Week 4

Reaction Mechanisms

4.1 TST and Overview of Mechanisms

- More TST theory.

    - We can intuitively rationalize concentration as q/V by thinking of the partition function in some way giving some information about the number of particles. When we divide this by V, we thus get *some* information about concentration.
    - δ is the finite window in which the activated complex is loosely defined to exist.
    - ν_c is the frequency of crossing the δ region in the energy diagram.
    - We substitute $[\mathrm{AB}^\ddagger] = [\mathrm{A}][\mathrm{B}]K_c^\ddagger/c^\circ$ from the equilibrium constant expression.
    - The translational partition function plays a role. Note that $m^\ddagger$ is the mass of the activated complex.

    $$q_{\mathrm{trans}} = \frac{\sqrt{2\pi m^\ddagger k_{\mathrm{B}} T}}{h}\delta$$

        - Dimensional analysis (as an analysis of units to help appreciate the term): $k_{\mathrm{B}}T$ is energy ($E \propto mv^2/2$) and $m^\ddagger$ is mass, so their product is momentum squared ($p^2 \propto mv^2$).
        - Thus, the top of the expression gives momentum, and h/δ also gives momentum.
        - Remember that the momentum is rather like that of the particle in a box.

    - We have that

    $$q^\ddagger = q_{\mathrm{trans}}^\ddagger \cdot q_{\mathrm{rot}}^\ddagger$$

    where $q^\ddagger$ is the partition function for the whole species, which we can split.

    - This permits

    $$
    \begin{aligned}
    K_c^\ddagger &= \frac{(q^\ddagger/V)c^\circ}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} \\
    &= \frac{\sqrt{2\pi m^\ddagger k_{\mathrm{B}} T}}{h}\delta\frac{(q_{\mathrm{int}}^\ddagger/V)c^\circ}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)}
    \end{aligned}
    $$

    and the following

    $$k = \nu_c\frac{\sqrt{2\pi m^\ddagger k_{\mathrm{B}} T}}{hc^\circ}\delta\frac{(q_{\mathrm{int}}^\ddagger/V)c^\circ}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)}$$

    - We now define the speed of the activated complex crossing the barrier top (gas collision). This is $\langle u_{\mathrm{ac}}\rangle$, where $\langle u_{\mathrm{ac}}\rangle = \nu_c\delta$ (the frequency x distance).

– We have that

$$\langle u_{\mathrm{ac}} \rangle = \int_0^\infty u f(u) \, \mathrm{d}u = \sqrt{\frac{m^\ddagger}{2\pi k_{\mathrm{B}}T}} \int_0^\infty u \mathrm{e}^{-m^\ddagger u^2 / 2k_{\mathrm{B}}T} \, \mathrm{d}u = \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m^\ddagger}}$$

and the following

$$k = \frac{k_{\mathrm{B}}T}{hc^\circ} \frac{(q_{\mathrm{int}}^\ddagger / V)c^\circ}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} = \frac{k_{\mathrm{B}}T}{hc^\circ} K^\ddagger$$

■ We start at zero instead of $-\infty$ because we're only considering the forward direction of the reaction. If we did $-\infty$, we'd be accounting for the reverse reaction as well.

– Introducing $\Delta^\ddagger G^\circ = -RT \ln K^\ddagger = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$ yields the **Eyring equation**

$$k(T) = \frac{k_{\mathrm{B}}T}{hc^\circ} \mathrm{e}^{-\Delta^\ddagger G^\circ / RT} = \frac{k_{\mathrm{B}}T}{hc^\circ} \mathrm{e}^{\Delta^\ddagger S^\circ / R} \mathrm{e}^{-\Delta^\ddagger H^\circ / RT}$$

– We can relate the Eyring equation to the Arrhenius equation by differentiating the logarithm.

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{T} + \frac{\mathrm{d}\ln K^\ddagger}{\mathrm{d}T} \qquad\qquad \frac{\mathrm{d}\ln K_c}{\mathrm{d}T} = \frac{\Delta U^\circ}{RT^2}$$

gives

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

– This all serves to relate thermodynamics and kinetics.

– Additionally, since $\Delta^\ddagger H^\circ = \Delta^\ddagger U^\circ + \Delta^\ddagger PV = \Delta^\ddagger U^\circ + \Delta^\ddagger nRT$, we have that

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{\Delta^\ddagger H^\circ + 2RT}{RT^2}$$

■ Note that $\Delta n = -1$ for bimolecular gas phase reactions.
■ $\Delta(PV)^\ddagger$ is the difference in the number of moles of gaseous products and reactants.
■ $\Delta n^\ddagger = 0$: Unimolecular.
■ $\Delta n^\ddagger = -1$: Bimolecular.
■ $\Delta n^\ddagger = -2$: Trimolecular.

– Comparing with the Arrhenius $\mathrm{d}\ln k / \mathrm{d}T = E_a / RT^2$ gives

$$E_a = \Delta^\ddagger H^\circ + 2RT$$

– Substituting into the Eyring equation yields

$$k(T) = \frac{\mathrm{e}^2 k_{\mathrm{B}}T}{hc^\circ} \mathrm{e}^{\Delta^\ddagger S^\circ / R} \mathrm{e}^{-E_a / RT}$$

– Gas, uni: $E_a = \Delta H^\ddagger + RT$, $A = \mathrm{e}k_{\mathrm{B}}T/h \cdot \mathrm{e}^{\Delta S^\ddagger / R}$.
– Gas, bi: $E_a = \Delta H^\ddagger + 2RT$, $A = \mathrm{e}^2 k_{\mathrm{B}}T/hc^\circ \cdot \mathrm{e}^{\Delta S^\ddagger / R}$.
– Gas, tri: $E_a = \Delta H^\ddagger + 3RT$, $A = \mathrm{e}^3 k_{\mathrm{B}}T/h(c^\circ)^2 \cdot \mathrm{e}^{\Delta S^\ddagger / R}$.

• Important things to memorize from TST.

– The Eyring equation.
– Don't worry about the partition function mathematics, but understand the dimensional analysis.
■ Know that we collapse two $k_{\mathrm{B}}T$ terms together; one from q_{trans} and one from $\langle u_{\mathrm{ac}} \rangle$.

• Consider cyclohexane conformations.

– We have that

$$\Delta^{\ddagger}H^{\circ} = 31.38\,\text{kJ}\,\text{mol}^{-1} \qquad \Delta^{\ddagger}S^{\circ} = 16.74\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1} \qquad T = 325\,\text{K}$$

– We want to know $\Delta^{\ddagger}G^{\circ}$.

– But by the definition of the Gibbs energy,

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ} = 25.94\,\text{kJ}\,\text{mol}^{-1}$$

– It follows that

$$k = \frac{k_{\text{B}}T}{h}e^{-\Delta^{\ddagger}G^{\circ}/RT} = 4.59 \times 10^{8}\,\text{s}^{-1}$$

• Overview of key mechanism concepts.

– Reaction mechanisms can involve more than one elementary step.

– Reactions can be sequential (single- or multi-step).

– To establish a mechanism, we use several techniques, approaches, assumptions, and approximations.

– Establish rate determining steps: The rate law and rate constants associated with these steps tend to dominate the kinetics of the overall reaction.

– Invoke the steady-state approximation to help solve the complicated mathematics of reaction kinetics.

– Enzyme kinetics, Michaelis-Menten mechanism involves an SS approximation.

• Oftentimes, reactions are of the form

$$\text{E} + \text{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{k_r}{\longrightarrow} \text{P} + \text{E}$$
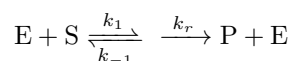
– Note that this form is very much analogous to the form analyzed in TST.

• **Elementary reaction**: A reaction that does not involve the formation of a reaction intermediate; the products must be formed directly from the reactants.

– Denoted by the double arrow.

– An elementary reaction can still be reversible.

• **Molecularity** (of an elementary reaction): The number of reactant molecules involved in the chemical reaction.

• **Unimolecular** (reaction): An elementary reaction with molecularity one. *General form*

$$\text{A} \Longrightarrow \text{products}$$
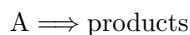
Rate law

$$v = k[\text{A}]$$

• **Bimolecular** (reaction): An elementary reaction with molecularity two. *General form*

$$\text{A} + \text{B} \Longrightarrow \text{products}$$
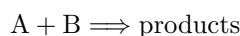
Rate law

$$v = k[\text{A}][\text{B}]$$

- **Termolecular** (reaction): An elementary reaction with molecularity three. *General form*

$$A + B + C \Longrightarrow \text{products}$$

  Rate law

$$v = k[A][B][C]$$

- No elementary reaction with molecularity greater than three is known, and the overwhelming majority of elementary reactions are bimolecular.

- When a complex reaction is at equilibrium, the rate of the forward process is equal to the rate of the reverse process for each and every step of the reaction mechanism.

  - We denote a reversible elementary reaction as follows.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$
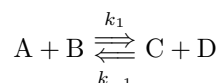
  - A reversible elementary reaction signifies that the reaction occurs in both the forward and reverse directions to a significant extent and that the reaction in each direction is an elementary reaction.
  - The rate laws are

$$v_1 = k_1[A][B] \qquad\qquad v_{-1} = k_{-1}[C][D]$$

  - At equilibrium,

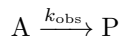$$k_1[A]_{\text{eq}}[B]_{\text{eq}} = k_{-1}[C]_{\text{eq}}[D]_{\text{eq}}$$
$$\frac{k_1}{k_{-1}} = \frac{[C]_{\text{eq}}[D]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} = K_c$$

- **Principle of detailed balance**: The following relationship, which holds for all reversible elementary reactions. *Given by*

$$K_c = \frac{k_1}{k_{-1}}$$

4.2   The Two-Step Consecutive Reaction Mechanism

4/20:   - Consider the general complex reaction

$$A \xrightarrow{k_{\text{obs}}} P$$

  - Suppose that the reaction occurs by the two step mechanism

$$A \xrightarrow{k_1} I \qquad\qquad\qquad I \xrightarrow{k_2} P$$

  - Because each step of this mechanism is an elementary reaction, the rate laws for each species are

$$\frac{d[A]}{dt} = -k_1[A] \qquad\qquad \frac{d[I]}{dt} = k_1[A] - k_2[I] \qquad\qquad \frac{d[P]}{dt} = k_2[I]$$

  - Thus, assuming that the initial concentrations at time $t = 0$ are $[A] = [A]_0$ and $[I]_0 = [P]_0 = 0$, we have that

$$[A] = [A]_0 e^{-k_1 t}$$
$$[I] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$
$$[P] = [A]_0 - [A] - [I] = [A]_0\left\{1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right\}$$

- Distinguishing the two-step consecutive reaction mechanism unambiguously from the one-step reaction.

  - For a single step reaction,
    $$[P] = [A]_0(1 - e^{-k_1 t})$$

  - The two-step consecutive reaction mechanism has the following alternate form.

    $$[P] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$

  - However, if $k_2 \gg k_1$, then

    $$[P] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$
    $$\approx [A]_0 \left\{ 1 + \frac{1}{-k_2} k_2 e^{-k_1 t} \right\}$$
    $$= [A]_0(1 - e^{-k_1 t})$$

  - If $k_1 \gg k_2$, he reaction reduces to
    $$[P] \approx [A]_0(1 - e^{-k_2 t})$$

  - Thus, the only ambiguous situation is $k_2 \gg k_1$.

- The steady-state approximation simplifies rate expressions.

  - We assume that $d[I]/dt = 0$, where I is a reaction intermediate.
  - Given the above differential equation for $d[I]/dt$, making the above assumption yields

    $$[I]_{SS} = \frac{k_1[A]}{k_2}$$
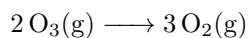
  - It follows that
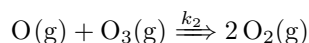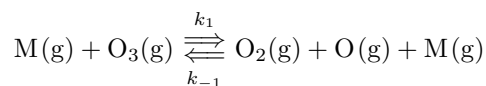 $$[I]_{SS} = \frac{k_1}{k_2}[A]_0 e^{-k_1 t}$$

  - Thus,
    $$\frac{d[I]_{SS}}{dt} = \frac{-k_1^2}{k_2}[A]_0 e^{-k_1 t}$$

  - We get $k_2 \gg k_1^2[A]_0$ and $[P] = [A]_0(1 - e^{-k_1 t})$.

- Example: Decomposition of ozone.
  $$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

  - The reaction mechanism is

    $$M(g) + O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) + M(g)$$

    $$O(g) + O_3(g) \overset{k_2}{\Longrightarrow} 2\,O_2(g)$$

    where M is a molecule that can exchange energy with the reacting ozone molecule through a collision, but M itself does not react.

  - The rate equations for $O_3(g)$ and $O(g)$ are

    $$\frac{d[O_3]}{dt} = -k_1[O_3][M] + k_{-1}[O_2][O][M] - k_2[O][O_3]$$
    $$\frac{d[O]}{dt} = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O][O_3]$$

– Invoking the steady-state approximation for the intermediate O yields

$$[\text{O}] = \frac{k_1[\text{O}_3][\text{M}]}{k_{-1}[\text{O}_2][\text{M}] + k_2[\text{O}_3]}$$

– Substituting this result into the rate equation for O_3 gives

$$\frac{\mathrm{d}[\text{O}_3]}{\mathrm{d}t} = -\frac{2k_1 k_2[\text{O}_3]^2[\text{M}]}{k_{-1}[\text{O}_2][\text{M}] + k_2[\text{O}_3]}$$

4.3   Complex Reactions

4/22:
- Expect the midterm to be 2 hours in length, available all next week, and to incorporate largely HW-like questions but also some open-ended, design-an-experiment questions. Completely open note.

- The rate law for a complex reaction does not imply a unique mechanism.
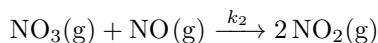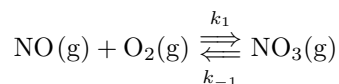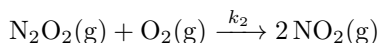
   – Consider the reaction
   $$2\,\text{NO}(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{k_{\text{obs}}} 2\,\text{NO}_2(\text{g})$$
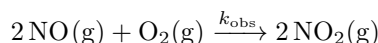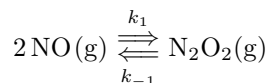
   – The rate law is
   $$\frac{1}{2}\frac{\mathrm{d}[\text{NO}_2]}{\mathrm{d}t} = k_{\text{obs}}[\text{NO}]^2[\text{O}_2]$$

   – Experimental studies confirm that the reaction is not an elementary reaction, but we can propose multiple mechanisms that would both yield the same rate law. Here are two examples.
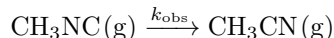
      ■ Mechanism 1.

      $$\text{NO}(\text{g}) + \text{O}_2(\text{g}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NO}_3(\text{g})$$

      $$\text{NO}_3(\text{g}) + \text{NO}(\text{g}) \xrightarrow{k_2} 2\,\text{NO}_2(\text{g})$$

      ■ Mechanism 2.

      $$2\,\text{NO}(\text{g}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N}_2\text{O}_2(\text{g})$$

      $$\text{N}_2\text{O}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{k_2} 2\,\text{NO}_2(\text{g})$$

   – One experiment to design is to capture or otherwise detect the intermediate species.
   – Through such an experiment, we can verify Mechanism 2.

- The Lindemann Mechanism explains how unimolecular reactions occur.

   – Consider the reaction
   $$\text{CH}_3\text{NC}(\text{g}) \xrightarrow{k_{\text{obs}}} \text{CH}_3\text{CN}(\text{g})$$

   – The following rate law is only correct at $[\text{CH}_3\text{NC}]$.
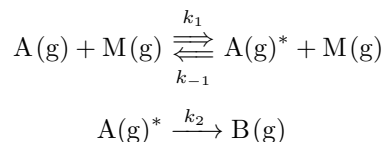 $$\frac{\mathrm{d}[\text{CH}_3\text{NC}]}{\mathrm{d}t} = -k_{\text{obs}}[\text{CH}_3\text{NC}]$$

   – At low $[\text{CH}_3\text{NC}]$, we have
   $$\frac{\mathrm{d}[\text{CH}_3\text{NC}]}{\mathrm{d}t} = -k_{\text{obs}}[\text{CH}_3\text{NC}]^2$$

   which is not the rate law for a unimolecular reaction.

– The Lindemann mechanism for unimolecular reactions of the form $A(g) \longrightarrow B(g)$ is

$$A(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A(g)^* + M(g)$$

$$A(g)^* \xrightarrow{k_2} B(g)$$

– The symbol $A(g)^*$ represents an energized reactant molecule. $M(g)$ is the collision partner.

– By the steady-state approximation, we have that

$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

$$[A^*] = \frac{k_1[M][A]}{k_2 + k_{-1}[M]}$$

so that

$$\frac{d[B]}{dt} = k_2[A^*]$$

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \underbrace{\frac{k_2 k_1[M]}{k_2 + k_{-1}[M]}}_{k_{obs}}[A]$$

– At high [M], we have that $k_{-1}[M][A^*] \gg k_2[A^*]$, or $k_{-1}[M] \gg k_2$. Thus,

$$k_{obs} = \frac{k_1 k_2}{k_{-1}}$$

– At low [M], we have that $k_2 \gg k_{-1}[M]$ so that
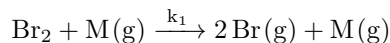
$$\frac{d[B]}{dt} = k_1[M][A]$$

$$= k_1[A]^2$$

– This mechanism was proposed by the British chemists J. A. Christiansen in 1921 and F. A. Lindemann in 1922. Their work underlies the current theory of unimolecular reaction rates.

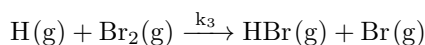• Some reaction mechanisms involve chain reactions.

– Chain reactions involve amplification.

– For example, $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ follows the ensuing mechanism.

  ■ Initiation.
$$Br_2 + M(g) \xrightarrow{k_1} 2Br(g) + M(g)$$

  ■ Propagation.

$$Br(g) + H_2(g) \xrightarrow{k_2} HBr(g) + H(g)$$

$$H(g) + Br_2(g) \xrightarrow{k_3} HBr(g) + Br(g)$$

  ■ Inhibition.

$$HBr(g) + H(g) \xrightarrow{k_{-2}} Br(g) + H_2(g)$$

$$HBr(g) + Br(g) \xrightarrow{k_{-3}} H(g) + Br_2(g)$$

■ Termination.

$$2\,\mathrm{Br} + \mathrm{M\,(g)} \xrightarrow{k_{-1}} \mathrm{Br_2(g)} + \mathrm{M\,(g)}$$
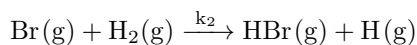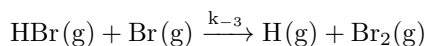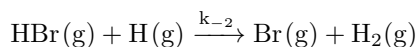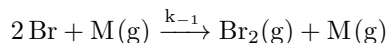
– The fifth step can be ignored.

– Notice that the inhibition and termination reactions are the reverse reactions of the propagation and initiation reaction(s), respectively.

■ Termination does not need to be the reverse of initiation, though. Termination just kills any reactive species.

■ Inhibition is the reverse of propagation, though.

– When you want to design a chain reaction species, make sure you have a reactive species (like bromine) for the initiation step. Notice, for instance, that hydrogen does not initiate.

– This leads to the experimentally determined rate law

$$\frac{1}{2}\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k'[\mathrm{HBr}][\mathrm{Br_2}]^{-1}}$$

– Deriving said rate law.

■ We have that

$$\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br_2}]$$

$$\frac{\mathrm{d[H]}}{\mathrm{d}t} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br_2}]$$

$$\frac{\mathrm{d[Br]}}{\mathrm{d}t} = 2k_1[\mathrm{Br_2}][\mathrm{M}] - k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br_2}]$$

■ We can apply the SS approximation to the second and third equations above, which both describe intermediate species.

$$0 = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br_2}]$$

$$0 = 2k_1[\mathrm{Br_2}][\mathrm{M}] - k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br_2}]$$

■ Solving the two equations above for [H] and [Br], respectively, is made substantially easier by noting that the negative of the first expression appears in its entirety in the second expression. Thus, we may simply substitute the former into the latter and solve to find an expression for [Br].

$$0 = 2k_1[\mathrm{Br_2}][\mathrm{M}] - k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - 0$$

$$[\mathrm{Br}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{Br_2}]^{1/2}$$

$$[\mathrm{Br}] = (K_{c,1})^{1/2}[\mathrm{Br_2}]^{1/2}$$

■ Resubstituting yields an expression for [H].

$$0 = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br_2}]$$

$$0 = k_2(K_{c,1})^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}] - (k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}])[\mathrm{H}]$$

$$[\mathrm{H}] = \frac{k_2(K_{c,1})^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}$$

■ Substituting these two expressions back into the original differential equation for [HBr] yields

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] - k_{-2}[HBr][H] + k_3[H][Br_2]$$

$$= k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2] - k_{-2}[HBr] \cdot \frac{k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

$$+ k_3 \cdot \frac{k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2]}{k_{-2}[HBr] + k_3[Br_2]} \cdot [Br_2]$$

$$= k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2] - \frac{k_2 k_{-2}(K_{c,1})^{1/2}[HBr][Br_2]^{1/2}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

$$+ \frac{k_2 k_3 (K_{c,1})^{1/2}[Br_2]^{3/2}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

$$= k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2] \left(1 - \frac{k_{-2}[HBr]}{k_{-2}[HBr] + k_3[Br_2]} + \frac{k_3[Br_2]}{k_{-2}[HBr] + k_3[Br_2]}\right)$$

$$= k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2] \left(\frac{k_{-2}[HBr] + k_3[Br_2]}{k_{-2}[HBr] + k_3[Br_2]} - \frac{k_{-2}[HBr] - k_3[Br_2]}{k_{-2}[HBr] + k_3[Br_2]}\right)$$

$$= k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2] \cdot \frac{2k_3[Br_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

$$\frac{1}{2}\frac{d[HBr]}{dt} = k_2(K_{c,1})^{1/2}[Br_2]^{1/2}[H_2] \cdot \frac{1}{(k_{-2}/k_3)[HBr][Br_2]^{-1} + 1}$$

$$= \frac{k_2(K_{c,1})^{1/2}[H_2][Br_2]^{1/2}}{1 + (k_{-2}/k_3)[HBr][Br_2]^{-1}}$$

$$= \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr][Br_2]^{-1}}$$

where we have substituted $k = k_2(K_{c,1})^{1/2}$ and $k' = k_{-2}/k_3$ in the last expression.

- Problem 29-24.
  - The reaction

$$CH_3CHO(g) \xrightarrow{k_{obs}} CH_4(g) + CO(g)$$

  proceeds by the mechanism

$$CH_3CHO(g) \xrightarrow{k_1} CH_3(g) + CHO(g)$$

$$CH_3(g) + CH_3CHO(g) \xrightarrow{k_2} CH_4(g) + CH_3CO(g)$$

$$CH_3CO(g) \xrightarrow{k_3} CH_3(g) + CO(g)$$

$$2\,CH_3(g) \xrightarrow{k_4} C_2H_6(g)$$
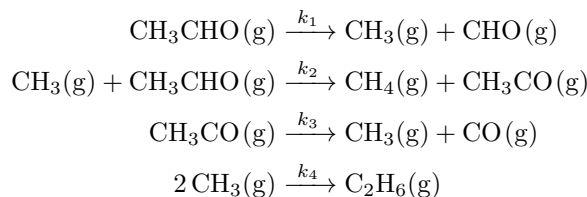
  - The initiation step is the first equation, the propagation steps are the second and third equations, and the termination step is the fourth equation.
  - We can write the rate laws

$$\frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO]$$

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - 2k_4[CH_3]$$

$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$$

– Applying the SS approximation to the last second and third equations yields (respectively)

$$[\mathrm{CH_3}] = \frac{k_1[\mathrm{CH_3CHO}] + k_3[\mathrm{CH_3CO}]}{k_2[\mathrm{CH_3CHO}] + 2k_4} \qquad\qquad [\mathrm{CH_3CO}] = \frac{k_2}{k_3}[\mathrm{CH_3}][\mathrm{CH_3CHO}]$$

– Substituting the right equation above into the left equation above and solving for $[\mathrm{CH_3}]$ yields an expression for $[\mathrm{CH_3}]$ purely in terms of $[\mathrm{CH_3CHO}]$.

$$[\mathrm{CH_3}] = \frac{k_1[\mathrm{CH_3CHO}] + k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}]}{k_2[\mathrm{CH_3CHO}] + 2k_4}$$

$$k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] + 2k_4[\mathrm{CH_3}] = k_1[\mathrm{CH_3CHO}] + k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}]$$

$$2k_4[\mathrm{CH_3}] = k_1[\mathrm{CH_3CHO}]$$

$$[\mathrm{CH_3}] = \frac{k_1}{2k_4}[\mathrm{CH_3CHO}]$$

– The final result is

$$\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = k_2\left(\frac{k_1}{2k_4}[\mathrm{CH_3CHO}]\right)[\mathrm{CH_3CHO}]$$

$$= k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}]^{3/2}$$

■ What's the issue here?

4.4   Chapter 26: Chemical Equilibrium

From McQuarrie and Simon (1997).

- "Thermodynamics enables us to predict with confidence the equilibrium pressures or concentrations of reaction mixtures" (McQuarrie & Simon, 1997, p. 963).

- Goal of this chapter: Derive a relationship between the standard Gibbs energy change and the equilibrium constant.

- We begin by considering the following general gas-phase reaction.

$$\nu_\mathrm{A}\,\mathrm{A(g)} + \nu_\mathrm{B}\,\mathrm{B(g)} \rightleftharpoons \nu_\mathrm{Y}\,\mathrm{Y(g)} + \nu_\mathrm{Z}\,\mathrm{Z(g)}$$

- **Extent of reaction**: A measure of how far along its reaction coordinate a chemical reaction is. *Denoted by* $\boldsymbol{\xi}$. *Units* **mol**. *Given by*

$$n_\mathrm{A} = n_\mathrm{A0} - \nu_\mathrm{A}\xi \qquad\qquad n_\mathrm{Y} = n_\mathrm{Y0} + \nu_\mathrm{Y}\xi$$
$$n_\mathrm{B} = n_\mathrm{B0} - \nu_\mathrm{B}\xi \qquad\qquad n_\mathrm{Z} = n_\mathrm{Z0} + \nu_\mathrm{Z}\xi$$

where n_j is the number of moles for each species at the time during the reaction corresponding to extent of reaction ξ and n_{j0} is the initial number of moles for each species.

  – As the reaction proceeds, ξ varies from zero to some maximum value.
  – An example of the units of ξ: If n_A0 equals ν_A moles and n_B0 equals ν_B moles, then ξ varies from zero moles to one mole over the course of the reaction.

- Relating the change in Gibbs energy to the change in extent of reaction.

- The Gibbs energy for this multicomponent system depends on T, P, and n_j for the two reactants and the two products. Thus,

$$
\begin{aligned}
\mathrm{d}G &= \left(\frac{\partial G}{\partial T}\right)_{P,n_j} \mathrm{d}T + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} \mathrm{d}P + \left(\frac{\partial G}{\partial n_\mathrm{A}}\right)_{T,P,n_{j\neq\mathrm{A}}} \mathrm{d}n_\mathrm{A} \\
&\quad + \left(\frac{\partial G}{\partial n_\mathrm{B}}\right)_{T,P,n_{j\neq\mathrm{B}}} \mathrm{d}n_\mathrm{B} + \left(\frac{\partial G}{\partial n_\mathrm{Y}}\right)_{T,P,n_{j\neq\mathrm{Y}}} \mathrm{d}n_\mathrm{Y} + \left(\frac{\partial G}{\partial n_\mathrm{Z}}\right)_{T,P,n_{j\neq\mathrm{Z}}} \mathrm{d}n_\mathrm{Z} \\
&= -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \mu_\mathrm{Y}\,\mathrm{d}n_\mathrm{Y} + \mu_\mathrm{Z}\,\mathrm{d}n_\mathrm{Z}
\end{aligned}
$$

- Taking T, P to be constant simplifies the above to

$$
\mathrm{d}G = \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \mu_\mathrm{Y}\,\mathrm{d}n_\mathrm{Y} + \mu_\mathrm{Z}\,\mathrm{d}n_\mathrm{Z}
$$

- Differentiating the equations used to define the extent of reaction yields

$$
\begin{aligned}
\mathrm{d}n_\mathrm{A} &= -\nu_\mathrm{A}\,\mathrm{d}\xi & \mathrm{d}n_\mathrm{Y} &= \nu_\mathrm{Y}\,\mathrm{d}\xi \\
\mathrm{d}n_\mathrm{B} &= -\nu_\mathrm{B}\,\mathrm{d}\xi & \mathrm{d}n_\mathrm{Z} &= \nu_\mathrm{Z}\,\mathrm{d}\xi
\end{aligned}
$$

so that

$$
\begin{aligned}
\mathrm{d}G &= -\nu_\mathrm{A}\mu_\mathrm{A}\,\mathrm{d}\xi - \nu_\mathrm{B}\mu_\mathrm{B}\,\mathrm{d}\xi + \nu_\mathrm{Y}\mu_\mathrm{Y}\,\mathrm{d}\xi + \nu_\mathrm{Z}\mu_\mathrm{Z}\,\mathrm{d}\xi \\
&= (\nu_\mathrm{Y}\mu_\mathrm{Y} + \nu_\mathrm{Z}\mu_\mathrm{Z} - \nu_\mathrm{A}\mu_\mathrm{A} - \nu_\mathrm{B}\mu_\mathrm{B})\,\mathrm{d}\xi \\
\left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= \nu_\mathrm{Y}\mu_\mathrm{Y} + \nu_\mathrm{Z}\mu_\mathrm{Z} - \nu_\mathrm{A}\mu_\mathrm{A} - \nu_\mathrm{B}\mu_\mathrm{B}
\end{aligned}
$$

- $\boldsymbol{\Delta_r G}$: The change in Gibbs energy when the extent of reaction changes by one mole. *Units* $\mathbf{J\,mol^{-1}}$. *Given by*

$$
\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \nu_\mathrm{Y}\mu_\mathrm{Y} + \nu_\mathrm{Z}\mu_\mathrm{Z} - \nu_\mathrm{A}\mu_\mathrm{A} - \nu_\mathrm{B}\mu_\mathrm{B}
$$

- Relating standard and nonstandard states.

  - Let all partial pressures be sufficiently low to assume ideality.
  - Then substituting the equation $\mu_j(T, P) = \mu_j^\circ(T) + RT\ln(P_j/P^\circ)$ yields

$$
\Delta_r G = \nu_\mathrm{Y}\mu_\mathrm{Y}^\circ(T) + \nu_\mathrm{Z}\mu_\mathrm{Z}^\circ(T) - \nu_\mathrm{A}\mu_\mathrm{A}^\circ(T) - \nu_\mathrm{B}\mu_\mathrm{B}^\circ(T) + RT\left(\nu_\mathrm{Y}\ln\frac{P_\mathrm{Y}}{P^\circ} + \nu_\mathrm{Z}\ln\frac{P_\mathrm{Z}}{P^\circ} - \nu_\mathrm{A}\ln\frac{P_\mathrm{A}}{P^\circ} - \nu_\mathrm{B}\ln\frac{P_\mathrm{B}}{P^\circ}\right)
$$

$$
= \underbrace{\nu_\mathrm{Y}\mu_\mathrm{Y}^\circ(T) + \nu_\mathrm{Z}\mu_\mathrm{Z}^\circ(T) - \nu_\mathrm{A}\mu_\mathrm{A}^\circ(T) - \nu_\mathrm{B}\mu_\mathrm{B}^\circ(T)}_{\Delta_r G^\circ} + RT\ln\underbrace{\frac{(P_\mathrm{Y}/P^\circ)^{\nu_\mathrm{Y}}(P_\mathrm{Z}/P^\circ)^{\nu_\mathrm{Z}}}{(P_\mathrm{A}/P^\circ)^{\nu_\mathrm{A}}(P_\mathrm{B}/P^\circ)^{\nu_\mathrm{B}}}}_{Q}
$$

- $\boldsymbol{\Delta_r G^\circ(T)}$: The change in standard Gibbs energy for the reaction between unmixed reactants in their standard states at temperature T and a pressure of one bar to form unmixed products in their standard states at the same temperature T and pressure of one par.

  - Note that since P° is taken to be $1\,\mathrm{bar}$, the P°'s are usually dropped in the definition of Q. However, they must be remembered in the sense that they make Q unitless whether shown or not.

- **Equilibrium**: The position of the reaction system at which the Gibbs energy is a minimum with respect to any displacement.

  - Mathematically, we have that at equilibrium, $\Delta_r G = 0$.

– It follows that at equilibrium,

$$0 = \Delta_r G^\circ(T) + RT \ln \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

$$\Delta_r G^\circ(T) = -RT \ln \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

- **Equilibrium constant**: A constant describing the relative pressures of reactants to products that will result in the reaction system achieving equilibrium. *Denoted by* $\boldsymbol{K_P(T)}$. *Given by*

$$K_P(T) = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

  – The value of the equilibrium constant depends on how we write the chemical equation for the reaction at hand. For instance, the equilibrium constant expression for $3\,H_2 + N_2 \rightleftharpoons 2\,NH_3$ is the square of the equilibrium constant expression for $\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftharpoons NH_3$.

- An equilibrium constant is a function of temperature only.

  – This is because in deriving the equilibrium constant expression, we set $\Delta_r G(T, P) = 0$, and pressure appears nowhere else in the equation $\Delta_r G^\circ(T) + RT \ln Q$.
  – In particular, the ratio that defines Q must remain constant at different initial pressures of reactants and products.

- Thinking through some equilibrium concepts in an example.

  – Consider the reaction
  $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

  – The equilibrium constant expression is
  $$K_P(T) = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}$$

  – If we initially have one mole of PCl_5 and no PCl_3 or Cl_2, then when the reaction occurs to an extent ξ, there will be $1 - \xi$ moles PCl_5 and ξ moles PCl_3 and Cl_2. This leads to an overall $1 + \xi$ moles of gas.

  – It follows that if ξ_{eq} is the extent of reaction at equilibrium, then the partial pressures of each gas at equilibrium are given by

$$P_{PCl_3} = P_{Cl_2} = \frac{\xi_{\text{eq}}}{1 + \xi_{\text{eq}}} P \qquad\qquad P_{PCl_5} = \frac{1 - \xi_{\text{eq}}}{1 + \xi_{\text{eq}}} P$$

  where P is the total pressure.

  – Thus, the equilibrium constant expression is

$$K_P(T) = \frac{\xi_{\text{eq}}^2}{1 - \xi_{\text{eq}}^2} P$$

  – While the above expression sure makes it seem like $K_P(T)$ depends on P, we know by the above that it can't. Thus, it must be the position of the equilibrium along the extent of reaction that changes as P changes.

  – In particular, as per **Le Châtelier's principle**, we can note that for $K_P > 1$, increasing pressure favors lesser extents of reaction (i.e., favors the reactants). This should make intuitive sense harkening back to AP Chemistry since it stands to reason that pressure increases would favor shifting the equilibrium to have fewer moles of gas. Now, however, we have a quantitative rule for how changes in pressure will affect the equilibrium.

- **Le Châtelier's principle**: If a chemical reaction at equilibrium is subjected to a change in conditions that displaces it from equilibrium, then the reaction adjusts toward a new equilibrium state.

- Note that we can also express the equilibrium constant in terms of concentration via the relationship $P = cRT$ where $c = n/V$ is the concentration.

$$K_P = \frac{c_Y^{\nu_Y} c_Z^{\nu_Z}}{c_A^{\nu_A} c_B^{\nu_B}} \left(\frac{RT}{P^\circ}\right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

- c°: The standard concentration. *Given by*

$$c^\circ = 1 \, \tfrac{\text{mol}}{\text{L}}$$

- The standard concentration enables the following definitions.

$$K_P = \underbrace{\frac{(c_Y/c^\circ)^{\nu_Y}(c_Z/c^\circ)^{\nu_Z}}{(c_A/c^\circ)^{\nu_A}(c_B/c^\circ)^{\nu_B}}}_{K_c} \left(\frac{c^\circ RT}{P^\circ}\right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

  - Note that both K_c and the term by which it is multiplied above are unitless.
  - As such, we have to be careful what units we use for R. In the standard situation of $P^\circ = 1 \, \text{bar}$ and $c^\circ = 1 \, \text{mol L}^{-1}$, we must use $R = 0.083\,145 \, \text{L bar mol}^{-1} \, \text{K}^{-1}$.

- By combining the two equations below (both given in derivations above), we can obtain a relation between the equilibrium constant K_p and the standard molar Gibbs energies (i.e., chemical potentials) of the relevant substances.

$$\Delta_r G^\circ(T) = -RT \ln K_P$$
$$\Delta_r G^\circ(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$$

  - Note that $\mu_j^\circ(T) = \Delta_f G^\circ[j]$ if we choose appropriate standard states.
  - Thus, we can use tables of standard molar Gibbs energies of formation to calculate equilibrium constants.

- Example: Deriving a function for the Gibbs energy of a reaction in terms of the extent of reaction.

  - Consider the following reaction, which occurs at $298.15 \, \text{K}$.

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$$
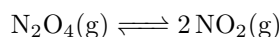
  - Let the initial conditions be one mole of N_2O_4 and no NO_2. Then

$$\begin{aligned} G(\xi) &= n_{\text{N}_2\text{O}_4} \overline{G}_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} \overline{G}_{\text{NO}_2} \\ &= (1-\xi)\overline{G}_{\text{N}_2\text{O}_4} + 2\xi \overline{G}_{\text{NO}_2} \\ &= (1-\xi)G_{\text{N}_2\text{O}_4}^\circ + 2\xi G_{\text{NO}_2}^\circ + (1-\xi)RT \ln P_{\text{N}_2\text{O}_4} + 2\xi RT \ln P_{\text{NO}_2} \end{aligned}$$

  - Let the reaction be carried out at a constant total pressure of one bar. This assumption combined with the fact that the total number of moles in the reaction mixture is $(1-\xi) + 2\xi = 1 + \xi$ reveals that

$$P_{\text{N}_2\text{O}_4} = x_{\text{N}_2\text{O}_4} P_{\text{total}} = \frac{1-\xi}{1+\xi} \cdot 1 = \frac{1-\xi}{1+\xi} \qquad P_{\text{NO}_2} = x_{\text{NO}_2} P_{\text{total}} = \frac{2\xi}{1+\xi} \cdot 1 = \frac{2\xi}{1+\xi}$$

    so that

$$G(\xi) = (1-\xi)G_{\text{N}_2\text{O}_4}^\circ + 2\xi G_{\text{NO}_2}^\circ + (1-\xi)RT \ln \frac{1-\xi}{1+\xi} + 2\xi RT \ln \frac{2\xi}{1+\xi}$$

– Choosing appropriate standard states, we can obtain the final form

$$G(\xi) = (1 - \xi)\Delta_f G^\circ_{N_2O_4} + 2\xi\Delta_f G^\circ_{NO_2} + (1 - \xi)RT \ln \frac{1 - \xi}{1 + \xi} + 2\xi RT \ln \frac{2\xi}{1 + \xi}$$

– Plugging in

$$\Delta_f G^\circ_{N_2O_4} = 97.787 \, \text{kJ mol}^{-1} \qquad\qquad \Delta_f G^\circ_{NO_2} = 51.258 \, \text{kJ mol}^{-1}$$

we can determine that the minimum of the curve occurs at $\xi_{eq} = 0.1892 \, \text{mol}$.

– Thus,

$$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{[2\xi_{eq}/(1 + \xi_{eq})]^2}{(1 - \xi_{eq})/(1 + \xi_{eq})} = \frac{4\xi^2_{eq}}{1 - \xi^2_{eq}} = 0.148$$

■ Note that this value compares exactly with the one obtained via the $-RT \ln K_P = \sum \nu_j \mu^\circ_j(T)$ method.

– Note that differentiating our final form for $G(\xi)$ wrt. ξ yields $\Delta_r G = \Delta_r G^\circ + RT \ln K_P$, as expected.

- **Reaction quotient**: A quantity describing the relative amounts of reactants and products present in the reaction system at a given instant in time. *Denoted by $\boldsymbol{Q_P}$. Given by*

$$Q_P = \frac{P^{\nu_Y}_Y P^{\nu_Z}_Z}{P^{\nu_A}_A P^{\nu_B}_B}$$

- We have that

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln Q_P \\ &= -RT \ln K_P + RT \ln Q_P \\ &= RT \ln \frac{Q_P}{K_P}\end{aligned}$$

– Thus, the ratio of the reaction quotient to the equilibrium constant determines the direction in which a reaction will proceed.

- The sign of $\Delta_r G$ and not that of $\Delta_r G^\circ$ determines the direction of reaction spontaneity.

– Indeed, the sign of $\Delta_r G^\circ$ determines the direction of reaction spontaneity only when all substances are mixed at one bar partial pressures (i.e., when $\Delta_r G = \Delta_r G^\circ$).

- "The fact that a process will occur spontaneously does not imply that it will necessarily occur at a detectable rate" (McQuarrie & Simon, 1997, p. 977).

– For example, the negative $\Delta_r G^\circ$ of water at one bar and $25\,°\text{C}$ tells us that the reaction $2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$ will occur spontaneously. However, experimental evidence reveals that a spark or catalyst is needed to convert hydrogen and oxygen to water; once said activation energy is introduced, the reaction proceeds explosively.

– Indeed, "the 'no' of thermodynamics is emphatic. If thermodynamics says that a certain process will not occur spontaneously, it will not occur. The 'yes' of thermodynamics, on the other hand, is actually a 'maybe'" (McQuarrie & Simon, 1997, p. 977).