The Third Law of Thermodynamics

The third law of thermodynamics:- states that the entropy of a pure crystalline substance is zero at absolute zero because the crystal arrangement must show the greatest orderliness at this temperature.

In other words, a pure perfect crystal has only one possible configuration, so that

$$S = K \ln O = k \ln(1) = 0$$

- The temperature of absolute zero (0 K) is not possible
- to reach the orientation of electron spins and nuclear spins can reach very low temperatures of 2×10^{-3} and 10^{-5} K, respectively.

The third law makes it possible to calculate the absolute entropies of pure substances from the following equation

$$S_T = \sum \frac{dq_{\mathrm{rev},i}}{T_i} + S_0 \qquad (3\text{–}49)$$

- S_0 is the molar entropy at absolute zero
- S_T is the absolute molar entropy at any temperature.

$$\text{đ}q_{rev} = C_P dT \quad \textit{at constant } p$$

so that **S_T may be determined from knowledge of the heat capacities and the entropy changes during a *phase change* melting (m) and vaporization (v):**

$$\boxed{S_T = \int_0^{T_\mathrm{m}} \frac{C_P\,dT}{T} + \frac{\Delta H_\mathrm{m}}{T_\mathrm{m}} + \int_{T_\mathrm{m}}^{T_\mathrm{v}} \frac{C_P\,dT}{T} + \frac{\Delta H_\mathrm{v}}{T_\mathrm{v}} + \int_{T_\mathrm{v}}^{T} \frac{C_P\,dT}{T}}$$

where $S_0 = 0$ has been omitted.

Free Energy Functions and Applications

the first and second laws of the thermodynamics and express both equilibrium (=) and spontaneity (<) conditions depending only on the properties of the system; therefore, they are of fundamental practical importance.

the ***Helmholtz free energy or work function A*** can be defined as

$$A = E - TS \qquad (3\text{–}56)$$

and the ***Gibbs free energy G***,

$$G = H - TS \qquad (3\text{–}57)$$

equilibrium and spontaneity conditions are reduced to only

$$\Delta A = 0 \qquad (\text{at } T = \text{const}, V = \text{const}) \qquad (3\text{–}58)$$

$$\Delta G = 0 \qquad (\text{at } T = \text{const}, P = \text{const}) \qquad (3\text{–}59)$$

Maximum Net Work

According to the first law of the thermodynamics expressed inequation *Q = ΔE - W*

at an isothermal process can be combined with second law the conservation of energy by substituting , yielding

$$\Delta E - W - T\Delta S = 0 \qquad (3\text{–}60)$$

In this case, *W* represents all possible forms of work available and not only *PV* work (i.e., expansion or compression of the system). The system does ***maximum work (W_{max})*** when it is working under reversible conditions;

$$\Delta A - W_{\max} = 0 \quad \text{or} \quad \Delta A = W_{\max} \qquad (3\text{–}61)$$

This equation explains the meaning of the

Helmholtz energy = *work function*

that is, **the *maximum work* produced in an isothermal transformation is equal to the change in the Helmholtz energy.**

Now if *W* is separated into the *PV* work and all other forms of ***work excluding expansion or compression, W_a (also called useful work) for an isothermal process at constant pressure*** equation **(**3-60**)** can be written as

$$\Delta E - W_a = P\Delta V - T\Delta S = 0 \qquad (3\text{–}62)$$

The definition of the Gibbs energy is

$$G = E + PV - TS \qquad (3\text{–}63)$$

For a reversible process equation, **(**3-62**)** transforms into

$$\Delta G - W_a = 0 \quad \text{or} \quad \Delta G = W_a \qquad (3\text{–}64)$$

This Equation expresses the fact that the change in Gibbs free energy at constant temperature and pressure equals the *useful* or *maximum network* (*W_a*)

Criteria of Equilibrium and Spontaneity

When ΔG = 0 ***the system is at equilibrium.***
When ΔG < 0 (negative) ***the process is a spontaneous***
When ΔG > 0 (positive) ***the process is not spontaneous.***

Table Criteria for Spontaneity and Equilibrium

Function	Restrictions	Spontaneous	Nonspontaneous	Equilibrium
	Total system,			
$\Delta S_{\text{universe}}$	$\Delta E = 0$, $\Delta V = 0$	+ or >0	- or <0	0
ΔG	$\Delta T = 0$, $\Delta P = 0$	- or <0	+ or >0	0
ΔA	$\Delta T = 0$, $\Delta V = 0$	- or <0	+ or >0	0

$$\boxed{\Delta G = \Delta H - T\,\Delta S \qquad (3\text{–}67)}$$

and therefore

$$\Delta G = -T\,\Delta S_{\text{universe}} \qquad (3\text{–}68)$$

despite the positive value of Δ*H*.
Now consider a **reaction**, we can then use the equation:

dΔG = ΔVdP – ΔSd

Example
Δ*H* and Δ*S* for the transition from liquid water to ice at -10°C and at 1 atm pressure are -1343 cal/mole and -4.91 cal/mole deg, respectively. Compute ΔG for the phase change at this temperature (-10°C = 263.2 K) and indicate whether the process is spontaneous. Write
Δ G = -1343 -[263.2 × (-4.91)] = -51 cal/mole
= -213 joules
The process is spontaneous, as reflected in the negative value of Δ*G*.

Pressure and Temperature Coefficients of Free Energy

The free energy change(ΔG) of an ideal gas undergoingan isothermal reversible or irreversible alteration can be givenaccording to the following equation:-

$$\Delta G = (G_2 - G_1) = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = 2.303 nRT \log \frac{P_2}{P_1} \qquad (3\text{–}78)$$

Example

What is the free energy change when 1 mole of an ideal gas is compressed from 1 atm to 10 atm at 25°C? We write

$$\Delta G = 2.303 \times 1.987 \times 298 \times \log \frac{10}{1}$$

$$\Delta G = 1364 \text{ cal}$$

The change in free energy of a solute when the concentration is altered is given by the equation

$$\Delta G = 2.303 nRT \log \frac{a_2}{a_1} \qquad (3\text{–}79)$$

in which *n* is the number of moles of solute and a_1 and a_2 are the initial and final activities of the solute, respectively.

Example 3-12

Borsook and Winegarden1 roughly computed the free energy change when the kidneys transfer various chemical constituents at body temperature (37°C or 310.2 K) from the blood plasma to the more concentrated urine. The ratio of concentrations was assumed to be equal to the ratio of activities in equation (3-79). They found The concentration of urea in the plasma is 0.00500 mole/liter; the concentration in the urine is 0.333 mole/liter. Calculate the free energy change in transporting 0.100 mole of urea from the plasma to the urine.

$$\Delta G = 2.303 \times 0.100 \times 1.987 \times 310.2 \times \log \frac{0.333}{0.00500}$$

$$\Delta G = 259 \text{ cal}$$

This result means that 259 cal of work must be done on the system, or this amount of network must be performed by the kidneys to bring about the transfer.

Fugacity

For pure solids or liquids the volume has little dependence on pressure, so it can be approached as constant.

$$\boxed{G = G^\circ + V(P - P^\circ) \quad \text{(for solids and liquids)} \quad (3\text{–}81)}$$

by applying the ideal gas equation *V* = *nRT*/*P*, the following equations can be obtain

$$\boxed{\begin{aligned} G - G^\circ &= \int_{P^\circ}^{P} = \frac{nRT}{P}dP \\ &= nRT\ln\left(\frac{P}{P^\circ}\right) \qquad \text{(for ideal gas)} \qquad (3\text{–}82) \end{aligned}}$$

assuming *P*° = 1 atm as the reference state. Then, dividing by the amount of substance *n* gives a new property (*G*/*n*) called *the* ***molar Gibbs energy*** or ***chemical potential***, defined by the letter μ,

$$\mu = \left(\frac{G}{n}\right) \qquad (3\text{–}83)$$

Thus, for an ideal gas

$$\mu = \mu^\circ + RT\ln\left(\frac{P}{1\ \text{atm}}\right) \qquad (3\text{–}84)$$

❖

❖ μ° depends only on the temperature and the nature of the gas and represents the chemical potential of 1 mole of the substance in the reference state where *P*° is equal to 1 atm.

$$\boxed{\mu = \mu^\circ + RT\ln f \qquad (3\text{–}85)}$$

❖ When a real gas does not behave ideally, a function known as the ***fugacity (f)*** can be introduced to replace pressure, just as activities are introduced to replace concentration *in non ideal solutions*

❖ the chemical potential of the solvent in the vapor state inequilibrium with the solution

$$\boxed{\mu_1 = \mu^\circ + RT\ln X_1 \qquad (3\text{–}109)}$$

for an ideal solution. The reference state μ° is equal to thechemical potential μ_1 of the pure solvent (i.e., $X_1 = 1$).

For nonideal solutions, equation **(**3-109**)** is modified by introducing the "***effective concentration" or activity*** of thesolvent to replace the mole fraction:

$$\boxed{\mu_1 = \mu^\circ + RT\ln a_1 \qquad (3\text{–}110)}$$

$$\boxed{a = \gamma X \qquad (3\text{–}111)}$$

and *γ* is referred to as the *activity coefficient*

Standard Free Energy and the Equilibrium Constant

- Many of the processes of pharmaceutical interest such as complexation, protein binding, the dissociation of a weak electrolyte, or the distribution of a drug between two immiscible phases are systems at equilibrium and can be described in terms of changes of the Gibbs free energy (Δ*G*).
- a closed system made up of several components. Therefore, at constant *T* and *P* the total free energy change of the products and reactants

$$\boxed{\Delta G = \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}} \qquad (3\text{–}121)}$$

- **Standard Free Energy** can be obtain as the following equation

$$\Delta G = \Delta G^{\circ} + RT \ln Q \qquad (3\text{–}130)$$

Where

$$Q = \frac{\sum a^{n}_{\text{products}}}{\sum a^{n}_{\text{reactants}}} \qquad (3\text{–}129)$$

Because Δ*G*° is a constant at constant *P* and constant *T*, *RT* is also constant. The condition for equilibrium is Δ*G* = 0, and therefore equation **(**3-130**)** becomes

$$0 = \Delta G^{\circ} + RT \ln K \qquad (3\text{–}131)$$

or

$$\boxed{\Delta G^{\circ} = -RT \ln K \qquad (3\text{–}132)}$$

where *Q* has been replaced by *K*, the equilibrium constant. Equation **(**3-132**)** is a very important expression, ***relating the standard free energy change of a reaction ΔG° to the equilibrium constant K.***

The van't Hoff Equation

$$\boxed{\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad (3\text{–}137)}$$

where Δ*H*° is the standard enthalpy of reaction.

- Equation **(**3-137**)** allows one to compute the enthalpy of a reaction if the equilibrium constants at T_1 and T_2 are available.
- it can be used to supply the equilibrium constant at a definite temperature if it is known at another temperature. Because Δ*H*° varies with temperature and equation **(**3-137**)** gives only an approximate answer.

- *The solubility of a solid in an ideal solution is a special type of equilibrium, and it is not surprising that the solubility can be* written as

$$\ln \frac{X_2}{X_1} = \frac{\Delta H_f}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad (3\text{–}138)$$

another form of the van't Hoff equation, can be written as:-

$$\ln K = -(\Delta H^\circ/R)1/T + \Delta S^\circ/R \qquad (3\text{–}139)$$

where $\Delta S^\circ/R$ is the intercept on the ln K axis of a plot of ln K versus $1/T$.

Clausius–Clapeyron Equation

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v (T_2 - T_1)}{R T_1 T_2} = 0$$

This equation is used to calculate the mean heat of vaporization of a liquid if its vapor pressure at two temperatures is available. Conversely, if the mean heat of vaporization and the vapor pressure at one temperature are known, the vapor pressure at another temperature can be obtained.
The Clausius–Clapeyron equations is important in the study of various phase transitions and in the development of the equations of some colligative properties.

Example 3-13

The average heat of vaporization of water can be taken as about 9800 cal/mole within the range of 20°C to 100°C. What is the vapor pressure at 95°C?
The vapor pressure P_2 at temperature T_2 = 373 K (100°C) is 78 cm Hg, and R is expressed as 1.987 cal/deg mole. Write

$$\log \frac{78.0}{P_1} = \frac{9800}{2.303 \times 1.987}\left(\frac{373 - 368}{368 \times 373}\right)$$

$$P_1 = 65 \text{ cm Hg}$$