

2106NSC

Physical & Analytical Chemistry

Thermodynamics 4

Free Energy

Motivation

For practical convenience

- ease of testing the 2nd Law of Thermodynamics
- working with multi-component systems
- working with real (i.e. non-ideal systems)

it is appropriate to introduce some new properties

- Gibbs free energy (G)
- Helmholtz free energy (A)
- fugacity (f)
- chemical potential (μ)
- activity (a)

First, we consider the **free energies**.

Josiah Willard Gibbs

Josiah Willard Gibbs was not paid a salary for the first 9 years of his job at Yale.

Once he had a job offer from Johns Hopkins University in Maryland, Yale began to pay him.

He gained little recognition for his work during his lifetime mainly because of his inability to communicate his ideas so that others could understand the concepts he was discussing.

J Willard Gibbs, 1839-1903

The Gibbs function ... as introduced in the previous lecture

Whether or not a reaction has a tendency to occur under specified conditions depends on the value of ΔS_{total} .

ΔS_{total} is composed of two parts: the entropy change in the reaction vessel
 the extent of dispersal in the surroundings.

Entropy change in the reaction vessel: ΔS_{sys}

Extent of dispersal in the surroundings is the energy dissipated (enthalpy $\Delta H = \Delta Q$) at a

given temperature T : $\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$

Therefore: $\Delta S_{\text{total}} = -\Delta H_{\text{sys}} / T + \Delta S_{\text{sys}}$
 $T \cdot \Delta S_{\text{total}} = -\Delta H_{\text{sys}} + T \cdot \Delta S_{\text{sys}}$

$$-T \cdot \Delta S_{\text{total}} = \Delta H_{\text{sys}} - T \cdot \Delta S_{\text{sys}} = \Delta G \quad \text{Gibbs free energy}$$

A reaction with a tendency to occur naturally has a Gibbs free energy change of $\Delta G < 0$.

The Gibbs free energy

Useful for constant T and p situations.

Definition: $G = H - T \cdot S$

Differential: $dG = dH - d(T \cdot S)$

$$dG = dH - T \cdot dS - S \cdot dT \quad \text{Product rule}$$

at constant temperature: $T = \text{const.} \Rightarrow dT = 0$

$$dG = dH - T \cdot dS - S \cdot 0$$

$$dG = dH - T \cdot dS \quad ; \quad T, p = \text{const.}$$

Free energy available to do useful work

From the definition of entropy, we know that

$$\Delta Q_{\text{rev}} = T \cdot \Delta S$$

Therefore:

$$\Delta G = \Delta H - T \cdot \Delta S = \Delta H - \Delta Q_{\text{rev}}$$

We also know that the maximum work is done when a process is carried out reversibly.

Thus,

$$\Delta G = \Delta H - \Delta Q_{\text{rev}} = \Delta W_{\text{add,max}}$$

is the **maximum additional non-expansion* work** done by a system during a process **at constant temperature**.

*since the free energy G is based on enthalpy H !

Gibbs free energy – entropy of the universe

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

We derived in the last lecture that

$$\Delta H_{\text{system}} = - T \cdot \Delta S_{\text{surroundings}}$$

Therefore:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} - (\Delta H_{\text{system}} / T)$$

$$\Delta S_{\text{universe}} = - (\Delta G_{\text{system}} / T)$$

Gibbs: $\Delta G = \Delta H - T \cdot \Delta S$

$$\Rightarrow (\Delta G / T) = (\Delta H / T) - \Delta S$$

$$\Rightarrow -(\Delta G / T) = \Delta S - (\Delta H / T)$$

For a reversible or equilibrium process:

$$\Delta S_{\text{universe}} = 0 \Rightarrow \Delta G = 0$$

For a spontaneous process:

$$\Delta S_{\text{universe}} > 0 \Rightarrow \Delta G < 0$$

The Helmholtz free energy

Useful for constant T and V situations.

Definition: $A = U - T \cdot S$

Differential: $dA = dU - d(T \cdot S)$

$$dA = dU - T \cdot dS - S \cdot dT$$

at constant temperature: $T = \text{const.} \Rightarrow dT = 0$

$$dA = dU - T \cdot dS - S \cdot 0$$

$$dA = dU - T \cdot dS; \quad T, V = \text{const.}$$



Hermann von Helmholtz

1821 - 1894

Product rule

Free energy available to do useful work

From the definition of entropy, we know that

$$\Delta Q_{\text{rev}} = T \cdot \Delta S$$

Therefore:

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We also know that the maximum work is done when a process is carried out reversibly.

Therefore,

$$\Delta A = \Delta U - \Delta Q_{\text{rev}} = \Delta W_{\text{add,max}}$$

is the **maximum additional work** done by a system during a process **at constant temperature**.

ΔG for a reaction

Consider the chemical reaction:



The change in free energy of this system is given by:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

and changes with the concentrations of reactants and products:

$$\Delta G = \Delta G^\ominus + R \cdot T \cdot \ln Q$$

Q is the reaction quotient:

$$Q = \frac{\text{concentrations (products)}}{\text{concentrations (reactants)}} = \frac{\prod_{i=1}^{N(\text{products})} c_i^{v_i}}{\prod_{j=1}^{N(\text{reactants})} c_j^{v_j}}$$

ΔG at equilibrium

We derived earlier that at equilibrium $\Delta G = 0$.

Therefore: $\Delta G = \Delta G^\ominus + R \cdot T \cdot \ln Q_{\text{eq}} = 0$

$$\Rightarrow \ln Q_{\text{eq}} = \ln K = \frac{-\Delta G^\ominus}{R \cdot T}$$

At equilibrium, the reaction quotient

$Q = Q_{\text{eq}} = K$, with K called the **equilibrium constant**.

It follows that

$$K = e^{-\frac{\Delta G^\ominus}{R \cdot T}}$$

Thermodynamic relations

The functions U , H , S and G (or A) of a system vary with changes in T and p (or V).

Since all the thermodynamics properties are inter-related, we can consider any property as a function of two others (if the composition is unchanged).

We can then use calculus to obtain expressions for any property in terms of the others.

This allows us to find relationships between properties that are not apparently related (**Maxwell equations**).

For illustration, we will just look at G as a function of pressure here.

Gibbs free energy as a function of pressure

We can use our standard definitions to see how properties vary with temperature and pressure :

$$H = U + p \cdot V$$

$$G = H - T \cdot S$$

$$dU = dQ + dW$$

The third relationship is true under all conditions, including reversible processes. For reversible processes, the heat change is $dQ = dQ_{\text{rev}}$, and the work done is $dW = dW_{\text{rev}}$.

$$dQ_{\text{rev}} = T \cdot dS \quad ; \quad dW_{\text{rev}} = p \cdot dV$$

Therefore: $dU = T \cdot dS - p \cdot dV$

$$\Rightarrow dG = dH - T \cdot dS - S \cdot dT \quad \text{cont ...}$$

Gibbs free energy as a function of pressure

$$dG = dH - T \cdot dS - S \cdot dT$$

$$dG = dU + p \cdot dV + V \cdot dp - T \cdot dS - S \cdot dT$$

$$dG = T \cdot dS - p \cdot dV + p \cdot dV + V \cdot dp - T \cdot dS - S \cdot dT$$

$$dG = V \cdot dp - S \cdot dT$$

At constant temperature: $T = \text{const.} \Rightarrow dT = 0$

$$\Rightarrow dG = V \cdot dp$$

$$\Rightarrow \Delta G = \int_{G_i}^{G_f} dG = \int_{p_i}^{p_f} V dp ; V \text{ depends on the pressure } p!$$

For an ideal gas: $p \cdot V = n \cdot R \cdot T$; therefore:

$$\Delta G = G_f - G_i = \int_{p_i}^{p_f} \frac{n \cdot R \cdot T}{p} dp = n \cdot R \cdot T \cdot \ln \frac{p_f}{p_i}$$

Gibbs free energy as a function of pressure

The standard state of a gas is defined as the gas at a pressure of $p^\ominus = 1 \text{ bar}$.

A special symbol ($^\ominus$) is used to denote a property of a substance in its standard state.

Let the initial state be the standard state ; so $p_i = p^\ominus = 1 \text{ bar}$).

Then G at any pressure is given by:

$$G(p) = G^\ominus + n \cdot R \cdot T \cdot \ln \frac{p}{p^\ominus}$$

with $G^\ominus = G(1 \text{ bar})$.

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.
Sections II.2.1-II.2.7

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.
Section 3.5 (pp. 113-120)