# ChemE 2200 – Physical Chemistry II for Engineers

## Solutions to Calculation Session 10 Exercises

1. Define $k_1$ and $k_{-1}$ as the forward and reverse rate constants, respectively.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \mathrm{B}$$

The rate equation for the reaction is

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}]$$

At the start of the reaction, [B] = 0, thus the rate equation becomes

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]$$

$$k_1 = \frac{-d[\mathrm{A}]/dt}{[\mathrm{A}]} = \frac{5.25\times10^{-4}\ \mathrm{mol/(L\cdot sec)}}{0.0384\ \mathrm{mol/L}} = 0.0137\ \mathrm{sec}^{-1}$$

After a long time, the reaction reaches equilibrium. The rate falls to zero.

$$-\frac{d[\mathrm{A}]}{dt} = 0 = k_1[\mathrm{A}]_{\mathrm{eq}} - k_{-1}[\mathrm{B}]_{\mathrm{eq}}$$

$$k_{-1}[\mathrm{B}]_{\mathrm{eq}} = k_1[\mathrm{A}]_{\mathrm{eq}}$$

$$k_{-1} = k_1\frac{[\mathrm{A}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}} = (0.0137\ \mathrm{sec}^{-1})\frac{0.0107\ \mathrm{mol/L}}{0.0384-0.0107\ \mathrm{mol/L}} = 0.0053\ \mathrm{sec}^{-1}$$

Summary: $k_1 = 0.0137\ \mathrm{sec}^{-1}$ and $k_{-1} = 0.0053\ \mathrm{sec}^{-1}$.

Some used a graphical solution, as follows. First, convert eqn (1) into the form of a straight line, in terms of [A] and $d[\mathrm{A}]/dt$. From a mol balance (mols are conserved in the reaction A ↔ B), $[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}]$. Substitute into eqn (1).

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \qquad (1)$$

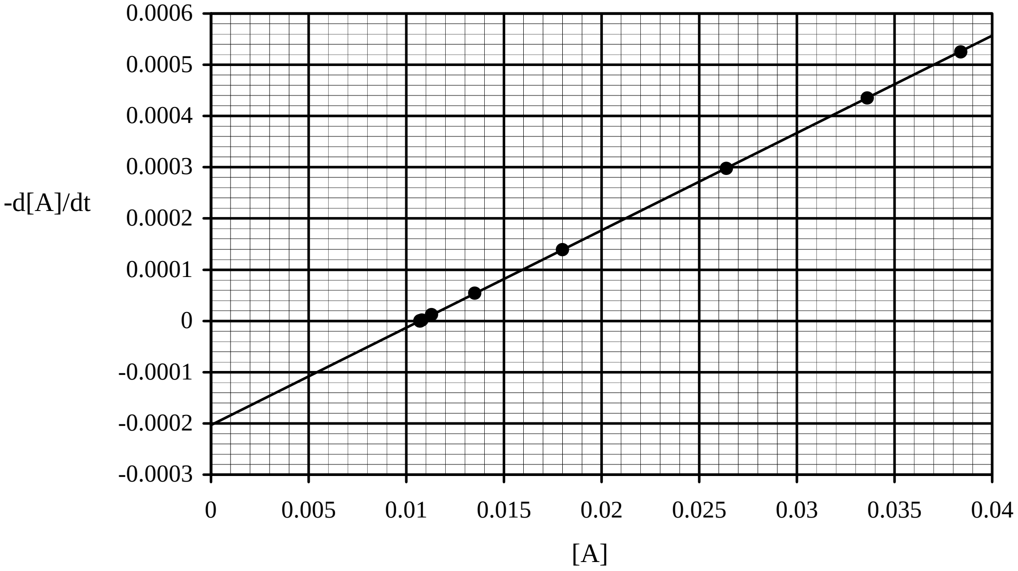
$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}([\mathrm{A}]_0 - [\mathrm{A}])$$

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_0 \qquad (2)$$

This is the form of a straight line, $y = mx + b$, for a plot of $d[\mathrm{A}]/dt$ vs. [A]. Plot the data and draw a straight line - shown on the next page.

The intercept is –0.00020, so $k_{-1} = -(-0.00020)/[\mathrm{A}]_0 = -(-0.00020)/0.0384 = 0.0052\ \mathrm{sec}^{-1}$. The slope is 0.0190, so $k_1 = \text{slope} - k_{-1} = 0.0190 - 0.0052 = 0.0138\ \mathrm{sec}^{-1}$.

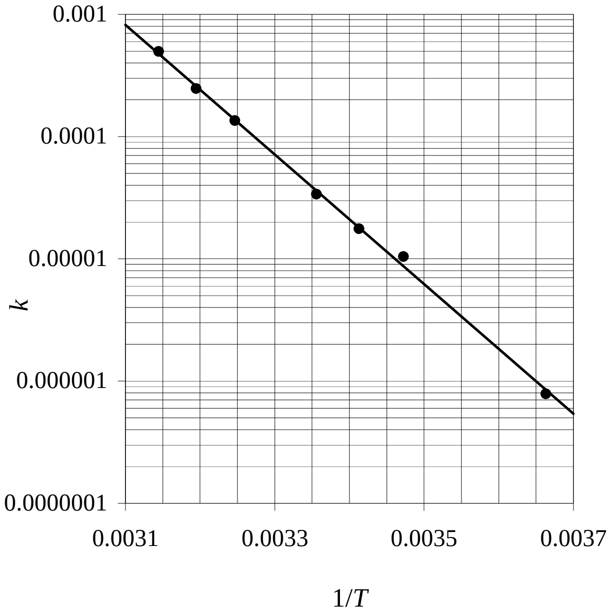
Or one could plug any two pairs of $d[\mathrm{A}]/dt$ and [A] data into eqn (2), which yields two equations and two unknowns. A two-point calculation is less accurate than using the entire data set, if the data have significant experimental error. In this case, the data are exact.



2. As derived in lecture, the activation energy may be extracted from the slope of a straight line drawn through a plot of $\log_{10}k$ vs. $1/T$.

$$\text{slope} = \frac{-E_a}{2.303R}$$

Draw a straight line through the points.



Use the intersections at the left and right borders to calculate the slope. The straight line passes through the points (0.0031, 0.0008) and (0.0037, 0.00000055).

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\log_{10} 0.00000055 - \log_{10} 0.0008}{0.0037 - 0.0031} = -5300\text{ K}$$

$$E_a = 2.303R \times 5300\text{ K} = 2.303\frac{8.31\text{ J}}{\text{K}\cdot\text{mol}}5300\text{ K} = 100\text{ kJ/mol}$$

There are at most two significant figures, so the activation energy is $1.0 \times 10^2$ kJ/mol.

To calculate the preexponential, we calculate the preexponential at each temperature and take the average.

| $T$ (K) | $k$ (sec$^{-1}$) | $A = k\,\mathrm{e}^{E_a/RT}$ |
|---|---|---|
| 273 | $7.87 \times 10^{-7}$ | $2.0 \times 10^{13}$ |
| 288 | $1.04 \times 10^{-5}$ | $2.6 \times 10^{13}$ |
| 293 | $1.76 \times 10^{-5}$ | $2.1 \times 10^{13}$ |
| 298 | $3.38 \times 10^{-5}$ | $2.0 \times 10^{13}$ |
| 308 | $1.35 \times 10^{-4}$ | $2.2 \times 10^{13}$ |
| 313 | $2.47 \times 10^{-4}$ | $2.1 \times 10^{13}$ |
| 318 | $4.98 \times 10^{-4}$ | $2.3 \times 10^{13}$ |

The average value is $A \approx 2 \times 10^{13}$. Because $A$ is extremely sensitive to the activation energy and the activation energy is somewhat uncertain, there will be considerable variation in this value, perhaps as much as a factor of 2.

3. The key feature in the Arrhenius plot is the slope of each line, which is $-E_a/R$. Line 1 has the steeper slope, so line 1 corresponds to the larger activation energy. Line 1 corresponds to the reaction X → Y + Z.

   So why is the rate constant for reaction 2 larger than the rate constant for reaction 1? It is likely that reaction 2 has a larger preexponential factor, $A$. Unimolecular decay typically has a preexponential factor in the range $10^{15}$ to $10^{17}$, whereas bimolecular collisions at room temperature and standard pressure typically have a preexponential factor in the range $10^{9}$ to $10^{11}$.

4. There are several approaches to this exercise. One is to consider the principle of detailed balance; the equilibrium constant equals the ratio of the forward and reverse rate constants.

$$\frac{[\cdot\mathrm{CH_3}]_{\mathrm{eq}}[\cdot\mathrm{Cl}]_{\mathrm{eq}}}{[\mathrm{CH_3Cl}]_{\mathrm{eq}}} = K_1 = \frac{k_1}{k_{-1}} \qquad (1)$$

$$\frac{[\cdot\mathrm{CH_2Cl}]_{\mathrm{eq}}[\cdot\mathrm{H}]_{\mathrm{eq}}}{[\cdot\mathrm{CH_3}]_{\mathrm{eq}}[\cdot\mathrm{Cl}]_{\mathrm{eq}}} = K_2 = \frac{k_2}{k_{-2}} \qquad (2)$$

$$\frac{[\mathrm{CH_3Cl}]_{\mathrm{eq}}}{[\cdot\mathrm{CH_2Cl}]_{\mathrm{eq}}[\cdot\mathrm{H}]_{\mathrm{eq}}} = K_3 = \frac{k_3}{k_{-3}} \qquad (3)$$

Multiply eqns (1), (2), and (3).

$$\frac{[\cdot\mathrm{CH_3}]_{\mathrm{eq}}[\cdot\mathrm{Cl}]_{\mathrm{eq}}}{[\mathrm{CH_3Cl}]_{\mathrm{eq}}}\,\frac{[\cdot\mathrm{CH_2Cl}]_{\mathrm{eq}}[\cdot\mathrm{H}]_{\mathrm{eq}}}{[\cdot\mathrm{CH_3}]_{\mathrm{eq}}[\cdot\mathrm{Cl}]_{\mathrm{eq}}}\,\frac{[\mathrm{CH_3Cl}]_{\mathrm{eq}}}{[\cdot\mathrm{CH_2Cl}]_{\mathrm{eq}}[\cdot\mathrm{H}]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}}\,\frac{k_2}{k_{-2}}\,\frac{k_3}{k_{-3}}$$

$$1 = \frac{k_1}{k_{-1}}\,\frac{k_2}{k_{-2}}\,\frac{k_3}{k_{-3}}$$

Solve for the ratio of $k_3$ to $k_{-3}$.

$$\frac{k_{-1}}{k_1}\,\frac{k_{-2}}{k_2} = \frac{k_3}{k_{-3}}$$

$$\frac{10^{-6}}{10^{-8}}\,\frac{10^{-5}}{10^{-7}} = \frac{k_3}{k_{-3}}$$

$$10^{+4} = \frac{k_3}{k_{-3}}$$

Thus ratio of $k_3$ to $k_{-3}$ should be $10^4$. The measured value is $10^{-7}/10^{-12} = 10^5$. Either $k_3$ or $k_{-3}$ or both must be wrong.

Another approach is to use $\Delta G_{\mathrm{rxn}}$. From thermodynamics we know that $\Delta G_{\mathrm{rxn}} = 0$ for the cycle.

$$0 = \Delta G_{\mathrm{cycle}} = \Delta G_{\mathrm{rxn\,1}} + \Delta G_{\mathrm{rxn\,2}} + \Delta G_{\mathrm{rxn\,3}}$$

One can obtain the same equation by Hess's Law. The sum of the reactions A → B plus B → C equals A → C. Note that the reaction A → C is the reverse of reaction 3, C → A. Thus,

$$\Delta G_{\text{rxn}\,1} + \Delta G_{\text{rxn}\,2} = -\Delta G_{\text{rxn}\,3}$$
$$\Delta G_{\text{rxn}\,1} + \Delta G_{\text{rxn}\,2} + \Delta G_{\text{rxn}\,3} = 0$$

Or if one draws a reaction-coordinate energy-level diagram, one can obtain the above relation. Now replace $\Delta G_{\text{rxn}}$ with the equilibrium constant.

$$\begin{aligned}\Delta G_{\text{rxn}\,1} + \Delta G_{\text{rxn}\,2} + \Delta G_{\text{rxn}\,3} &= 0\\ RT\ln K_{\text{rxn}\,1} + RT\ln K_{\text{rxn}\,2} + RT\ln K_{\text{rxn}\,3} &= 0\\ \ln K_{\text{rxn}\,1} + \ln K_{\text{rxn}\,2} + \ln K_{\text{rxn}\,3} &= 0\end{aligned}$$

$$\begin{aligned}\ln(K_{\text{rxn}\,1}K_{\text{rxn}\,2}K_{\text{rxn}\,3}) &= 0\\ K_{\text{rxn}\,1}K_{\text{rxn}\,2}K_{\text{rxn}\,3} &= 1\\ \frac{k_1}{k_{-1}}\frac{k_2}{k_{-2}}\frac{k_3}{k_{-3}} &= 1\end{aligned}$$

From here one proceeds as above - solve for the ratio of $k_3$ to $k_{-3}$, etc.

5. As suggested by the hint, there are two parallel mechanisms for the oxidation of this polymer. Consider two first-order reactions in parallel, for example.

$$\text{A} \overset{k_1}{\rightarrow} \text{product 1}$$

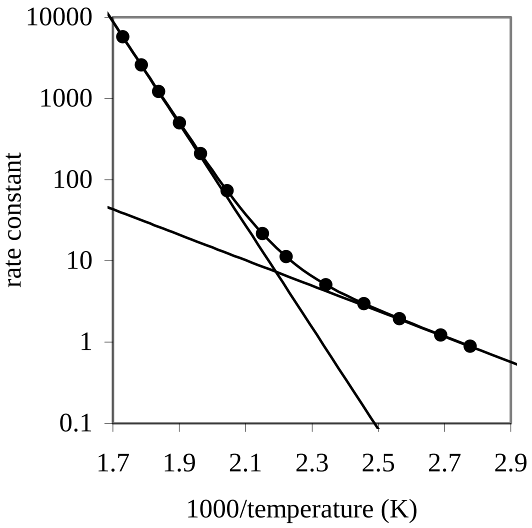
$$\text{A} \overset{k_2}{\rightarrow} \text{product 2}$$

The rate equation for [A] is

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}] - k_2[\text{A}] = -(k_1 + k_2)[\text{A}]$$

The apparent rate constant is the sum of $k_1$ and $k_2$.

In this example, one mechanism has a small activation energy (30 kJ/mol) and a small Arrhenius preexponential ($2 \times 10^4$). The other mechanism has a large activation energy (120 kJ/mol) and a large Arrhenius preexponential ($4 \times 10^{14}$). Arrhenius plots of these individual rate constants are shown by straight lines in the plot below. The sum of the straight lines is the line through the data.



Oxidation is dominated by the large-activation-energy mechanism at high temperatures, above 450 K (1000/450 = 2.2). Oxidation is dominated by the small-activation-energy mechanism at temperatures below 400 K (1000/415 = 2.4). At 300 K, the rate constant is obtained by extrapolating the straight line fit to the four right-most data points. The rate constant at 300 K is about 0.12, which is about 8 times slower than the rate measured at 360 K, which was tediously slow to measure.

It would be inaccurate to extrapolate by drawing a single straight line through the data.

It would be inaccurate to extrapolate by drawing a curve that continues to slope upward at low temperatures.

6. Elementary reactions usually meet one of the following criteria:

   reaction breaks one bond,

   reaction makes one bond,

   reaction breaks one bond and makes one bond.

   Also, termolecular reactions are unlikely because the simultaneous collision of three molecules is rare, and it is improbable that the three molecules have the correct orientation. An exception is the collision between three atoms, or two atoms and a third body. Because a diatomic cannot be formed by the collision of two atoms, the three-body collision is the next-best route. Remember, "When you have eliminated all which is impossible, then whatever remains, however improbable, must be the truth." Sherlock Holmes in *The Blanched Soldier*.

(A) McQuarrie and Simon in exercise 29.11. The overall reaction is

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

The first step in the mechanism,

$$N_2O_5 \leftrightarrow NO_2 + NO_3$$

breaks one bond. It is likely an elementary reaction. The second step in the mechanism,

$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$$

breaks two bonds and makes one bond. It is unlikely to be an elementary reaction. The third step in the mechanism,

$$NO_3 + NO \rightarrow 2NO_2$$

breaks one bond and makes one bond. It is likely to be an elementary reaction.

Although the second reaction is unlikely to be elementary, the proposed mechanism may be correct. That is, it is possible that alternative reactions are less likely, or not consistent with the observed rate equation, or not consistent with observed intermediates.

(B) McQuarrie and Simon in exercise 29.17. The overall reaction is

$$2H_2 + 2NO \rightarrow N_2 + 2H_2O$$

The first step in the mechanism,

$$H_2 + NO + NO \rightarrow N_2O + H_2O$$

breaks two bonds ($H_2$ bond and NO bond) and makes three bonds (N-N bond in $N_2O$ and two H-O bonds in $H_2O$). The first step is also a termolecular collision. It is not likely an elementary reaction. The second step in the mechanism,

$$H_2 + N_2O \rightarrow N_2 + H_2O$$

breaks two bonds and makes two bonds. It is unlikely to be an elementary reaction.

(C) McQuarrie and Simon in exercise 29.18. The overall reaction is

$$2H_2 + 2NO \rightarrow N_2 + 2H_2O$$

The first step in the mechanism,

$$NO + NO \rightarrow N_2O_2$$

makes one bond. It is likely an elementary reaction. The second step in the mechanism,

$$H_2 + N_2O_2 \rightarrow N_2O + H_2O$$

breaks two bonds and makes two bonds. It is unlikely to be an elementary reaction. The third step in the mechanism,

$$H_2 + N_2O \rightarrow N_2 + H_2O$$

breaks two bonds and makes two bonds. It is unlikely to be an elementary reaction.

Although the second reaction is unlikely to be elementary, the proposed mechanism may be correct. That is, it is possible that alternative reactions are less likely, or not consistent with the observed rate equation, or not consistent with observed intermediates.

7.(A) Use reaction (1) to write a rate equation.

$$r_{\mathrm{rxn}} = k_1[\mathrm{N}][\mathrm{A}]$$

There is typically some confusion about the +/- sign on $d[\mathrm{A}]/dt$. To determine the sign, write reaction 1 as a chemical equation.

$$0 = 2\mathrm{A} - \mathrm{A} - \mathrm{N} = \mathrm{A} - \mathrm{N}$$

Thus the stoichiometric coefficients are $\nu_\mathrm{A} = +1$ and $\nu_\mathrm{N} = -1$.

$$r_{\mathrm{rxn}} = \frac{1}{\nu_\mathrm{A}}\frac{d[\mathrm{A}]}{dt} = \frac{1}{\nu_\mathrm{N}}\frac{d[\mathrm{N}]}{dt} = \frac{1}{1}\frac{d[\mathrm{A}]}{dt} = \frac{1}{-1}\frac{d[\mathrm{N}]}{dt}$$

Finally, we have

$$\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{N}][\mathrm{A}]$$

We now separate and integrate. Because N is in excess, we can assume that [N] is constant.

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]} = k_1[\mathrm{N}]dt$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = k_1[\mathrm{N}]\int_0^t dt$$

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -k_1[\mathrm{N}]t$$

$$[\mathrm{A}] = [\mathrm{A}]_0\, e^{k_1[\mathrm{N}]t}$$

The infection grows exponentially.

(B) Use reactions (1) and (2) to write a rate equation.

$$\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{N}][\mathrm{A}] - k_2[\mathrm{W}][\mathrm{A}]$$

Because W is not consumed in reaction (2), [W] is constant. Separate and integrate.

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]} = \left(k_1[\mathrm{N}] - k_2[\mathrm{W}]\right)dt$$

$$[\mathrm{A}] = [\mathrm{A}]_0\, e^{\left(k_1[\mathrm{N}] - k_2[\mathrm{W}]\right)t}$$

(C) [A] grows exponentially unless the exponent is less than zero. The requirement is thus,

$$k_1[\mathrm{N}] - k_2[\mathrm{W}] < 0$$

$$[\mathrm{W}] > \frac{k_1}{k_2}[\mathrm{N}]$$

## Team Competition: Reaction-Coordinate Energy-Level Diagrams

# Calculation Session 10 Team Champions!

# Team “No Pain no GANE” Gee Tam, Emma Nam, Neha Chopade, and Anirudh Tenneti

## Perfect Score: 20/20!

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**Team Competition Solution:**

Identify corresponding groups of reactants, intermediates, or products. Consecutive energy levels must have the same atoms, albeit in different combinations. This rule collects the list of 19 groups into six sets:

1. $H_2 + I_2$ and 2HI (two H’s and two I’s)
2. $H_2 + \frac{1}{2}O_2$, $H_2 + \cdot O\cdot$, $H\cdot + \cdot OH$, and $H_2O$ (two H’s and one O)
3. $3O_2$ and $2O_3$ (only O’s)
4. $2NO + O_2 + \cdot O\cdot$, $NO + NO_2 + \cdot O\cdot$, $NO + NO_3$, and $2NO_2$ (two N’s and four O’s)
5. $CH_4 + \frac{1}{2}O_2$, $CH_4 + \cdot O\cdot$, $\cdot CH_3 + \cdot OH$, and $CH_3OH$ (four H’s, one C, and one O)
6. $CH_3CH_3$, $CH_3 + \cdot CH_3$, $\cdot CH_2CH_3 + \cdot H$, and $CH_2{=}CH_2 + H_2$ (six H’s and two C’s)

Use chemical thermodynamics and chemical kinetics to match compounds with the levels on the reaction-coordinate energy-level diagrams.

Chemical Thermodynamics:

Is the reaction exothermic or endothermic? $CH_3CH_3$, $\rightarrow \cdot CH_3 + \cdot CH_3$ is endothermic and $2O_3 \rightarrow 3O_2$ is exothermic. $H_2 + I_2 \rightarrow 2HI$ is approximately nonthermic.

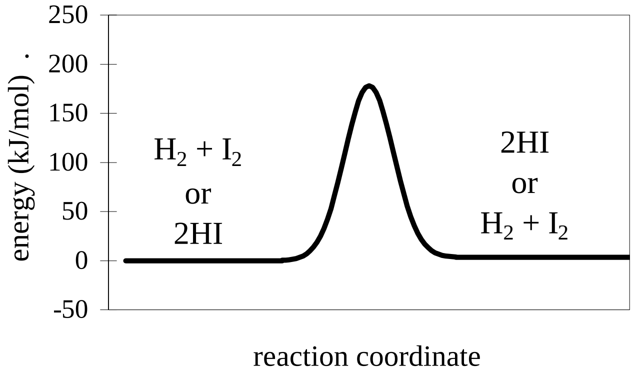
Is the energy level at 0? If so, the level is likely elements in their natural state, such as $H_2$, $O_2$ and $I_2$.

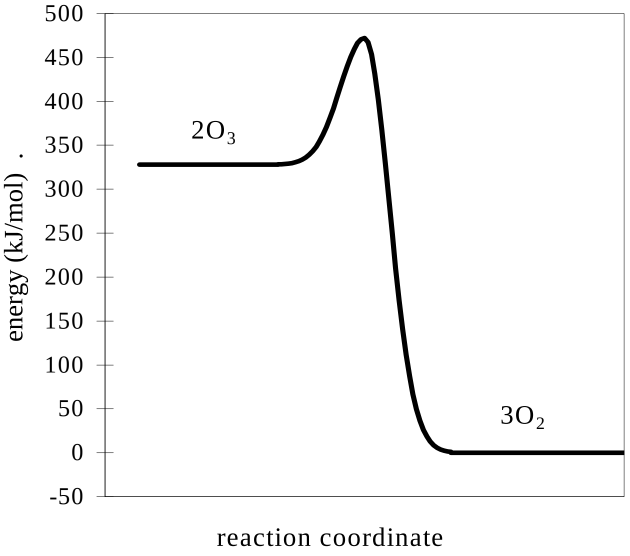
Chemical Kinetics:

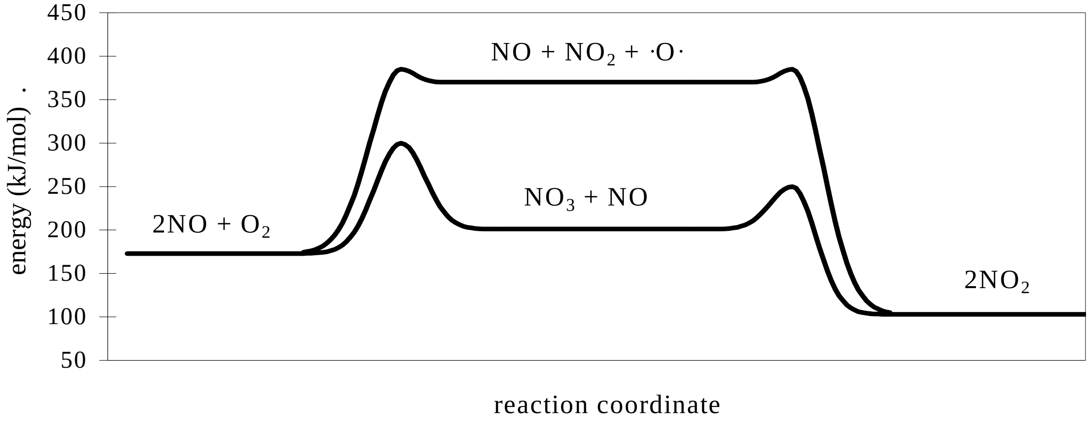
If the activation energy barrier is small (~10 kJ/mol) the reaction likely involves radicals combining or fragile molecules ($O_3$ or $XeF_2$) decomposing.

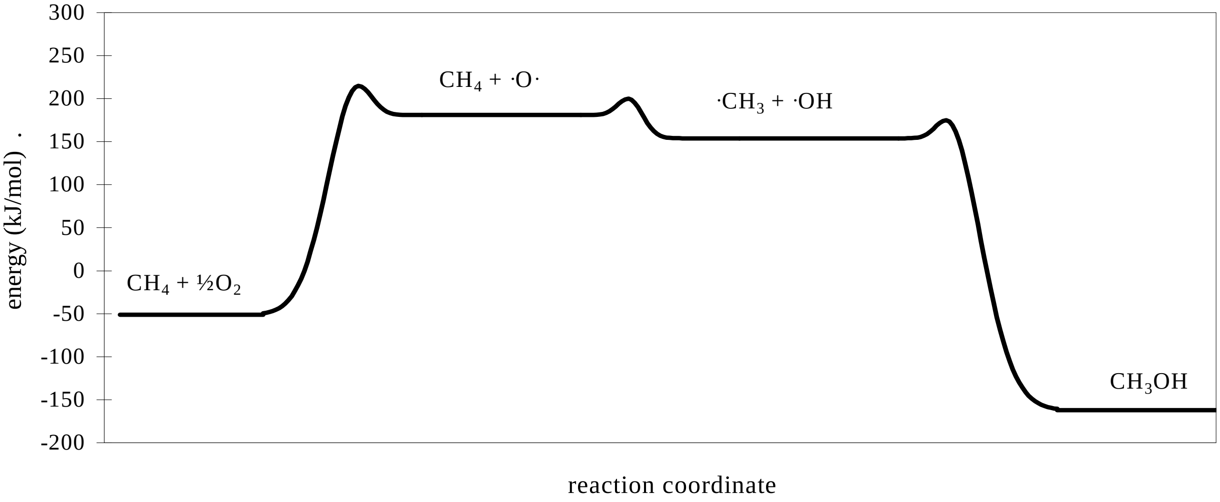
If the activation energy barrier is large (>100 kJ/mol) the reaction likely involves breaking molecular bonds in stable molecules.

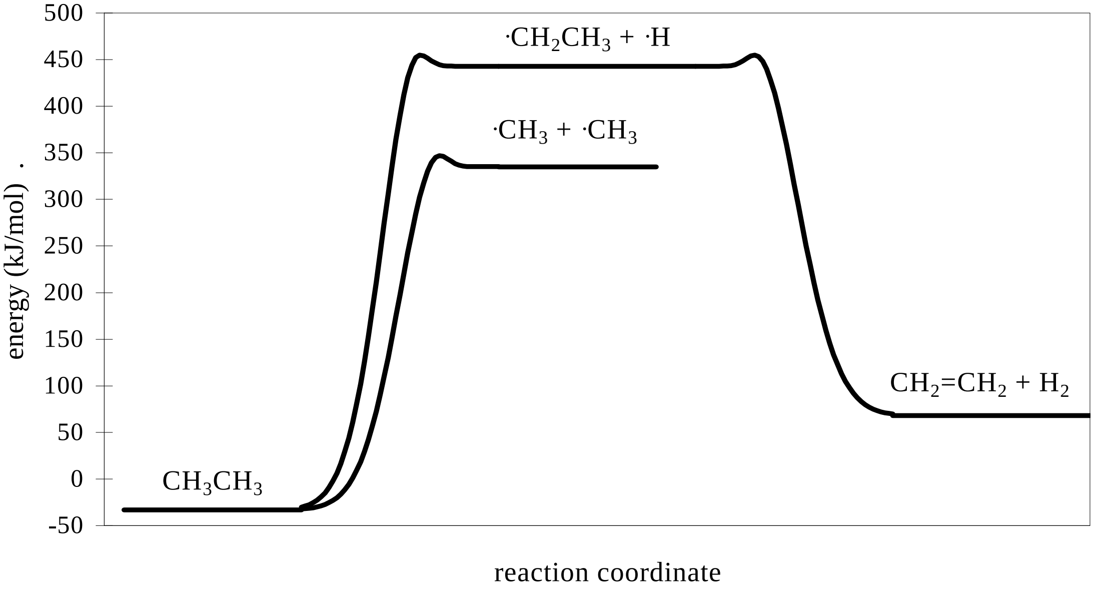
These principles (and the Gibbs Energies of the molecules and radicals) yield the following assignments:

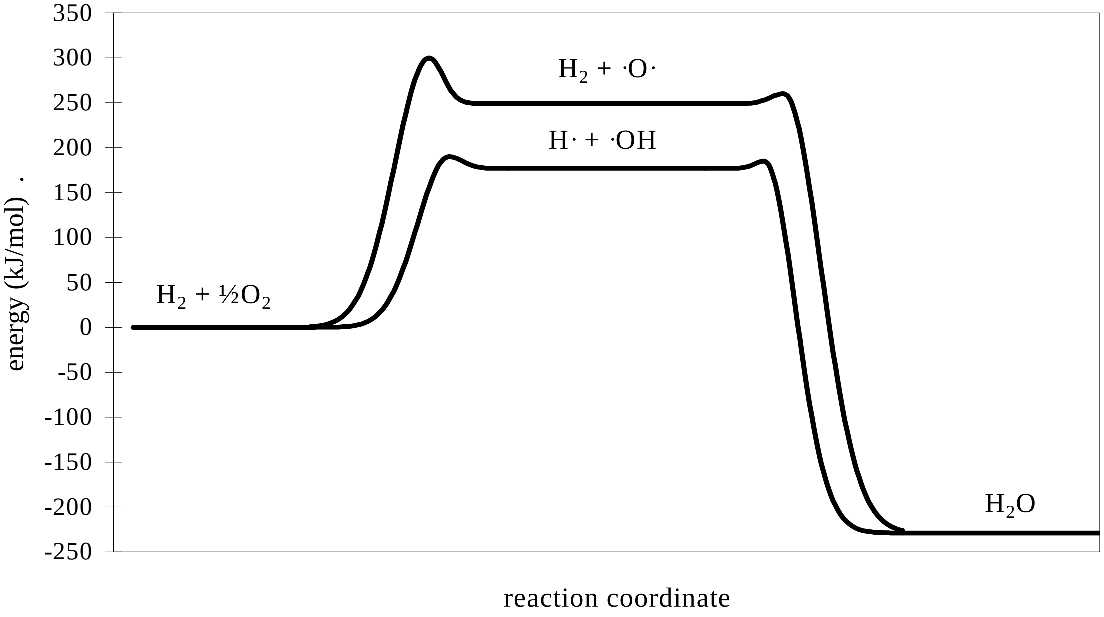







300
250
200
150
100
50
0
-50
-100
-150
-200
energy (kJ/mol)
CH$_4$ + ½O$_2$
CH$_4$ + ·O·
·CH$_3$ + ·OH
CH$_3$OH
reaction coordinate


500
450
400
350
300
250
200
150
100
50
0
-50
energy (kJ/mol)
·CH$_2$CH$_3$ + ·H
·CH$_3$ + ·CH$_3$
CH$_3$CH$_3$
CH$_2$=CH$_2$ + H$_2$
reaction coordinate


350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
energy (kJ/mol)
H$_2$ + ½O$_2$
H$_2$ + ·O·
H· + ·OH
H$_2$O
reaction coordinate