Chapter 6::Chemical equilibrium

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March 15, 2023

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 concentraations 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.

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

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::

- $\Delta G < 0 \implies \sigma \equiv spont \implies exergonic$

- $\Delta G > 0 \implies \sigma \equiv \neg spont \implies endergonic$

- 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 infinitessimal 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.

$$R : C_6H_6(l) + O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$
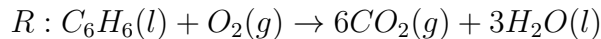
To calculate maximum nonexpansion work, simply calculate ΔG

$$\Delta G = 3\Delta G(H_2O, l) + 6\Delta G(CO_2, g) - \Delta G(G_6H_6, l) \approx 3202.2kJ$$

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

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

Helmholtz energy and spontaneity

This property is derived for processes occuring at $V \equiv const \wedge T \equiv const$. 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::

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

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

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

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::

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

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::

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

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

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

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 $P \equiv const, dG = -SdT$. When $P \equiv const$, 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,

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

Assume that $\Delta H \wedge \Delta S$ are independent of T and that $P = 1atm$. 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 $T \equiv const$, 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 $V \equiv const$ and the process concerns liquids and solids, we have that::

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

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 $P_1 = 1bar$ and set $P_2 = P$, therefore,

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

If $\forall products, reactants \in \sigma((products \equiv ((s) \lor (l))) \lor (reactants \equiv ((s) \lor (l))))$, 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 $\exists product \lor reactant \in \sigma(product \lor reactant \equiv (g))$, then the volume of solids and liquids is ignored, and::
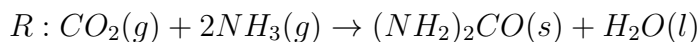
$$\Delta G = G(P_2) - G(P_1) = \Delta nRT \ln\left(\frac{P_2}{P_1}\right)$$

Hess's law for Gibbs energy

It's the same thing as enthalpy.

Example

For the synthesis of urea::

$$R : CO_2(g) + 2NH_3(g) \rightarrow (NH_2)_2CO(s) + H_2O(l)$$

a) Calculate $\Delta_r G$ for the reaction at $298K$ and $1bar$ (Ans: $-6.8kJ$)

b) 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.

$$\Delta G(10bar) = \Delta G(1bar) + \Delta nRT \ln\left(\frac{P_2}{P_1}\right)$$

$$= (6800Jmol^{-1}) + (-3)(8.314JK^{-1}mol^{-1})(298K)(\ln\left(\frac{10}{1}\right) = -23.9kJmol^{-1})$$

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

Haber process

Equilibrium

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

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

All chemical reactions are reversible, i.e. $\forall R, R_1 \to R_2 \iff R_2 \to R_1$ 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.

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

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 sandard 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,

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

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

ΔG of a reaction mixture

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

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

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

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

$$R : aA(g) + bB(g) \leftrightharpoons cC(g) + dD(g) | \Delta G_R = \Delta G_R^\circ + RT \ln(Q)$$

The Q value is a ratio of pressures::

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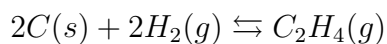
What is the point?

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

- $Q_C < K_C \implies rxts \to prods$

- $Q_C > K_C \implies prods \to rxts$

- $Q_C = K_C \implies \varnothing$

Example

Take the reaction for the formation of ethylene from carbon and hydrogen at $25°C$. $P_{H_2} = 100atm, P_{C_2H_4} = 0.1atm$
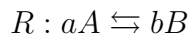
$$2C(s) + 2H_2(g) \leftrightharpoons C_2H_4(g)$$

So here,

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

Relating ΔG to equilibrium

Suppose we have a reaction

$$R : aA \leftrightharpoons bB$$

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::

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

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::

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