Today

**Kinetics**

How fast are reactions?
What are the rates?

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**Thermodynamics vs. Kinetics**

Diamond → Graphite

\[ \Delta_R G^\circ = -3 \text{ kJ mol}^{-1} \]

Graphite is lower in free energy than Diamond
Reaction of Diamond to Graphite is spontaneous

THE REACTION IS JUST VERY VERY SLOW

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**Thermodynamics**

- Compares Free energy of reactants and products
- This is the ideal case assuming everything can find its lowest energy state (time is irrelevant)

- Diamonds are unstable

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**Kinetics**

- What is actually happening
- How long does it take convert reactants to products

- Diamonds are "kinetically trapped" in the unstable state

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**What prevents reactions from going "downhill" in energy?**

- Thermodynamics deals with the initial and final states
- Kinetics deals with the path between them

\[ 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \]
Why is there a "barrier"?

You have to break the "old" bonds before you can form the "new" ones.

How do you speed up a reaction?

Raise the temperature (more molecules over the barrier)
Add a catalyst (lower the barrier)

How do we know how fast a reaction is?

We look at the rate

Rate is change per time
Reaction rate is change in concentration per time

For this reaction

A. the rate for all the species is constant
B. the rate is largest at the start of the reaction
C. the rate is largest at equilibrium
D. the rate is randomly fluctuating

Rate is change in concentration per unit time
Rate is the slope of the graph of concentration vs time

Steepest slow at the start
at equilibrium rate = 0 (reaction has stopped)
If you know the rate of one reactant or product, you know them all.

For this reactions

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

the rate of production of \( \text{NH}_3 \) is

A. 2 times the rates of consumption of \( \text{H}_2 \)
B. 1.5 times the rate of consumption of \( \text{H}_2 \)
C. \( \frac{2}{3} \times \text{rate of consumption of H}_2 \)

\[ 2 \times \text{N}_2 \quad \frac{2}{3} \times \text{H}_2 \]
Characterizing rates

We want the slope

\[ \frac{\Delta [C]}{\Delta t} \approx \frac{d[C]}{dt} \]

Note
Rate is changing with concentration

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Rate Laws

How does the rate depend on the concentrations?

Rate is some function of the concentration of the reactant molecules

What is the function?

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| Table 15.1 Concentrations of Reactant and Products as a Function of Time for the Reaction 2NO\(_2\)(g) \rightarrow 2NO(g) + O\(_2\)(g) (at 300°C) |
|---------------------------------|--------|--------|--------|
| Time (± 1 s) | NO\(_2\) | NO     | O\(_2\) |
| 0             | 0.0100 | 0      | 0      |
| 30            | 0.0079 | 0.0021 | 0.0011 |
| 100           | 0.0065 | 0.0035 | 0.0018 |
| 150           | 0.0055 | 0.0045 | 0.0023 |
| 200           | 0.0048 | 0.0052 | 0.0026 |
| 250           | 0.0043 | 0.0057 | 0.0029 |
| 300           | 0.0038 | 0.0062 | 0.0031 |
| 350           | 0.0034 | 0.0066 | 0.0033 |
| 400           | 0.0031 | 0.0069 | 0.0035 |

\[2NO_2(g) \rightarrow NO(g) + O_2(g)\]

unknown constant

\[ \text{Rate} = k[NO_2]^n \]

unknown exponent

k is the "rate constant"

n is the "reaction order" with respect to NO\(_2\)