**Chemistry IB – Reaction Rates & Thermodynamics Notes**

- **Rates of Reaction:**

 - Collision Theory:

 - **rate**—measures the speed of change within a given interval of

 time

 - usually expressed as amount of reactant changing per unit

 time

- **Collision Theory**—*atoms, ions and molecules can react to*

 *form products when they collide, provided that the particles*

 *have enough kinetic energy*



- **activation energy**—the minimum amount of energy that

 particles must have in order to react



- **activated complex**—the arrangement of atoms at the peak of

 the activation energy barrier

- the activated complex is sometimes also called the

 **TRANSITION STATE**

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 - **Factors Affecting Reaction Rate:**

 1) **Temperature**—usually raising the temperature INCREASES

 the rate and decreasing temperature usually DECREASES

 the rate ***{NOT true for ENZYMES (biological catalysts)}***

 

 2) **Concentration**—the HIGHER the concentration (more

 particles) the FASTER the reaction rate

3) **Particle Size**—the SMALLER the particles, the MORE

 SURFACE AREA is available to react, so the FASTER the

 reaction rate

  

4) **Catalysts**—speeds up a reaction WITHOUT being used up

in the reaction by LOWERING the activation energy

 - enzymes—biological catalysts

 - need specific temperatures to function properly

 - inhibitor—a substance that interferes with the action

 of a catalyst



This type of inhibition is called COMPETITIVE inhibition because the inhibitor binds to the ACTIVE SITE (same as the substrate so it COMPETES for the binding site!!)



This type of inhibition is called NON COMPETITIVE inhibition because the inhibitor binds to a DIFFERENT site which CHANGES the ACTIVE SITE (so the substrate CANNOT bind to the binding site!!)

- **Reversible Reactions and Equilibrium**

 - Reversible Reactions:

 - **reversible reaction**—occurs simultaneously in both directions

 - **2 SO2(g) + O2(g) ↔ 2 SO3(g)**

 - at start of reaction, proceeds in forward direction only

 - as more SO3 forms, the concentration increases and it

 starts speeding up in the reverse direction

- eventually the forward and reverse rates are **EQUAL** so

 **CHEMICAL EQUILIBRIUM** is reached



 - Factors Affecting Equilibrium:

 - **Le Chatelier’s principle:** *If a stress is applied to a system in*

 *dynamic equilibrium, the system changes to relieve the stress*

- if equilibrium is disrupted in some way, the system will

 change until a **NEW EQUILIBRIUM** is reached



1) **Concentration**—changing the amount of any reactant or

 product will affect the equilibrium

 **H2CO3(aq) ↔ CO2(aq) + H2O(l)**

 - add more CO2 and the reaction shifts to favor the

 **REVERSE** reaction

- if you remove CO2 the reaction shifts to favor the

 **FORWARD** reaction

2) **Temperature**—increasing the temperature causes the

 equilibrium position to shift in the direction that absorbs

 heat

 **2 SO2(g) + O2(g) ↔ 2 SO3(g) + heat**

 - add heat and the reaction shifts to favor the **REVERSE**

 - take heat away and the reaction shifts to favor the

 **FORWARD**

 3) **Pressure**—changing pressure on a system ONLY affects an

 equilibrium that has a UNEQUAL number of moles of

 gaseous reactants and products

 **N2(g) + 3 H2(g) ↔ 2 NH3(g)**

 - increase pressure and the reaction shifts to favor the

 **FORWARD** because the products have ***less total***

 ***particles***

 - decrease pressure and the reaction shifts to favor the

 **REVERSE** (***more particles*** to compensate for less

 pressure)

 - **Equilibrium Constants:**

 - **Equilibrium Constant**—a ratio of the product concentrations

 to the reactant concentrations at equilibrium

 - ***a*A + *b*B ↔ *c*C + *d*D**

  **[C]c [D]d**

 **Keq = ------------**

 **[A]a [B]b**

 - if Keq < 1 then reactants are favored at equilibrium

 - if Keq > 1 then products are favored at equilibrium

 - *A liter of a gas mixture of dinitrogen tetroxide and nitrogen*

 *dioxide are at equilibrium at 10oC. The mixture contains*

 *0.0045 moles N2O4 and 0.030 moles NO2. Calculate the*

 *equilibrium constant for this mixture of gases.*

**N2O4(g) < -- > 2 NO2(g)**

 0.0045 M 0.030 M

$$K\_{EQ}= \frac{\left[NO\_{2}\right]^{2}}{[N\_{2}O\_{4}]}= \frac{\left(0.030\right)^{2}}{\left(0.0045\right)} = \frac{0.00090}{0.0045} =0.20$$

* *A closed system initially containing 0.00100 M H2 and 0.00200 M I2 at 448oC is allowed to reach equilibrium and at equilibrium the [HI] is 0.00187 M. Calculate the value of Keq at 448oC.*

|  |  |
| --- | --- |
|  | **H2(g)  + I2(g) < -- > 2 HI(g)** |
|  **I = Initial** | **0.00100 M** | **0.00200 M** | **0** |
|  **C = Change** | **- x** | **- x** | **+ 2x** |
| **E = Equilibrium** | **0.00100 – x M** | **0.00200 – x M**  | **0 + 2x = 2x = 0.00187M** |

 **So since we know that 2x = 0.00187 🡪 x = 0.000935**

 **So that means the equilibrium [H2] = 0.00100 – 0.000935 = 0.000065 M**

 **And the equilibrium [I2] = 0.00200 – 0.000935 = 0.001065 M**

|  |  |
| --- | --- |
|  | **H2(g)  + I2(g) < -- > 2 HI(g)** |
|  **I = Initial** | **0.00100 M** | **0.00200 M** | **0** |
|  **C = Change** | **- x** | **- x** | **+ 2x** |
| **E = Equilibrium** | **0.00100 – x M = 0.000065 M** | **0.00200 – x M = 0.001065 M**  | **0 + 2x = 2x = 0.00187M** |

**So …** $K\_{EQ}= \frac{\left[HI\right]^{2}}{\left[H\_{2}\right][I\_{2}]}= \frac{\left(0.00187\right)^{2}}{(0.000065)(0.001065)}=51$

* *The following reversible reaction at equilibrium has a Keq of 1.67 x 10-7* *at 800*oC. *What are the concentrations at equilibrium if you react 0.0250 M H2S??*

***2 H2S(g) < -- > 2 H2(g) + S2(g)***

|  |  |
| --- | --- |
|  | **2 H2S(g)  < -- > 2 H2(g) + S2(g)** |
|  **I = Initial** | **0.0250 M** | **0** | **0** |
|  **C = Change** | **- 2x** | **+ 2x** | **+ x** |
| **E = Equilibrium** | **0.0250 – 2x ≈ 0.0250M** | **2x** | **x** |

***So if we plug these EQUILIBRIUM values into our formula for KEQ we will end up with an x3 term, an x2 term, an x and a constant value and that is very difficult to solve BUT since KEQ is very small in comparison to the initial [H2S] we can IGNORE THE “– X” term (even – 2x)!! and that will simplify the calculation a lot!***

$$K\_{EQ}= \frac{\left[H\_{2}\right]^{2}[S\_{2}]}{\left[H\_{2}S\right]^{2}}= \frac{\left(2x\right)^{2}(x)}{\left(0.0250\right)^{2}}= \frac{4x^{3}}{0.000625}=1.67 x 10^{-7}$$

$$4x^{3}=1.04 x 10^{-10}$$

$$x^{3}=2.60 x 10^{-11}\rightarrow x= \sqrt[3]{2.60 x 10^{-11} } $$

$$x=2.96 x 10^{-4}M\rightarrow \left[S\_{2}\right]$$

$$\left[H\_{2}\right]=2x=2\left(2.96 x 10^{-4}\right)=5.92 x 10^{-4} M$$

- **Determining Whether A Reaction Will Occur:**

 - Free Energy And Spontaneous Reactions:

 - **Free Energy**—the energy that is available to do work

 - not all energy that is available can be used efficiently

 - some energy is always lost

 - **Spontaneous Reactions**—reactions that naturally favor the

 formation of the products at the specified conditions

- **Nonspontaneous Reactions**—do NOT favor the formation of

 the products at the specified conditions

- whether a reaction is spontaneous or not says ***NOTHING***

 about the rate of the reaction!!

 - **Entropy:**

 - **entropy (S)**—the amount of disorder in a system

 - both enthalpy (H) and entropy (S) determine whether or not a

 reaction is spontaneous

 - processes tend to favor higher entropy (more disorder)



 - Factors that increase Entropy:

 1) solid 🡪 liquid 🡪 gas

 2) dividing into smaller parts

 3) total number of product particles > reactants

 4) temperature increases

 - you can’t measure entropy directly, only the CHANGE in

 entropy (ΔS)

 - **Heat, Entropy and Free Energy:**

 - **Gibbs Free Energy Change (ΔG)**—the maximum amount of

 energy that may be coupled to another process to do useful

 work

- **ΔG = ΔH - T ΔS**

- if ΔG = (-) then the reaction is spontaneous

- if ΔG = (+) then the reaction is nonspontaneous

|  |
| --- |
| **Relating Enthalpy, Entropy & Free Energy** |
| **∆H** | **∆S** | **∆G** |
| **(-) exothermic** | **(+) INCREASE disorder** | **ALWAYS (-) (spontaneous)** |
| **(-) exothermic** | **(-) DECREASE disorder** | **(-) at lower T** |
| **(+) endothermic** | **(+) INCREASE disorder** | **(-) at higher T** |
| **(+) endothermic** | **(-) DECREASE disorder** | **ALWAYS (+) (nonspontaneous)** |

 - *Determine whether the reaction 2 Na(s) + Cl2(g) 🡪 2NaCl(s) is*

 *spontaneous at the standard states.*

*This could be solved a number of ways depending on the information that is given!*

*GIVEN: ΔH: Na(s) = 0 kJ/mol Cl2(g) = 0 kJ/mol NaCl(s) = - 411.12 kJ/mol*

 *ΔS: Na(s) = 51.21 J/molK Cl2(g) = 223.08 J/molK NaCl(s) = 72.11 J/molK*

$$∆H\_{f}^{0}= \sum\_{}^{}∆H\_{f PRODUCTS}^{0}- \sum\_{}^{}∆H\_{f REACTANTS}^{0}$$

$$∆H\_{f}^{0}=\left[\left(2 mol NaCl\right)\left(-411.12\frac{kJ}{mol}\right)\right]-\left[\left(2 mol Na\right)\left(0\frac{kJ}{mol}\right)+\left(1 mol Cl\_{2}\right)\left(0\frac{kJ}{mol}\right)\right]$$

$$∆H\_{f}^{0}=\left[-822.24 kJ\right]-\left[0 kJ+0 kJ\right]= -822.24 kJ$$

And

$$ $$

$$∆S\_{f}^{0}= \sum\_{}^{}∆S\_{f PRODUCTS}^{0}- \sum\_{}^{}∆S\_{f REACTANTS}^{0}$$

$$∆S\_{f}^{0}=\left[\left(2 mol NaCl\right)\left(72.11\frac{J}{molK}\right)\right]-\left[\left(2 mol Na\right)\left(51.21\frac{J}{molK}\right)+\left(1 mol Cl\_{2}\right)\left(223.08\frac{J}{molK}\right)\right]$$

$$∆S\_{f}^{0}=\left[144.22\frac{J}{K}\right]-\left[102.42\frac{J}{K}+223.08\frac{J}{K}\right]$$

$$= 144.22\frac{J}{K} - 325.50\frac{J}{K} = -181.28\frac{J}{K}$$

*So if ΔH = -822.24 kJ and ΔS = -181.28 J/K then…*

$$∆G= ∆H-T∆S$$

$$∆G=\left(-822.24 kJ\right)-\left(298 K\right)\left(-0.18128\frac{kJ}{K}\right) = -822.24 kJ+54.02 kJ= -768.22 kJ$$

*GIVEN:* *ΔG: Na(s) = 0 kJ/mol Cl2(g) = 0 kJ/mol NaCl(s) = - 384.04 kJ/mol*

$$∆G\_{f}^{0}= \sum\_{}^{}∆G\_{f PRODUCTS}^{0}- \sum\_{}^{}∆G\_{f REACTANTS}^{0}$$

$$∆G\_{f}^{0}=\left[\left(2 mol NaCl\right)\left(-384.04\frac{kJ}{mol}\right)\right]-\left[\left(2 mol Na\right)\left(0\frac{kJ}{mol}\right)+\left(1 mol Cl\_{2}\right)\left(0\frac{kJ}{mol}\right)\right]$$

$$∆G\_{f}^{0}=\left[-768.08 kJ\right]-\left[0 kJ+0 kJ\right]= -768.08 kJ$$

- **The Progress Of Chemical Reactions:**

 - Rate Laws:

 - the rate of a reaction depends in part on the concentrations of

 the reactants

- A 🡪 B

- rate = ΔA / Δt or:

- Rate = k [A]

- k = the specific rate constant



- first order reaction—the rate is directly proportional to only

 ONE reactant’s concentration



- aA + bB 🡪 cC + dD

- rate = k [A]a [B]b

- add the exponents a and b to get the overall order of a more

 complex reaction (order = a + b)



- *The rate law for the one step reaction aA 🡪 B is of the form*

 *Rate = k[A]a. From the data in the following table, find the*

 *kinetic order of the reaction with respect to A and the overall*

 *order of the reaction*

Initial [A] (mol/L) Initial Rate (mol/L•sec)

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 0.050 3.0 x 10-4

 0.100 1.2 x 10-3

 0.200 4.8 x 10-3

*So in order to solve here, we are going to work with the RATIO of the rate laws for different trials and use algebra to solve for the exponent (a)*

*I will focus on a ratio of RATE3 and RATE2 because it is a little easier to see what is happening with the numbers.*

$$\frac{RATE\_{3}}{RATE\_{2}} = \frac{k\left[A\right]\_{3}^{a}}{k\left[A\right]\_{2}^{a}} = \frac{\left(k\right)\left(0.200\right)^{a}}{\left(k\right)\left(0.100\right)^{a}} =\left(\frac{.200}{.100}\right)^{a}=2^{a}= \frac{4.8 x 10^{-3}}{1.2 x 10^{-3}}$$

**So …** $2^{a}=4\rightarrow a=2 \rightarrow RATE=k\left[A\right]^{2} \left(second order\right)‼$