

Chapter 6::Chemical equilibrium

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Gibbs energy

Abstract

We would like to determine the spontaneity of a reaction mixture to approach equilibrium, along with deriving the thermodynamic equilibrium constant K_P and equilibrium concentrations of reactants and products in a mixture of reactive ideal gases. We define Gibbs energy (ΔG), which expresses spontaneity in terms of properties of the system alone.

Suppose we have an arbitrary system σ in thermal equilibrium with the surroundings. What determines the directions of a spontaneous change? Well, it would be the tendency of a system to minimize energy.

$$-dq_\sigma = dq_{surr} \implies dS_\sigma + dS_{surr} \geq 0 \implies dS_\sigma + \frac{dq_{surr}}{T} \geq 0$$

Definition

$$\Delta G_\sigma = \Delta H_\sigma - T\Delta S_\sigma \implies dG_\sigma = dH_\sigma - TdS_\sigma$$

If we graph this relation, we notice that ΔG is a function of T . ΔH would be ΔG_0 and the slope would be ΔS .

Gibbs energy holds the following properties::

- $\Delta G < 0 \implies \sigma \equiv \textit{spont} \implies \textit{exergonic}$
- $\Delta G > 0 \implies \sigma \equiv \neg \textit{spont} \implies \textit{endergonic}$
- Gibbs energy is an extensive property, and is a state function.

When a problem concerns Gibbs energy, we only care about **what happens in the system, not the surroundings**.

Differential forms of U , H , and G

For an infinitesimal process::

$$G = H + TS \implies dG = dH - TdS - SdT$$

According to the first law::

$$dH = dU + PdV + VdP \implies dU = dq + dw \implies dU = dq - PdV$$

For a reversible process::

$$dq_{rev} = TdS, dU = TdS - PdV$$

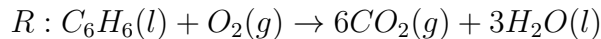
So,

$$dH = TdS + VdP, dG = VdP - SdT, dU = TdS - PdV$$

This only applies for **expansion** work.

Example

Calculate the maximum nonexpansion work that can be gained from the combustion of benzene (l) and of H_2 (g) on a per gram and a per mole basis under standard conditions. Is it apparent from this calculation why fuel cells based on hydrogen oxidation are under development for mobile applications? Thermodynamic values available in appendix.



To calculate maximum nonexpansion work, simply calculate ΔG

$$\Delta G = 3\Delta G(H_2O, l) + 6\Delta G(CO_2, g) - \Delta G(C_6H_6, l) \approx 3202.2 kJ$$

The above value is per mole, so we need to multiply by molar mass ($\frac{1mol}{78.18g}$). In the end, we get $-40.99 \frac{kJ}{g}$

For formation of water, we have that

$$\Delta G = \Delta G(H_2O, l) = -237.1 kJmol^{-1} \implies -237.1 kJmol^{-1} \left(\frac{1mol}{2g} \right) = -117.6 kJg^{-1}$$

Helmholtz energy and spontaneity

This property is derived for processes occurring at $V \equiv \text{const} \wedge T \equiv \text{const}$. We use A to represent the quantity.

$$A = U - TS$$

Gibbs free energy gives **maximum nonexpansion work**, whereas Helmholtz energy gives **maximum overall work**.

Exact differentials and Maxwell relations

Take a function $z = f(x, y)$ where $dz = M(x, y)dx + N(x, y)dy$

Recall that by Euler's theorem, a function is a state function if and only if::

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

The total differentials for $U(S, V)$, $H(S, P)$, $G(T, P)$ can be modelled as follows::

$$dU = TdS - PdV = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV|_T = \frac{\partial U}{\partial S}, -P = \frac{\partial U}{\partial V}$$

$$dH = TdS + VdP = \frac{\partial H}{\partial S}dS + \frac{\partial H}{\partial P}dP|_T = \frac{\partial H}{\partial S}, V = \frac{\partial H}{\partial P}$$

$$dG = -SdT + VdP = \frac{\partial G}{\partial T}dT + \frac{\partial G}{\partial P}dP|_T = -S = \frac{\partial G}{\partial T}, V = \frac{\partial G}{\partial P}$$

Because dU is an exact differential,

$$\frac{\partial}{\partial V} \left(\frac{\partial U(S, V)}{\partial S} \right) = \frac{\partial}{\partial S} \left(\frac{\partial U(S, V)}{\partial V} \right)$$

It would follow that::

$$\frac{\partial T}{\partial V} = -\frac{\partial P}{\partial S}$$

Example

Derive the maxwell relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Because S and V are constant, we can use the exact differential::

$$dU = TdS - PdV$$

Now we can form the mixed derivative::

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial U(S, V)}{\partial S}\right)\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial U(S, V)}{\partial V}\right)\right)_V$$

Substituting $dU = TdS - PdV$, we have that

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial [TdS - PdV]}{\partial S}\right)\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial [TdS - PdV]}{\partial V}\right)\right)_V$$

After simplifying, we can conclude that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \blacksquare$$

Dependence of ΔG on T

Recall that $dG = VdP - SdT$. At $P \equiv \text{const}$, $dG = -SdT$. When $P \equiv \text{const}$, it also follows that

$$\frac{\partial G}{\partial T} = -S, S \geq 0$$

So it would follow that Gibbs energy **decreases as energy increases**.

The Gibbs-Helmholtz equation states that for a finite process,

$$\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T} = -\frac{\Delta H}{T^2}$$

Assume that $\Delta H \wedge \Delta S$ are independent of T and that $P = 1 \text{ atm}$. We can integrate both sides of the equation to give us that

$$\int d\left(\frac{\Delta G}{T}\right) = \int \Delta H d\frac{1}{T}$$

$$\frac{\Delta G(T)}{T} - \frac{\Delta G(298)}{298} \approx \left(\frac{1}{T} - \frac{1}{298}\right) \Delta H(298)$$

So in the end, we have that the Gibbs-Helmholtz equation can be approximated as::

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} \approx \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Delta H(T_1)$$

Dependence of ΔG on P

Recall that $dG = VdP - SdT$, then at $T \equiv \text{const}$, we have that $dG = VdP \implies \frac{\partial G}{\partial P} = V$.

We model dependence of ΔG on P as follows::

$$\Delta G = \int_1^2 dG = G_2 - G_1 = \int_{P_1}^{P_2} VdP$$

If $V \equiv \text{const}$ and the process concerns liquids and solids, we have that::

$$\Delta G = G(P_2) - G(P_1) = V(P_2 - P_1)$$

For $g \in \mathbb{C}$, we have that::

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

Now set $P_1 = 1\text{bar}$ and set $P_2 = P$, therefore,

$$G = G^\circ + nRT \ln(P) \implies \bar{G} = \bar{G}^\circ + RT \ln(P)$$

If $\forall products, reactants \in \sigma((products \equiv ((s) \vee (l))) \vee (reactants \equiv ((s) \vee (l))))$, then

$$\Delta G = G(P_2) - G(P_1) = V(P_2 - P_1) = V\Delta P$$

This is not very important, since we can just ignore the quantity altogether.

However, if $\exists product \vee reactant \in \sigma(product \vee reactant \equiv (g))$, then the volume of solids and liquids is ignored, and::

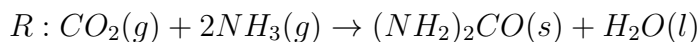
$$\Delta G = G(P_2) - G(P_1) = \Delta nRT \ln \left(\frac{P_2}{P_1} \right)$$

Hess's law for Gibbs energy

It's the same thing as enthalpy.

Example

For the synthesis of urea::



- Calculate $\Delta_r G$ for the reaction at $298K$ and $1bar$ (Ans: $-6.8kJ$)
- Assume $g \in \mathbb{C}$, calculate $\Delta_r G$ at $P = 10bar$.

To calculate $\Delta G(10bar)$, we can plug in the values into the equation we derived.

$$\begin{aligned} \Delta G(10bar) &= \Delta G(1bar) + \Delta nRT \ln \left(\frac{P_2}{P_1} \right) \\ &= (6800Jmol^{-1}) + (-3)(8.314JK^{-1}mol^{-1})(298K) \left(\ln \left(\frac{10}{1} \right) \right) = -23.9kJmol^{-1} \end{aligned}$$

So it would suffice to say that a reaction at higher pressure is **more spontaneous** than at lower pressure.

Equilibrium

The following equation provides the relationship between ΔG_T and ΔG_T° at partial pressures $P = 1\text{bar}$. When $\Delta G = 0$, the system is at equilibrium.

$$\Delta G_T = \Delta G_T^\circ + RT \ln \left(\frac{\left(\frac{P_E}{P^\circ}\right)^b}{\left(\frac{P_A}{P^\circ}\right)^a} \right)$$

All chemical reactions are reversible, i.e. $\forall R, R_1 \rightarrow R_2 \iff R_2 \rightarrow R_1$ since they can go both ways. Reactions that proceed **nearly** to completion. Often times, the reverse of these reactions are too slow to detect experimentally.

The **equilibrium point** is the point in time where a concentration of a reactant or product in the system stops changing.

Reaction rates

When a system is at equilibrium, the forward and reverse reactions occur at the same rate, i.e. for gases, $\frac{\Delta P_1}{\Delta T} = \frac{\Delta P_2}{\Delta T} = 0$. For solids and liquids, use concentration instead.

The equilibrium constant

The equilibrium constant of a reaction is represented as a ratio of concentrations.

$$K_c = \frac{\prod_{[E] \in \text{react}} [E]_i}{\prod_{[E] \in \text{prod}} [E]_j} | i, j \in \mathbb{N}$$

For i reactants and j products. If we have multiple reactions taking place with distinct equilibrium constants, we can multiply them together to find the overall equilibrium constant. Say we have $R_1, R_2 \in \sigma$ each with their own K_1, K_2 , then $K_3 = K_1 K_2$.

For gas exclusive systems, we have that::

$$K_P = K_C(RT)^{\Delta n}$$

Thermodynamic equilibrium constant (unitless)

In thermodynamics we want to relate equilibrium to reaction spontaneity. This would require us to have a unitless description of the equilibrium constant using a concept called activity. Activity is measured as the standard deviation from the standard state.

$$a_X = \frac{[E]}{1M}, a_X = \frac{P_X}{1bar}$$

For solutes and gases respectively. For pure liquids and solids, $a_X = 1$. For an arbitrary reaction,

$$bB + cC \rightleftharpoons dD + eE | K = \frac{a_D^d a_E^e}{a_B^b a_C^c} \implies K = \frac{\prod a_{prod}}{\prod a_{rxt}}$$

Recall that if $K \rightarrow \infty$, the system would contain mostly products, and if $K \rightarrow 0$, the system would contain mostly reactants.

ΔG of a reaction mixture

In a reaction, G would depend on the number of moles $\forall \zeta \in \sigma$, i.e.

$$G = G(T, P, n_1, n_2 \dots n_i) | i = |\sigma| \in \mathbb{N}$$

The chemical potential of the i th element in the reaction can be expressed as $\mu_i = \frac{\partial G}{\partial n_i}, i \in \mathbb{N}$

Once concentration equilibrium has been reached with respect to the reactants, we have that::

$$\mu_{pure}(H_2) = \mu_{mixture}(H_2)$$

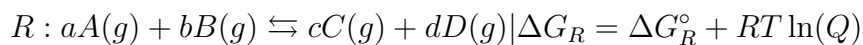
So,

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP + \sum_{i \in \mathbb{N}} \mu_i dn_i$$

With respect to temperature and pressure,

$$\mu_A^{mixture}(T, P) = \mu_A^{pure}(T, P) + RT \ln(\chi_A)$$

For an arbitrary gaseous reaction, we have that



The Q value is a ratio of pressures::

$$Q = \frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b}$$

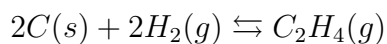
What is the point?

Q can tell us how reaction concentrations must change in order to reach equilibrium (where $Q = K$). In summary,

- $Q_C < K_C \implies rxns \rightarrow prods$
- $Q_C > K_C \implies prods \rightarrow rxns$
- $Q_C = K_C \implies \emptyset$

Example

Take the reaction for the formation of ethylene from carbon and hydrogen at $25^\circ C$.
 $P_{H_2} = 100 atm, P_{C_2H_4} = 0.1 atm$

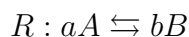


So here,

$$Q_P = \frac{P_{C_2H_4}}{P_{H_2}^2}, \Delta G = 68.1 + (8.314)(298) \left(\ln \left(\frac{0.1}{100^2} \right) \right) = 39.6 kJ mol^{-1}$$

Relating ΔG to equilibrium

Suppose we have a reaction



Suppose G changes by a small amount (δG) and the reaction progresses by a small amount ($\delta \xi$). We have that the change in G is::

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi \implies \Delta G = \frac{\delta G}{\delta \xi} = \mu_B - \mu_A$$

in $kJmol^{-1}$.

So let us summarize,

- $\mu_A > \mu_B \implies R \equiv spont(\rightarrow)$
- $\mu_A = \mu_B \implies equilibrium$
- $\mu_B > \mu_A \implies R \equiv spont(\leftarrow)$

We can rewrite the equation as::

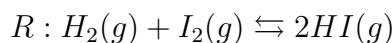
$$\Delta G_T = -RT \ln(K) + RT \ln(Q) = RT \ln\left(\frac{Q}{K}\right)$$

Chemical equilibria of ideal gases (ice tables)

Suppose $1.00mol$ of H_2 and $2.00mol$ of I_2 are placed in a $1.00L$ vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at $458^\circ C$? The equilibrium constant K_c at this temperature is $49.7^\circ C$.

Solution

We have that $[H_2] = 1M$ and $[I_2] = 2M$ since volume is $1L$.



$$K_c = \frac{2x^2}{(1-x)(2-x)} = 49.7 \implies 0.92x^2 - 3x + 2 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{3 \pm \sqrt{9 - 4(0.92)(2)}}{2(0.92)} \approx 1.63 \pm 0.7$$

Since $x_1 = 2.33$ would give us a negative concentration, we reject it. So we can plug in $x_2 = 0.93$ to check if our values work::

$$K_c = \frac{1.86^2}{(0.07)(1.07)} = 49.7$$

It is indeed the same number, so our solution is correct.

The Van't Hoff equation

We want to find a relationship between K and T_2 if K is known for T_1

$$\begin{aligned}\Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S \\ \Delta_r G^\circ &= -RT \ln(K) \\ -RT \ln(K) &= \Delta_r H^\circ - T \Delta_r S \\ \ln(K) &= \frac{-\Delta H}{RT} + \frac{\Delta S}{R}\end{aligned}$$

So we have found a relationship for K_1, T_1 and K_2, T_2

$$\ln(K) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (2)$$

Example

A polypeptide can exist in either the helical or random coil forms. The equilibrium constant for equilibrium reaction of the helix to random coil transition is 0.86 at $40^\circ C$ and 0.35 at $60^\circ C$. Calculate values of ΔH and ΔS for the reaction.

Solution

Assuming ΔH and ΔS are independent of T , then we can use the equation

$$\ln\left(\frac{0.35}{0.86}\right) = -\frac{\Delta H}{333K} \left(\frac{1}{333K} - \frac{1}{313K}\right) \implies \Delta H = -3.9E4 kJmol^{-1}$$

Use the values at $40^\circ C$ to calculate ΔG and ΔS

$$\Delta G = -RT \ln(K) = -(8.314)(313) \ln(0.86) = 391 J mol^{-1}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-3.9E4 - 392}{313K} = -1.3E2 JK^{-1} mol^{-1}$$

Example 2

If the reaction $R : FeN_2(s) + \frac{3}{2}H_2(g) \rightarrow 2Fe(s) + NH_3(g)$ comes to equilibrium at a total pressure of $1bar$, analysis of the gas shows that at $700K$ and $800K$, $\frac{P(NH_3)}{P(H_2)} = 2.165$ and 1.083 , respectively, if only $H_2(g)$ was initially present in the gas phase and $Fe_2N(s)$ was in excess.

- a) Calculate K_P at $700K$ and $800K$. We know that if $P_\Sigma = 1bar$, then $P_{NH_3} + P_{H_2} = 1bar$. So at $700K$,

$$1atm = 2.165P_{H_2} + P_{H_2} = 3.165P_{H_2}$$

$$P_{H_2} = 0.316atm, P_{NH_3} = 0.684atm$$

$$K_P(700K) = \frac{0.684}{(0.316)^{\frac{3}{2}}} = 3.85$$

At $800K$,

$$1atm = 1.083P_{H_2} + P_{H_2} = 2.083P_{H_2}$$

$$P_{H_2} = 0.480atm, P_{NH_3} = 0.520atm$$

$$K_P(800K) = \frac{0.520}{(0.480)^{\frac{3}{2}}} = 1.56$$

- b) Calculate $\Delta_r S^\circ$ at $700K$ and $800K$ and $\Delta_r H^\circ$ assuming it is independent of temperature.

$$\ln \left(\frac{K_P(800)}{K_P(700)} \right) = -\frac{\Delta H}{R} \left(\frac{1}{800} - \frac{1}{700} \right)$$

After some plugging in and calculations, we have that::

$$\Delta H = -42.1 \text{ kJ mol}^{-1}$$

To find ΔS , we need ΔG first.

$$\Delta G(700\text{K}) = -RT \ln(K_P(700\text{K})) = -7.81 \text{ kJ mol}^{-1}$$

$$\Delta G(800\text{K}) = -RT \ln(K_P(800\text{K})) = -2.91 \text{ kJ mol}^{-1}$$

Now we can calculate ΔS .

$$\Delta S(700\text{K}) = \frac{\Delta H(700) - \Delta G(700)}{700\text{K}} = 48.9 \text{ J mol}^{-1} \text{ K}^{-1} = \Delta S(800\text{K})$$

Note that the values of ΔS at 700K and 800K are nearly equal because $|\Delta G_r| \lll |\Delta H_r|$

c) Calculate ΔG_r at 298K

$$\ln(K_P(298.15\text{K})) = \ln(K_P(700\text{K})) - \frac{\Delta H}{R} \left(\frac{1}{298} - \frac{1}{700} \right) = 11.1$$

So now we can calculate our ΔG .

$$\Delta G = -RT \ln(K_P(298\text{K})) = -(8.314)(298.15)(11.1) = -27500 \text{ J mol}^{-1} = -27.5 \text{ kJ mol}^{-1}$$

Le Chatelier's principle

We want to know what happens when we perturb a system that is at equilibrium. Changing the amount of reactants and products in addition to changing volume, pressure, and temperature are all different ways to perturb the system. In general,

- The concentration stress of an **added reactant** or product is relieved by **consuming** the added substance.
- The concentration stress of a **removed** reactant or product is relieved by **replenishing** the removed substance

A special case is if we add **inert** gases to the system. Then no changes will occur because no reactions will be taking place to increase/decrease pressure/volume.