and p_N.

To calculate $k_u(T,P)$ for any pressure, interpolate $\log k_u$ as a linear function of $\log p$. If p is between p_i and p_{i+1} for any temperature (Fig.1), a rate constant can be find from

$$\log k_u(T,p)=\log k_{u,i}+(\log p-\log p_i)\frac{\log k_{u,i+1}-\log k_{u,i}}{\log p_{i+1}-\log p_i} \qquad (3)$$

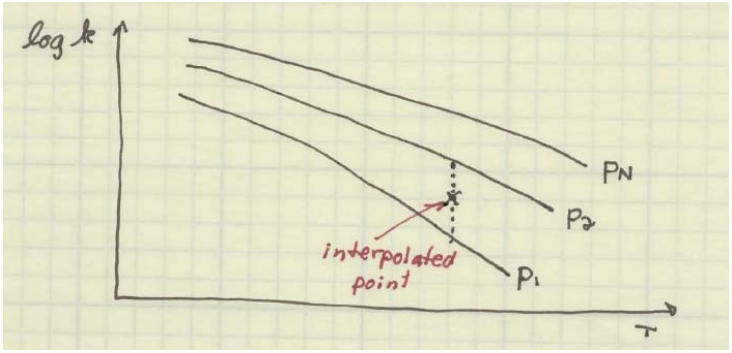

Fig.1 Linear interpolation of rate constant

To include the differences of the third-body efficiency, in principle, one could use

$$k_u=\sum_l X_l k_{u,l} \qquad (4)$$

for different third-body, where X_l is the mole fraction of the *l*th third-body.

2. PLOG CHEMKIN II and III chemistry library and interpreter

CKINTERP_PLOG.f is programmed to generate a chem.bin with PLOG reactions. This program is fully compatible with the original CKINTERP.f. An example of the input format for the PLOG reactions in chem.inp is given below,

```
C3H4+H=CH3CCH2      9.2E+38   -8.65   7000.  !(This is a dummy reaction rate for Chemkin)
 PLOG  /0.1     9.2E+38   -8.65   7000./
 PLOG  /1.      9.5E+42   -9.43   11200./
 PLOG  /10.     1.5E+45   -9.69   15100./
 PLOG  /100.    1.8E+43   -8.78   16800./
 PLOG  /1.0E+5  4.4E+09   1.45    2400./
```

The numbers on the first reaction line are dummies. Reaction Design wanted them there for formatting conformity. The numbers in each subsequent line give a pressure (atm) followed by a set of modified Arrhenius parameters. If a pressure is repeated, the rate coefficient is the sum of all the expressions listed. The current code allows up to N=12 pressure inputs.

To use the chem.bin generated by the CKINTERP_PLOG.f interpreter for ignition and flame computations, a in this file, a new PLOG Chemkin library Fortran code is developed to replace the orginal Chemkin library. This can be done by replacing,

```
!Call CKINIT (LENI, LENR, LENC, LINC, Lout, ICKWRK, RCKWRK,CCKWRK)
```

and using

```
Call CKINIT_PLOG(LENI, LENR, LENC, LINC, Lout, ICKWRK, RCKWRK,CCKWRK)
```

3. Using PLOG chemistry library (chem.bin) in CHEMKIN II and III softwares

To use chem.bin generated by CKINTERP_PLOG.f in CHEMKIN II and III softwares such as PREMIX.f, a new cklib-plog.f and a few other modifications in driv.f and premix.f are needed to calculate flame speed. A summary of these changes are listed below;

I. Use Cklib-plog.f to replace the original Cklib.f,
II. In DRIV.f, the following module needs to be added;

```
MODULE VAR_PLOG
PARAMETER (LENI_PLOG=200000, LENR_PLOG=99000000)
DIMENSION I_PLOG(LENI_PLOG)
REAL*8  R_PLOG(LENR_PLOG) !ADD FOR PLOG BY GXL,  MUST be REAL*8
Common /pressure/PinATM
END MODULE
```

III. In PREMIX.f,

a. Use CALL CKINIT_PLOG(LENI, LENR, LENC, LINK, LOUT,I, R, C) to replace
CALL CKINIT (LENI, LENR, LENC, LINK, LOUT, I, R, C).

b. PinATM is the pressure (atm) and its initial value needs to be given.

c. This pressure of PinATM in premix.f should be given to PATM in the SUBROUTINE CALK_PLOG of cklib-plog.f.

References

[1] J. Troe, J. Phys. Chem., 1979, 83, 114
[2] James A. Miller, Personal communication, 2010.
[3] R.J.Kee, F.M.Rupley, J.A.Miller, 'CHRMKIN-II: A FORTRAN Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics', SAND89-8009B, UC-706, Sandia National Laboratories, Albuquerque, New Mexico, (1993a).