

# 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 ( $\Delta G$ ), which expresses spontaneity in terms of properties of the system alone.

Suppose we have an arbitrary system  $\sigma$  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  $\Delta G$  is a function of  $T$ .  $\Delta H$  would be  $\Delta G_0$  and the slope would be  $\Delta S$ .

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::

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

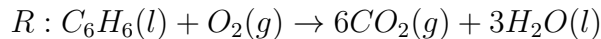
So,

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

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  $\Delta G$**

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

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 $\Delta G$ 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 $\Delta G$ 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  $\Delta G$  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::

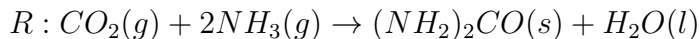
$$\Delta G = G(P_2) - G(P_1) = \Delta nRT \ln \left( \frac{P_2}{P_1} \right)$$

## Hess's law for Gibbs energy

It's the same thing as enthalpy.

## Example

For the synthesis of urea::



- 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.

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

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

## Haber process