

The Laws of Thermodynamics in Review

1. The **internal energy, U**, of an isolated system is **constant**. There are only **two** ways to change internal energy – **heat** and **work**.

$$\Delta U = q + w$$

Internal energy (U): total energy in the system:

chemical bonds
intermolecular forces
motion (kinetic energy)

2. The **entropy** of the universe **increases** in any spontaneous process.

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

3. The **entropy** of a perfect crystal approaches **zero** as the **temperature** approaches absolute **zero**.

1st Law: Heat and Work in Review

Heat and work are **path functions** (not state functions).

By definition, **Heat** at a **constant pressure** is called **Enthalpy**.

$$q = \Delta H$$

Ex) Imagine a reaction done in a **balloon**. The **volume** of the balloon may change over the course of the reaction.

i) If the balloon **shrinks**, work has been done **on** the system.

ii) If the balloon **expands**, work has been done **by** the system.

The amount of work done **on the system** depends on **P** and the change in **V**.

At **constant** pressure:

$$W = -P\Delta V$$

1st Law: Heat and Work

Recalling that: $\Delta U = q + w$

and that: $q = \Delta H$

At constant pressure, we can **relate** enthalpy and internal energy:

$$q = \Delta U - w$$

Therefore, **enthalpy** under constant pressure is:

$$\Delta H = \Delta U + P\Delta V$$

2nd Law: Gibbs Free Energy

Recall: at constant **T**,
the change in entropy is:

$$\Delta S = \frac{q_{rev}}{T}$$

Also recall that at constant **P**:

$$q_{system} = \Delta H_{system}$$

Hence at constant **P** and **T**:

$$\Delta S_{system} = \frac{\Delta H_{system}}{T}$$

The heat **absorbed** by the **system**
will be the same as the heat **released**
by the **surroundings** , hence:

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

2nd Law: Gibbs Free Energy

Recall that:
$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

Therefore:
$$\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

Furthermore:
$$-T\Delta S_{universe} = -T\Delta S_{system} + \Delta H_{system}$$

Which means that for any **spontaneous** reaction

$$-T\Delta S_{universe} < 0 \text{ (negative).}$$

2nd Law: Gibbs Free Energy

$-T\Delta S_{\text{universe}}$ is **defined** in terms of the **system** only, and is used to define a **new** term:

The **Gibbs free energy** (G), as:

$$G = H - TS$$

i) At **constant** T and P ,

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

since ΔH is only meaningful at constant pressure.

ii) For any **spontaneous** reaction, $\Delta G < 0$.

iii) Gibbs free energy is a **state function**.

Gibbs Free Energy and the Standard State

Changes in **Gibbs free energy** are determined by **reaction conditions**.

Hence **free energy** values are always made in reference to **standard states**.

Standard temperature and pressure (STP) are defined as:

i) $T = 25\text{ }^{\circ}\text{C}$

ii) $P = 1\text{ bar (100 kPa)}$

Standard states are defined as:

i) A **solid** is in the standard state if it is at STP.

ii) A **liquid** is in the standard state if it is at STP.

iii) A **gas** is in the standard state if it is at STP and behaves ideally.

iv) A **solution** is in the standard state if it has one solute with a concentration of 1 mol/L, is at STP and behaves ideally.

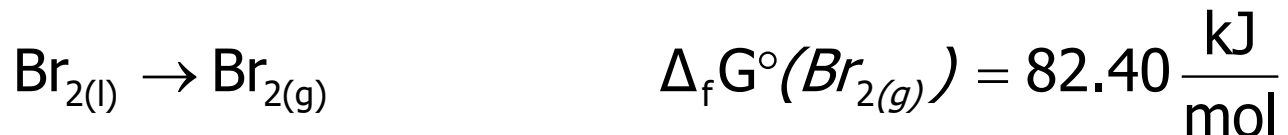
Note: a **liquid** is not the same as a **solution**.

Gibbs Free Energy and the Standard State

Standard molar Gibbs free energies of formation (ΔG_f°) are **tabulated** alongside ΔH_f° and ΔS° .

ΔG_f° : when **1 mole** of a compound is made from **pure elements** in their **standard states**.

e.g.



Note: If a substance is a **pure element** in its **standard state**, this means that:

$$\Delta G_f^\circ = 0.$$

Gibbs Free Energy and Predicting Spontaneity

As the Gibbs free energy is a **state** function, it is used to calculate the **free energy change** for any **reaction** (ΔG_r°) under standard state conditions.

e.g.



$$\Delta_f G^\circ(\text{H}_2\text{O}_{(l)}) = -237.1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{SO}_{3(g)}) = -371.1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{H}_2\text{SO}_{4(aq)}) = -744.5 \frac{\text{kJ}}{\text{mol}}$$

-136.3 kJ/mol

Gibbs Free Energy and Predicting Spontaneity

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

Analogous to Hess's Law !!

Note: The **state** of matter is important.

i) Only one **allotrope** of any element can have $\Delta_f G^\circ = 0$.

Most often the one that is **most stable** under STP.

ex) graphite, $O_{2(g)}$, *etc.*

ii) As **ions** cannot exist in **isolation** hence without **counterions**;

Therefore the standard state $H^+_{(aq)}$ (1 M at STP) is used as the **reference** for ions.

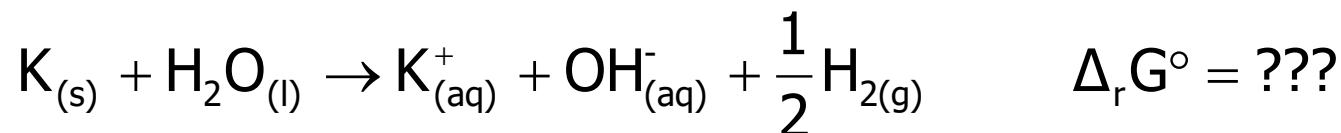
ie. $\Delta_f G^\circ(H^+_{(aq)}) = 0$.

Gibbs Free Energy and Predicting Spontaneity

A well known **spontaneous** reaction occurs when potassium metal is added to water.

What is the **free energy change** for this reaction under **standard conditions**?

e.g.



$$\Delta_f G^\circ(\text{H}_2\text{O}_{(l)}) = -237.1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{K}_{(aq)}^+) = -283.3 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{OH}_{(aq)}^-) = -157.2 \frac{\text{kJ}}{\text{mol}}$$

-203.4 kJ/mol

Gibbs Free Energy and Predicting Spontaneity

A reaction between H_2 and N_2 **doesn't readily proceed** to make NH_3 .

What is the **free energy change** for this reaction under standard conditions?

$$\Delta_f G^\circ(NH_{3(g)}) = -16.45 \frac{kJ}{mol}$$

The free energy change tells us that this process is **avored thermodynamically**?

It does not tell us if there is a **direct** path from reactants to products without a **larger positive free energy** in between.

It does therefore **not predict** whether the reaction will take place under standard conditions.

Gibbs Free Energy and Activity

The **Haber-Bosch** process **isn't** performed under standard conditions so this free energy value doesn't apply in this case.

Reaction conditions: 450 °C, 100 atm, catalyst: magnetite (Fe_3O_4)

Frequently reactions are run under **nonstandard** conditions.

Under nonstandard conditions we consider the **activity (a)** of the substances involved.

Activity is a measure of a substance's **deviation** from the standard state:

i) Any substance in the standard state will have **a = 1**.

Recall: that the standard state requires that gases and solutes behave Ideally.

ii) Activities are **dimensionless** (*i.e.* they have no units.)

Gibbs Free Energy and Activity

For **ideal** substances, activity is relatively straightforward:

- i) Pure **solids** have $a = 1$
- ii) Ideal **gases** have $a = P/P^\circ$ where $P^\circ = 1 \text{ bar}$
- iii) Ideal **solutes** have $a = c/c^\circ$ where $c^\circ = 1 \text{ mol/L}$
- iv) Ideal **solvents** have $a = X$ where X is the **mole fraction** of solvent molecules.

For **nonideal** substances, activity must be modified by an **activity coefficient** (γ):

- i) **Nonideal** solutes have $a = \gamma c/c^\circ$ where $c^\circ = 1 \text{ mol/L}$
- ii) **Activity coefficients**, γ , are **concentration-dependent** as they account for such **nonideal** behaviour arising from **intermolecular forces** between different particles of solute.

Thus, the activity coefficient will **tend** towards **1** with dilution.

Gibbs Free Energy & Nonstandard Conditions

To **calculate** the ΔG° of a reaction under **nonstandard** conditions:

Use the free energy under standard conditions **and** the deviation from the standard state conditions:

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$

$\Delta_r G_m$ is the molar Gibbs free energy change **under the given conditions**,

R is the ideal gas constant, **T** is the given temperature (in K) and

Q is the **reaction quotient**:

$$Q = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$

There is a **similarity** between the formula for **Q** and the formula for **K**.

K describes the system at **equilibrium** only.

Gibbs Free Energy & Nonstandard Conditions

Calculate the molar Gibbs free energy change for the **rusting of iron** under atmospheric conditions.

$$\Delta_f G^\circ(Fe_2O_{3(s)}) = -742.2 \frac{kJ}{mol}$$

$$P_{O_2} = 0.21 \text{ bar}$$

$$T = 25^\circ\text{C}$$

$$Q = 10.39$$

$$\Delta G = -736.4 \text{ kJ/mol}$$

Gibbs Free Energy & Nonstandard Conditions

Calculate the molar Gibbs free energy change for **dissolving** carbon dioxide in a **soft drink** under atmospheric conditions.

$$\Delta_f G^\circ(\text{CO}_{2(g)}) = -394.4 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{H}_2\text{O}_{(l)}) = -237.1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{H}_2\text{CO}_{3(aq)}) = -623.1 \frac{\text{kJ}}{\text{mol}}$$

$$P_{\text{CO}_2} = 0.038 \text{ bar}$$

$$[\text{H}_2\text{CO}_3] = 0.1 \text{ M}$$

$$[\text{sugar}] = 0.6 \text{ M}$$

$$[\text{H}_2\text{O}] = 55.33 \text{ M}$$

$$T = 25 \text{ }^\circ\text{C}$$

$$Q = 2.66$$

$$\Delta G = 10.8 \text{ kJ/mol}$$

Gibbs Free Energy & Nonstandard Conditions

Repeat the calculation for dissolving carbon dioxide in a soft drink with a **higher pressure** for carbon dioxide (5.0 bar).

$$\Delta_f G^\circ(\text{CO}_{2(g)}) = -394.4 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{H}_2\text{O}_{(l)}) = -237.1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{H}_2\text{CO}_{3(aq)}) = -623.1 \frac{\text{kJ}}{\text{mol}}$$

$$P_{\text{CO}_2} = 5.0 \text{ bar}$$

$$[\text{H}_2\text{CO}_3] = 0.1 \text{ M}$$

$$[\text{sugar}] = 0.6 \text{ M}$$

$$[\text{H}_2\text{O}] = 55.33 \text{ M}$$

$$T = 25 \text{ }^\circ\text{C}$$

$$Q = 0.0202$$

$$\Delta G = -1.26 \text{ kJ/mol}$$

Free Energy Change and Equilibrium

Recall: The free energy change for a reaction under any conditions ($\Delta_r G$) can be calculated from the free energy change of the same reaction under standard conditions ($\Delta_r G^\circ$):

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$

where **Q** is the reaction quotient:

$$Q = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$

We also know that:

- i) The **forward** reaction is spontaneous if $\Delta_r G < 0$.
- ii) The **reverse** reaction is spontaneous if $\Delta_r G > 0$.

What if $\Delta_r G = 0$?

Free Energy Change and Equilibrium

When $\Delta_r G = 0$, we can say that:

$$\Delta_r G_m = \Delta_r G_m^o + RT \ln Q = 0$$

Which rearranges to give:

$$\Delta_r G_m^o = -RT \ln Q$$

The **forward** and **reverse** reactions are in balance, *i.e.* **at equilibrium!**

Therefore:

$$Q = K$$

Hence:

$$\Delta_r G_m^o = -RT \ln K$$

Free Energy Change and Equilibrium

I) If we know the **equilibrium constant** for a reaction, we can calculate its **standard molar free energy** change:

$$\Delta_r G_m^\circ = -RT \ln K$$

II) If we know the **standard molar free energy change** for a reaction, we can therefore calculate its **equilibrium constant**:

$$K = e^{\frac{-\Delta_r G_m^\circ}{RT}}$$

Note: these equations refer to $\Delta_r G^\circ$ (standard conditions)

NOT

to $\Delta_r G$ (which is ZERO at equilibrium!)

Q vs. K

Consider a very generic equilibrium reaction: $A \rightleftharpoons B$

i) When does $Q = K$?

at equilibrium $K = Q = a_B/a_A$

ii) When is $Q < K$?

When there is **excess A** or a **depletion of B**:

w.r.t equilibrium $a_A > a_A(\text{eq})$ or $a_B < a_B(\text{eq}) \Rightarrow Q < K$

Reaction proceeds forward

iii) When is $Q > K$?

When there is **excess B** or a **depletion of A**

w.r.t equilibrium $a_A < a_A(\text{eq})$ or $a_B > a_B(\text{eq}) \Rightarrow Q > K$

Reaction proceeds in reverse

Free Energy Change and Equilibrium

Consider the **dimerization** of NO_2 :



Calculate the equilibrium constant for this reaction at 25 °C.

$$\Delta_f G^\circ(\text{NO}_{2(g)}) = 51.31 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ(\text{N}_2\text{O}_{4(g)}) = 97.89 \frac{\text{kJ}}{\text{mol}}$$

$$K = 6.74$$

Free Energy Change and Equilibrium

Is the **dimerization** of NO_2 **spontaneous** at 25 °C if:

the **partial pressure** of NO_2 is 0.4 bar

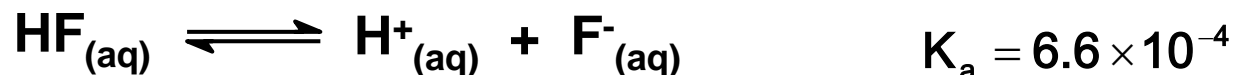
and the **partial pressure** of N_2O_4 is 1.8 bar?

$$Q = 11.25$$

Free Energy Change and Equilibrium: Acids

The **acid ionization constant**, K_a , is the **equilibrium constant** for the reaction in which an acid ionizes.

e.g.



$\text{p}K_a$ is a measure of **strength** of an acid:

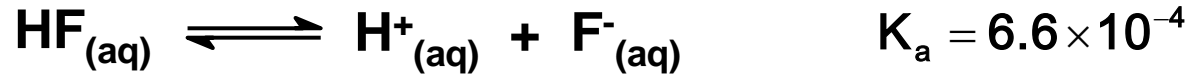
- 1)** An acid with a **low** $\text{p}K_a$ is **stronger** than an acid with a **high** $\text{p}K_a$.
- 2)** The $\text{p}K_a$ value for an acid comes from its acid ionization constant:

$$\text{p}K_a = -\log K_a$$

(Even a **big** K_a value is pretty small. K_a values range from about 10^{-50} to 10^{10} .)

Free Energy Change and Equilibrium: Acids

1) Calculate the standard molar free energy of formation for $\text{HF}_{(\text{aq})}$.



$$\Delta_f G^\circ(\text{H}^+_{(\text{aq})}) = 0 \frac{\text{kJ}}{\text{mol}} \quad \Delta G_r^\circ = 18.15 \text{ kJ/mol}$$

$$\Delta_f G^\circ(\text{F}^-_{(\text{aq})}) = -278.8 \frac{\text{kJ}}{\text{mol}} \quad \Delta G_f^\circ(\text{HF}_{(\text{aq})}) = -296.95 \text{ kJ/mol}$$

2) Calculate the concentration of $\text{H}^+(\text{aq})$ at 298 K in a 1.00 M solution of HF.

$$[\text{H}^+(\text{aq})] = 0.0254$$

$$\text{pH} = 1.60$$