

# Chapter 5 Part 1

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# Equilibrium

## Dynamic Equilibrium

- An equilibrium where forward and reverse reactions are occurring at the same rate such that there is no overall change in the chemical identity of the system.

## Static Equilibrium

- An equilibrium where nothing is happening such as a rock once its rolled to the bottom of a hill

# Dynamic vs. Static Equilibrium

Describe the following situations as either static or dynamic equilibria.

- A. The level of water in a fish tank, as the water is constantly passing through the filter.
- B. A rocking chair that has stopped rocking.
- C. Acetic acid, a weak acid, that is ionized only to the extent of about 2% in aqueous solution.
- D. A bank account that maintains an average monthly balance of \$1000 despite numerous withdrawals and deposits.

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- B. A rocking chair that has stopped rocking. **Static**
- C. Acetic acid, a weak acid, that is ionized only to the extent of about 2% in aqueous solution. **Dynamic**
- D. A bank account that maintains an average monthly balance of \$1000 despite numerous withdrawals and deposits. **Dynamic**

# Extent of a reaction

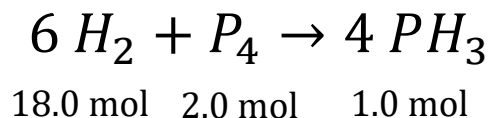
- We can define the extent of a reaction as,  $\xi$ , where

$$\xi = \frac{n_i - n_{i,0}}{v_i}$$

- $n_{i,0}$  is the number of moles of the  $i$ th chemical species at time  $t = 0$
- $n_i$  is the number of moles of the  $i$ th chemical species at some time  $t$
- $v_i$  is the stoichiometric coefficient of the  $i$ th chemical species in the reaction
  - $v_i$  is positive for products and negative for reactants
- The possible numerical values of  $\xi$  may vary depending on the initial conditions and the reaction stoichiometry, but at any point in the reaction  $\xi$  will have the same value no matter which species is used

# Extent of Reaction

The following reaction is set up with the initial amounts of each substance listed below:



In each of the following scenarios, show that no matter which species is used to determine  $\xi$ , the value for  $\xi$  is the same.

- A. All the  $P_4$  reacts to form products
- B. All the  $PH_3$  reacts to form reactants

# Extent of Reaction

$$\xi = \frac{6.0 \text{ mol} - 18.0 \text{ mol}}{-6} = 2.0 \text{ mol using H}_2$$

$$\xi = \frac{0.0 \text{ mol} - 2.0 \text{ mol}}{-1} = 2.0 \text{ mol using P}_4$$

$$\xi = \frac{9.0 \text{ mol} - 1.0 \text{ mol}}{+4} = 2.0 \text{ mol using PH}_3$$

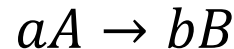
$$\xi = \frac{19.5 \text{ mol} - 18.0 \text{ mol}}{-6} = -0.25 \text{ mol using H}_2$$

$$\xi = \frac{2.25 \text{ mol} - 2.0 \text{ mol}}{-1} = -0.25 \text{ mol using P}_4$$

$$\xi = \frac{0.0 \text{ mol} - 1.0 \text{ mol}}{+4} = -0.25 \text{ mol using PH}_3$$

# Equilibrium

- For a gas phase reaction



we can define the reaction coefficient,  $Q$ , as

$$Q = \frac{\prod_{\text{i products}} \left( \frac{p_i}{p^\circ} \right)^{|v_i|}}{\prod_{\text{j reactants}} \left( \frac{p_j}{p^\circ} \right)^{|v_j|}}$$

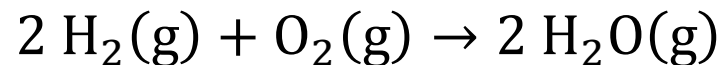
- Further, we can use the reaction coefficient to relate  $\Delta G$  in nonstandard conditions to  $\Delta G^\circ$  ( $\Delta G$  under standard conditions)

$$\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^\circ + RT \ln Q$$



## Using $\Delta G$ and $Q$

For molar amounts, the standard Gibbs free energy of reactions for the following reaction at 25°C is  $-457.14$  kJ:



In a system where  $p_{\text{H}_2} = 0.775$  bar,  $p_{\text{O}_2} = 2.88$  bar, and  $p_{\text{H}_2\text{O}} = 0.556$  bar, determine  $\Delta_{\text{rxn}} G$  in kJ. Use 1.00 bar as the standard pressure.

## Using $\Delta G$ and $Q$

$$Q = \frac{\left(\frac{p_{H_2O}}{1.00 \text{ bar}}\right)^2}{\left(\frac{p_{H_2}}{1.00 \text{ bar}}\right)^2 \left(\frac{p_{O_2}}{1.00 \text{ bar}}\right)} = \frac{\left(\frac{0.556 \text{ bar}}{1.00 \text{ bar}}\right)^2}{\left(\frac{0.775 \text{ bar}}{1.00 \text{ bar}}\right)^2 \left(\frac{2.88 \text{ bar}}{1.00 \text{ bar}}\right)} = 0.179$$

$$\begin{aligned}\Delta_{\text{rxn}} G &= \Delta_{\text{rxn}} G^\circ + RT \ln Q \\ &= -457.14 \text{ kJ} + \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) (298.15 \text{ K}) \ln(0.179) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -461 \text{ kJ}\end{aligned}$$

# $\Delta G$ and Equilibrium

- When  $\Delta G = 0$ , the system is said to be at equilibrium
- Accordingly, at equilibrium, the equation below

$$\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^{\circ} + RT \ln Q$$

becomes

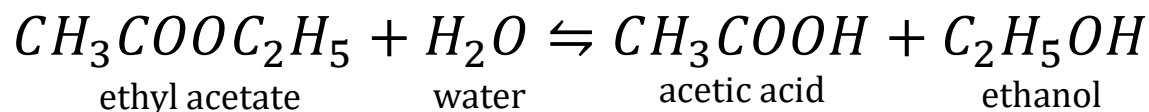
$$\Delta_{\text{rxn}} G^{\circ} = -RT \ln K$$

where  $K$  is the equilibrium constant.

- Large values of  $K$  suggest more products than reactants at equilibrium
- Small values of  $K$  suggest more reactants than products at equilibrium

# ICE tables: A familiar hope

For the gas-phase reaction

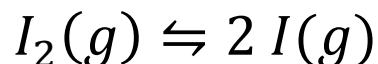


The equilibrium constant is 4.0 at 120°C.

- A. If you start with 1.00 bar of both ethyl acetate and water in a 10.0-L container, what is the extent of the reaction at equilibrium
- B. What is  $\Delta_{rxn}G$  at equilibrium?
- C. What is  $\Delta_{rxn}G^\circ$  at equilibrium?

# The ICE Table strikes back

Molecular iodine dissociates into atomic iodine at relatively moderate temperatures. At 1000 K, for a 1.00-L system that has  $6.00 \times 10^{-3}$  moles of  $I_2$  present initially, the final equilibrium pressure is 0.750 atm. Determine the equilibrium amounts of  $I_2$  and atomic I, calculate the equilibrium constant, and determine  $\xi$  if the relevant equilibrium is



Assume ideal gas behavior under these conditions. Use atm as the standard unit for pressure.