Chemical Thermodynamics III

- In this lecture, we shall analyze the ***temperature dependence*** of chemical reactions (***Arrhenius' law***).
- We shall also analyze ***light dependence*** of some reactions, such as the ***hydrogen-bromine reaction***.
- Finally, we shall discuss the influence of external sources of energy, such as ***mechanical energy*** in a ***Continuous Stirred Tank Reactor (CSTR)***, or such as ***electrical energy*** in ***electrolysis***.

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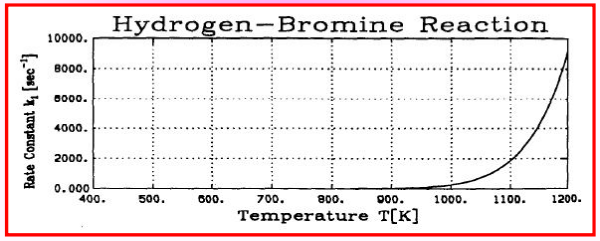
Temperature Dependence of Chemical Reaction Systems I

- It can be observed that the reaction rates of essentially all reactions change in function of the temperature that the reactants are at, for example:



Temperature Dependence of Chemical Reaction Systems II

- How can this be explained? Most reactions require ***activation energy*** to take place. Without this activation energy, they could not occur, because otherwise, they would occur rather violently.
- Thus, a reaction such as:

$$Br2 \xrightarrow{k_i} 2Br^{\cdot}$$

- should probably be written as:

$$Br2 + M \xrightarrow{k_i} 2Br^{\cdot} + M$$

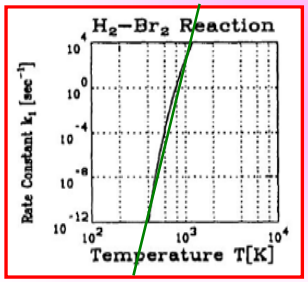
- where ***M*** is a ***catalyst*** that does not otherwise participate in the reaction. It only provides the necessary activation energy for the reaction to take place.

Temperature Dependence of Chemical Reaction Systems III

- ***Temperature*** is only a statistical quantity, i.e., the different molecules vary in the amount of energy that they possess. Temperature is a measure of the ***average microscopic kinetic energy*** (***Brown's movement***) that a molecule possesses.
- If two high-energized molecules collide, they react, because they can borrow the necessary activation energy from the microscopic kinetic energy, i.e., from the thermal domain.
- In the case of the Br_2 decaying reaction, it probably will never occur, unless one Br_2 molecule collides with another molecule, from which it can borrow the necessary activation energy.
- The higher the ***temperature*** of the reactants, the more highly energized the average molecule will be, and the more likely it will overcome the activation energy. Thus, the reaction rate constants are always functions of temperature.

Arrhenius' Law I

- We can redraw the previous figure using a double-logarithmic scale.



Arrhenius discovered that the temperature dependence for many reactions is approximately linear, if depicted using a double-logarithmic scale.

$$\Rightarrow \quad k = A \cdot \exp(-\frac{E_a}{R \cdot T})$$

A = frequency factor (frequency of collisions)
E_a = activation energy

Arrhenius' Law II

- Notice that, although the temperature dependence of chemical reaction rates is physically interpretable, ***Arrhenius' law*** is purely empirical, and no physical explanation can be provided that would support the precise nature of the ***Arrhenius equation***. Indeed, the equation is often modified to:

$$k = k_0 \cdot T^m \cdot \exp(-\frac{E_a}{R \cdot T})$$

- Notice that no external energy was added here in order to speed up the reactions. The modulation of the reaction rates is purely internal. It is caused by the heat stored in the system.

The Hydrogen-Bromine Reaction

- The following experimental rates have been found to describe well the ***hydrogen-bromine reaction***:

$$ak_1 = 1.39 \cdot 10^8 \cdot \sqrt{T} \cdot (\frac{189243.0}{R \cdot T})^{1.97}$$
$$k_1 = ak_1 \cdot \exp(\frac{-189243.0}{R \cdot T})$$
$$k_2 = \frac{k_1}{K(T)}$$
$$k_3 = 10^{11.43} \cdot \exp(\frac{-82400.0}{R \cdot T})$$
$$k_5 = 10^{11.97} \cdot \exp(\frac{-149800.0}{R \cdot T})$$
$$k_4 = 0.1 \cdot k_5$$

Abs. Temperature T [K]	Equilibrium Const. K [mole m^{-3}]
300.0	7.7446×10^{-29}
400.0	1.9543×10^{-20}
500.0	2.2182×10^{-15}
600.0	5.2844×10^{-12}
700.0	1.3867×10^{-9}
800.0	9.0782×10^{-8}
900.0	2.3768×10^{-6}
1000.0	3.2509×10^{-5}
1100.0	2.7861×10^{-4}
1200.0	1.6788×10^{-3}
1300.0	7.6913×10^{-3}
1400.0	2.8510×10^{-2}
1500.0	8.8716×10^{-2}
1600.0	2.4044×10^{-1}
1700.0	5.8344×10^{-1}
1800.0	1.7947
1900.0	2.6061
2000.0	4.9431

Arrhenius' Law III

- We need to ask ourselves one more question: If the participating reactants are at different temperature values, which value do we use in the ***Arrhenius equation***?
- Remember that ***temperature*** is only a ***statistical quantity***. It is a measure for the average microscopic kinetic energy contained in a molecule of a substance.
- Consequently, if two reactant substances are at different temperature values, we can safely use the ***average value of their temperatures*** in satisfying the ***Arrhenius equation***.

Pressure Dependence of Reaction Rates

- In the light of what we have learnt about temperature dependence of reaction rates, a ***pressure dependence*** should also be expected.
- If the pressure of a gas rises, this means that more molecules are present per unit volume. Consequently, the probability of collisions among molecules should increase as well.
- Although a pressure dependence certainly exists, it isn't explored much in the chemical engineering literature.

Light Sensitivity of Reaction Rates I

- Some reaction rates have been found to be sensitive to light, i.e., the reaction rates increase in the ***presence of light***, and decrease when the reactants are kept in the dark.
- For example, this is most certainly true for the ***hydrogen-bromine reaction***.
- The explanation of this phenomenon is simple: photons collide with reactants and provide the necessary activation energy for the reaction to take place.
- In the ***hydrogen-bromine reaction***, it is the decaying reaction of the bromine gas that is influenced by collisions with photons.

Light Sensitivity of Reaction Rates II

- However, in this case, there is ***external energy***, namely ***optical energy***, that is added to the system.
- Thus, contrary to the previously discussed types of reaction rate dependencies, here the bond graph will need to change, since external energy is added to the system.

$$P_{opt} = (h \cdot \nu) \cdot I$$

h = Planck constant ($h = 6.625 \cdot 10^{-34}$ *J sec*)
ν = Frequency (color) of the light
I = Intensity (number of photons per time unit) of the light

- We choose: $\frac{h \cdot \nu}{I}$ ↘

Light Sensitivity of Reaction Rates III

- The photons add energy to the microscopic kinetic motion of the molecules, i.e., the optical energy is adding energy to the thermal side.
- Consequently, the ***Gibbs equation*** is modified as follows:

$$T \cdot \dot{S}_{k1} = p \cdot q_{k1} + (h \cdot n) \cdot I - \mu \cdot \nu_{k1}$$

Increase in light increases the thermal power.

- The additional entropy is entered at reaction k_1, since this is the reaction that is influenced by the photon flux. Yet this is arbitrary, since the photons collide with all molecules.

Light Sensitivity of Reaction Rates IV

- Furthermore, the reaction rates need to be modified:

$$\begin{aligned}
\nu_{Br_2} &= -\nu_{k_1} + \nu_{k_2} - \nu_{k_5} - k_1' \cdot I \cdot n_{Br_2} \\
\nu_{Br\cdot} &= 2\nu_{k_1} - 2\nu_{k_2} - \nu_{k_3} + \nu_{k_4} + \nu_{k_5} + 2k_1' \cdot I \cdot n_{Br_2} \\
\nu_{H_2} &= -\nu_{k_3} + \nu_{k_4} \\
\nu_{H\cdot} &= \nu_{k_3} - \nu_{k_4} - \nu_{k_5} \\
\nu_{HBr} &= \nu_{k_3} - \nu_{k_4} + \nu_{k_5}
\end{aligned}$$

- At room temperature, k_1 is almost equal to 0, but k_1' is not.

Electrolysis I

- Chemical reactions can also be influenced by applying an electrical field. In a solution, molecules are often ionized, i.e., they either lack or have a surplus of negatively charged electrons. ***Ions*** are thus either positively or negatively charged.
- For example, ***salts*** dissolve in aqueous solutions into individual ions.

Positively charged ion *Negatively charged ion*

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

- Since ions are electrically charged, they can be physically separated from each other by applying an electrical field.

Electrolysis II

- In water, there exists an equilibrium between water molecules, and positively and negatively charged ***ions***.

$$2H_2O \rightleftharpoons H_3O^+ + HO^-$$

- If the ***pH value*** of the water is changed by adding a drop of either an acid, such as ***sulphuric acid***, H_2SO_4, or alkali, such as ***potash lye***, KOH, the number of ions in the solution will be drastically enhanced.
- If two metal plates are dipped into the water and an electric field is created by connecting a voltage source to these two plates, the negatively charged ions will migrate towards the ***anode***, whereas the positively charged ions will migrate towards the ***cathode***.

Electrolysis III

- In the ***electrolysis of water***, the following reactions take place:

$$4H_3O^+ + 4e^- \xrightarrow{k_1} 2H_2 + 4H_2O$$
$$4OH^- \xrightarrow{k_1} 2H_2O + O_2 + 4e^-$$
$$2H_2O \xrightarrow{k_2} H_3O^+ + OH^-$$
$$H_3O^+ + OH^- \xrightarrow{k_3} 2H_2O$$

- Reactions k_2 and k_3 are fast equilibrium reactions.
- The surplus electrons from the second reaction k_1 wander from the ***anode*** through the voltage source back to the ***cathode***, where they are recycled in the first reaction.

Electrolysis IV

- It may be interesting to look at the reaction rate equations.
- Since the "meeting" of the 4 ions at the electrode is not stochastic, but driven by the electric field, the corresponding reaction rate does not go with the fourth power of the molar mass of these ions.
- A certain minimal voltage, u_0, is needed to polarize the ions, before they start migrating to the electrodes.
- Thus, we can write:

$$\nu_{k1a} = k_1 \cdot (u - u_0) \cdot n_{H_3O^+}$$

Electrolysis V

- Thus, the set of reaction rate equations can be written as:

$$\begin{aligned}
\nu_{H_3O^+} &= -4k_1(u-u_0)n_{H_3O^+} + k_2 \cdot (n_{H_2O})^2/V - k_3 \cdot n_{H_3O^+} \cdot n_{OH^-}/V \\
\nu_{OH^-} &= -4k_1(u-u_0)n_{OH^-} + k_2 \cdot (n_{H_2O})^2/V - k_3 \cdot n_{H_3O^+} \cdot n_{OH^-}/V \\
\nu_{H_2O} &= 4k_1(u-u_0)n_{H_3O^+} + 2k_1(u-u_0)n_{OH^-} - 2k_2 \cdot (n_{H_2O})^2/V \\
&\quad + 2k_3 \cdot n_{H_3O^+} \cdot n_{OH^-}/V \\
\nu_{H_2} &= 2k_1(u-u_0)n_{H_3O^+} \\
\nu_{O_2} &= k_1(u-u_0)n_{OH^-}
\end{aligned}$$

Electrolysis VI

- This can be rewritten as:

$$\begin{aligned}
\nu_{H_3O^+} &= -4\nu_{k1a} + \nu_{k2} - \nu_{k3} \\
\nu_{OH^-} &= -4\nu_{k1b} + \nu_{k2} - \nu_{k3} \\
\nu_{H_2O} &= 4\nu_{k1a} + 2\nu_{k1b} - 2\nu_{k2} + 2\nu_{k3} \\
\nu_{H_2} &= 2\nu_{k1a} \\
\nu_{O_2} &= \nu_{k1b}
\end{aligned}$$

$$\begin{aligned}
\nu_{k1a} &= k_1(u-u_0)n_{H_3O^+} \\
\nu_{k1b} &= k_1(u-u_0)n_{OH^-} \\
\nu_{k2} &= k_2 \cdot (n_{H_2O})^2/V \\
\nu_{k3} &= k_3 \cdot n_{H_3O^+} \cdot n_{OH^-}/V
\end{aligned}$$

- Since the two ions are always created in pairs:

$$n_{H_3O^+} = n_{OH^-} \quad \Rightarrow \quad \nu_{k1a} = \nu_{k1b}$$

Electrolysis VII

- Thus:

$$\begin{aligned} \nu_{H_3O^+} &= -4\nu_{k1} + \nu_{k2} - \nu_{k3} \\ \nu_{OH^-} &= -4\nu_{k1} + \nu_{k2} - \nu_{k3} \\ \nu_{H_2O} &= 6\nu_{k1} - 2\nu_{k2} + 2\nu_{k3} \\ \nu_{H_2} &= 2\nu_{k1} \\ \nu_{O_2} &= \nu_{k1} \end{aligned}$$

$$\begin{aligned} \nu_{k1} &= k_1 \cdot (u - u_0) \cdot n_{H_3O^+} \\ \nu_{k2} &= k_2 \cdot (n_{H_2O})^2/V \\ \nu_{k3} &= k_3 \cdot n_{H_3O^+} \cdot n_{OH^-}/V \end{aligned}$$

$$\Rightarrow \begin{bmatrix} \nu_{H_3O^+} \\ \nu_{OH^-} \\ \nu_{H_2O} \\ \nu_{H_2} \\ \nu_{O_2} \end{bmatrix} = \underbrace{\begin{bmatrix} -4 & +1 & -1 \\ -4 & +1 & -1 \\ +6 & -1 & +2 \\ +2 & 0 & 0 \\ +1 & 0 & 0 \end{bmatrix}}_{N\text{-matrix}} \cdot \begin{bmatrix} \nu_{k1} \\ \nu_{k2} \\ \nu_{k3} \end{bmatrix}$$

Electrolysis VIII

- We need to ask ourselves, what happens with the external electrical power that is introduced into the system.
- The power supply "sees" a resistor that consumes the power ***u·i***.
- Resistors usually generate heat. In fact, there really is no choice in the matter. The power that is introduced has to be accounted for in the Gibbs equation, which is used to determine the ***entropy flow***.
- Thus, the resistor indeed heats up the system.

$$T \cdot \dot{S}_{k1} = p \cdot q_{k1} + u \cdot i - \mu \cdot \nu_{k1}$$

Stirred Reactors I

- Until now, we always assumed that the reactants are ideally mixed.
- In gas reactions, this assumption holds true quite well. In liquid reactions, the same cannot be said. The more highly viscous a liquid is, the less likely it is homogeneous.
- We may need to stir, in order to mix the reactants well.
- Nothing really happens to the reaction equations, since these were created under the assumption of an ideal mixture.
- Yet, the stirring causes viscous friction, which creates heat.

Stirred Reactors II

- The entire ***power of stirring***, except for what is stored in the mechanical inertia of the paddle gets converted to heat.
- It is most convenient to add this entropy at the component side, more precisely at the ***0-junctions*** next to the ***CF-fields***, and simply split it among the reactants in proportion to their relative mass.

References

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