Chapter 5 Part 1

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Equilbrium

Dynamic Equilibrium	Static 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.	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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Extent of a reaction

- We can define the extent of a reaction as, ξ, where

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

  - $n_{i,0}$ is the number of moles of the ith chemical species at time $t = 0$
  - n_i is the number of moles of the ith chemical species at some time t
  - v_i is the stoichiometric coefficient of the ith chemical species in the reaction
    - v_i is positive for products and negative for reactants
- The possible numerical values of ξ may vary depending on the initial conditions and the reaction stoichiometry, but at any point in the reaction ξ 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:

$$6\,H_2 + P_4 \rightarrow 4\,PH_3$$

18.0 mol 2.0 mol 1.0 mol

In each of the following scenarios, show that no matter which species is used to determine ξ, the value for ξ 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

$$aA \rightarrow bB$$

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 ΔG in nonstandard conditions to ΔG° (ΔG under standard conditions)

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

Using ΔG and Q

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

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

In a system where $p_{H_2} = 0.775$ bar, $p_{O_2} = 2.88$ bar, and $p_{H_2O} = 0.556$ bar, determine $\Delta_{rxn}G$ in kJ. Use 1.00 bar as the standard pressure.

Using ΔG and Q

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

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

$$= -457.14\ \mathrm{kJ} + \left(8.314\,\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right)(298.15\ \mathrm{K})\ln(0.179)\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right)$$

$$= -461\ kJ$$

ΔG and Equilibrium

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

  $$\Delta_{\mathrm{rxn}} G = \Delta_{rxn} G° + RT \ln Q$$

  becomes

  $$\Delta_{rxn} G° = -RT \ln K$$

  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

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O} \leftrightharpoons \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

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 $\Delta_{rxn}G°$ 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 6.00×10^{-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 ξ if the relevant equilibrium is

$$I_2(g) \leftrightharpoons 2\, I(g)$$

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