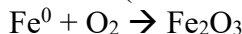


## Lecture 4: Thermodynamics

The following reaction is spontaneous (occurs without external energy input):



1. Why does this reaction occur? Will it also occur as  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + \text{O}_2$ ?
2. Answer: the energy change associated with the forward reaction is thermodynamically favorable

Thermodynamics – the study of energy transformation from one form to another

Energy (E) – the capacity to do work or produce heat

Work (w) – transfer of energy by mechanical interaction; energy transferred to the motion of objects (e.g. volume change of a gas)

Heat (q) – transfer of energy by thermal interaction; energy transferred to the motion of atoms and molecules

**1st Law of Thermodynamics:** Change in the internal energy of a closed system:  $\Delta E = dq - dw$   
dq = heat absorbed by a system from its surroundings; (-) heat lost from a system to its surroundings  
dw = work done by the system on its surroundings

The energy of the universe never changes (Law of Conservation of Energy)! Energy can be neither created or destroyed, only transformed. So a change in the energy of a system requires energy exchange between the system (user defined) and its surroundings (the rest of the universe).

Now we skip a lot of derivation and get straight to the point.

We are especially interested in *Gibbs Free Energy* – the amount of energy in a system that is available to do work (at constant temperature and pressure). We start at standard state ( $T = 25^\circ\text{C}$  and  $P = 1 \text{ atm}$ ).

For a given system:  $G = H - TS$

G = Gibbs free energy ( $\text{kJ mol}^{-1}$ )

H = Enthalpy ( $\text{kJ mol}^{-1}$ )

T = temperature (units Kelvin)

S = Entropy ( $\text{J mol}^{-1} \text{K}^{-1}$ )

### What is enthalpy?

Enthalpy (H) – describes the loss or gain of heat during a chemical reaction ( $\text{kJ/mol}$ )

The enthalpy change for a reaction ( $\Delta H_{\text{rxn}}^0$ ) is equal to the sum of the enthalpy of formation of all the products minus the sum of the enthalpy of formation of all the reactants:

$$\Delta H_{\text{rxn}}^0 = \sum (n_p \times \Delta H_{\text{f,p}}^0) - \sum (n_r \times \Delta H_{\text{f,r}}^0)$$

n – moles of a constituent; based on the stoichiometric chemical reaction

$\Delta H_f^\circ$  – standard enthalpy of formation; the amount of heat lost or gained when one mole of a compound is formed from its individual elements; values are reported in tables (see Stumm and Morgan pdf)

Since we cannot measure enthalpy directly, we measure the change in enthalpy from a baseline condition of an element in its most stable form at standard state

*Exothermic reaction* – releases heat ( $H < 0$ ); *Endothermic reaction* – absorbs heat ( $H > 0$ )

### What is entropy?

Entropy (S) – a measure of molecular randomness (or disorder); values are reported in tables (also see Stumm and Morgan pdf)

**2nd Law of Thermodynamics** – any spontaneous process increases the disorder of the universe

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

Why? The probability of an ordered arrangement is much smaller than the probability of a disordered arrangement.

$$\Delta S^\circ_{\text{reaction}} = \sum (n_p \times S^\circ_{\text{products}}) - \sum (n_r \times S^\circ_{\text{reactants}})$$

We are interested in the change in Gibbs free energy in a system associated with a chemical reaction *at standard state* (represented by the superscript 0):

$$\Delta G^\circ_{\text{rxn}} = (\Delta G^\circ_{f,p} - \Delta G^\circ_{f,r}) = (\Delta H^\circ_{f,p} - \Delta H^\circ_{f,r}) - T(S^\circ_p - S^\circ_r)$$
$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$$

### Why do we care?

All systems tend towards lowest possible energy (diagram)

$\Delta G < 0$  (a decrease in energy of the system!) indicates that the reaction is spontaneous.

$\Delta G > 0$  indicates that a reaction is not spontaneous; requires input of energy to proceed

$\Delta G = 0$  indicates that a reaction is at *chemical equilibrium* and the quantities of products and reactants do not change because the forward and backward chemical reaction occurs at the same rate

Nature is always trying to reach chemical equilibrium, but we depend on it not getting there.

Example problem: What is the change in free energy ( $\Delta G^\circ_{\text{rxn}}$ ) of the reaction  $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$  at standard state?

1. Balance the reaction:  $4 \text{Fe}^0 + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3$
2. Calculate the enthalpy change of the reaction:

$$\Delta H_f^\circ (\text{Fe}) = 0 \text{ kJ/mol}$$

$$\Delta H_f^\circ (\text{O}_2) = 0 \text{ kJ/mol}$$

$$\Delta H_f^\circ (\text{Fe}_2\text{O}_3) = -824.6 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} = (2 \times -825 \text{ kJ/mol}) - (4 \times 0 + 3 \times 0) = -1,650 \text{ kJ/mol}$$

The reaction releases heat, which is why this chemical reaction is used in hand warmers. A semi-permeable membrane allows oxygen to slowly diffuse into the pouch and oxidize Fe. The pouch also includes water to mediate the chemical reaction, activated charcoal to hold the water and distribute the heat, and vermiculite to insulate the reaction.

3. Calculate the entropy change of the reaction:

$$S^0(\text{Fe}) = 27.3 \text{ J/mol/K}$$

$$S^0(\text{O}_2) = 205 \text{ J/mol/K}$$

$$S^0(\text{Fe}_2\text{O}_3) = 87.4 \text{ J/mol/K}$$

$$\Delta S^0_{\text{rxn}} = S^0_{\text{prod}} - S^0_{\text{react}} = (2 \times 87.4) - (4 \times 27.3 + 3 \times 205) = -549 \text{ J/mol/K} = -0.549 \text{ kJ/mol/K}$$

4. Calculate the Gibbs free energy of reaction:

$$\Delta G^0_{\text{rxn}} = \Delta H^0_{\text{rxn}} - T\Delta S^0_{\text{rxn}}$$

$$= (-1,650 \text{ kJ/mol}) - (298 \text{ K}) \times (-0.549 \text{ kJ/mol/K}) = -1650 + 163 = -1,487 \text{ kJ/mol}$$

- The energy change in the system is negative, thus energy is released from the system to its surroundings
- Entropy of the system decreases (unfavorable), but this is overcome by the heat released

$\Delta H > T\Delta S$ : enthalpy driven reaction

$\Delta H < T\Delta S$ : entropy driven reaction

**Chemical Potential – or how can I use this information in a real system that does not abide by stoichiometry or standard state conditions?**

Chemical potential is used to practically apply thermodynamics to chemical reactions:

$$\mu_i = (dG_i/dn_i)_{T,P}$$

$$\text{aka } dG_i = dn_i \times \mu_i$$

$G$  is an *extensive property*, i.e. depends on the amount of material in the system ( $G = \sum n_i \mu_i$ )

$\mu$  is an *intensive property*, i.e. does not depend on the amount of material in the system

- Defined as the amount per mole that  $G$  changes with the *addition* of an infinitesimal amount of a particular component (slope of  $G_i$  vs  $n_i$ )
- Also referred to as partial molar Gibbs free energy

In a one-component system, the chemical potential of a component  $i$  is equal to:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

OR 
$$\mu_i = \mu_i^0 + RT \ln f_i \quad (\text{for gases})$$

$\mu_i^0$  = the chemical potential of  $i$  at standard state

$R$  = the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  = temperature (K)

$a_i$  = activity of component  $i$  in the system (solutes/solids)

$f_i$  = fugacity; the effective pressure of a component  $i$  in the gas phase

## What is activity?

The effective concentration of a component  $i$  in liquid or solid phase

$$a_i = \gamma_i \times m_i$$

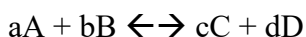
$\gamma_i$  – activity coefficient; controlled by ionic strength (next time)

$m_i$  – concentration in molal units (moles per mass of solution)

In an infinitely dilute ideal solution,  $\gamma_i \rightarrow 1$ , so  $a_i \rightarrow m_i$

In reality, activity is usually lower than molality due to intermolecular interactions.

What does this matter for chemical reactions?



(lower case letters are coefficients; upper case letters are the species)

$$\mu_A = \mu_A^0 + RT \ln a_A$$

$$\mu_B = \mu_B^0 + RT \ln a_B$$

$$\mu_C = \mu_C^0 + RT \ln a_C$$

$$\mu_D = \mu_D^0 + RT \ln a_D$$

$$\begin{aligned} \Delta G_{\text{rxn}} &= G_{\text{products}} - G_{\text{reactants}} = [c\mu_C + d\mu_D] - [a\mu_A + b\mu_B] \\ &= [c(\mu_C^0 + RT \ln a_C) + d(\mu_D^0 + RT \ln a_D)] - [a(\mu_A^0 + RT \ln a_A) + b(\mu_B^0 + RT \ln a_B)] \\ &= c\mu_C^0 + cRT \ln(a_C) + d\mu_D^0 + dRT \ln(a_D) - a\mu_A^0 - aRT \ln(a_A) - b\mu_B^0 - bRT \ln(a_B) \end{aligned}$$

Let's simplify! Condense standard state chemical potentials into one term:

$$\Delta G_{\text{rxn}}^0 = G_{\text{products}}^0 - G_{\text{reactants}}^0 = (c\mu_C^0 + d\mu_D^0) - (a\mu_A^0 + b\mu_B^0) \quad (\text{standard conditions})$$

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

The change in free energy of a reaction is equal to the change in free energy of the reaction at standard state plus the ratio of the activities of the products to the activities of the reactants

\*\*the thermodynamic favorability of a reaction also depends on the chemistry of your system

## Equilibrium Constant

At equilibrium,  $\Delta G_{\text{rxn}} = 0$ , thus:

$$\begin{aligned} -\Delta G_{\text{rxn}}^0 &= RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right) \\ e^{\left( -\frac{\Delta G_{\text{rxn}}^0}{RT} \right)} &= \frac{a_C^c a_D^d}{a_A^a a_B^b} = K_{eq} \end{aligned}$$

$$\ln(K_{eq}) = -\frac{\Delta G_{\text{rxn}}^0}{RT}$$

**The equilibrium constant ( $K_{eq}$ ) for a reaction is equal to the ratio of products to reactants at equilibrium AND can be calculated from  $\Delta G^\circ_{rxn}$ .**

But  $K_{eq}$  varies as a function of temperature (within  $\sim 20$  deg C of 25 deg C).

We use the van't Hoff equation to calculate how  $K_{eq}$  changes as a function of T, using a known  $K_{eq}$  at a known T

- $\Delta H^\circ$  and  $\Delta S^\circ$  remain constant over the range of temperatures we examine

$$\ln(K_{T_2}) - \ln(K_{T_1}) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Example: Temperature dependence of calcite precipitation:  $\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{H}^+$   
 What is the equilibrium constant for calcite precipitate at 35°C? Does an increase in temperature favor calcite precipitation ( $K_{eq}$  increases) or calcite dissolution ( $K_{eq}$  decreases)?

Solving for  $K_{T_2}$ . What values do we need?

$K_{T_1}$ ,  $\Delta H^\circ$ , R (= 8.314 J mol<sup>-1</sup> K<sup>-1</sup> = 0.008314 kJ mol<sup>-1</sup> K<sup>-1</sup>),  $T_1$  (= 298 K),  $T_2$  (= 308 K)

	$G^\circ_f$ (kJ mol <sup>-1</sup> )	$H^\circ_f$ (kJ mol <sup>-1</sup> )
CaCO <sub>3</sub> (calcite)	-1128.8	-1207.4
H <sup>+</sup>	0	0
HCO <sub>3</sub> <sup>-</sup>	-586.8	-692.0
Ca <sup>2+</sup> <sub>(aq)</sub>	-553.5	-542.8

Calculate  $\Delta H^\circ = \sum H_{f,p}^\circ - \sum H_{f,r}^\circ$

$$\Delta H^\circ = [(-1207.4) + 0] - [(-542.8) + (-692.0)] = 27.43 \text{ kJ/mol}$$

Calculate  $\ln(K_{T_1}) = -\Delta G^\circ_{rxn}/RT$  (standard state)

$$\Delta G^\circ = \sum G_{f,p}^\circ - \sum G_{f,r}^\circ$$

$$\Delta G^\circ = [(-1128.8) + 0] - [(-586.8) + (-553.5)] = 11.5 \text{ kJ/mol}$$

$$\ln(K_{T_1}) = (-11.5)/(0.008314 \times 298) = -4.64 \text{ (unitless)}$$

$$K_{T_1} = e^{-4.64} = 9.66 \times 10^{-3}$$

Now use the van't Hoff equation:

$$\ln(K_{T_2}) = -4.64 + (27.43/0.008314) \times [(1/298) - (1/308)] = -4.64 + 0.359$$

$$\ln(K_{T_2}) = -4.28$$

$$K_{T_2} = e^{-4.28} = 1.38 \times 10^{-2}$$

Solution:

$K_{T_2} > K_{T_1}$ ; an increase in temperature shifts the reaction towards the products (towards calcite precipitation)

Reaction requires heat input ( $\Delta H > 0$ ); reaction goes towards products at increased temperature.

**WHAT WE LEARNED TODAY:**

1. Chemical reactions result in the transfer of energy between a system and its surroundings
2. Reactions occur spontaneously when energy is lost from a system to its surroundings.
3. Gibbs free energy of a reaction at standard state ( $\Delta G^0$ ) can be calculated from changes in enthalpy (heat) and entropy (disorder)
4. The Gibbs free energy of a reaction ( $\Delta G$ ) depends on the activities (or fugacities) of the reaction components, i.e. how far away the system is from equilibrium
5. A system is at equilibrium when the energy of the system is minimized,  $\Delta G_{\text{rxn}} = 0$  and the  $a_{\text{products}}/a_{\text{reactants}} = K_{\text{eq}}$  (the equilibrium constant)

**NEXT TIME:**

What is activity, and how do we know what the activity of a species in solution is?