Entropy Change of Reactions
at
Constant Temperature and Pressure

☞ For a chemical reaction run at constant temperature and pressure, the reaction's effect on the entropy of the surroundings can be calculated by the equation

$$\Delta S_{\text{surroundings}} = -\Delta H/T$$

where ΔH is the reaction's enthalpy, and the negative sign is inserted to show the reaction's effect on the surroundings.

✔ Substituting into $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \Delta H/T$$

✔ Multiplying through by T and defining $\Delta S_{\text{system}} = \Delta S$

$$T\Delta S_{\text{total}} = T\Delta S_{\text{system}} - \Delta H$$

$$T\Delta S_{\text{total}} = T\Delta S - \Delta H$$

Gibbs Free Energy, *G*

J. Willard Gibbs (1839-1903)

- ☞ The Gibbs free energy is defined by the relationship

$$G = H - TS$$

- ☞ For a chemical reaction at constant pressure and temperature,

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

- ✔ From our previous result $T\Delta S_{\text{total}} = T\Delta S - \Delta H$, we see

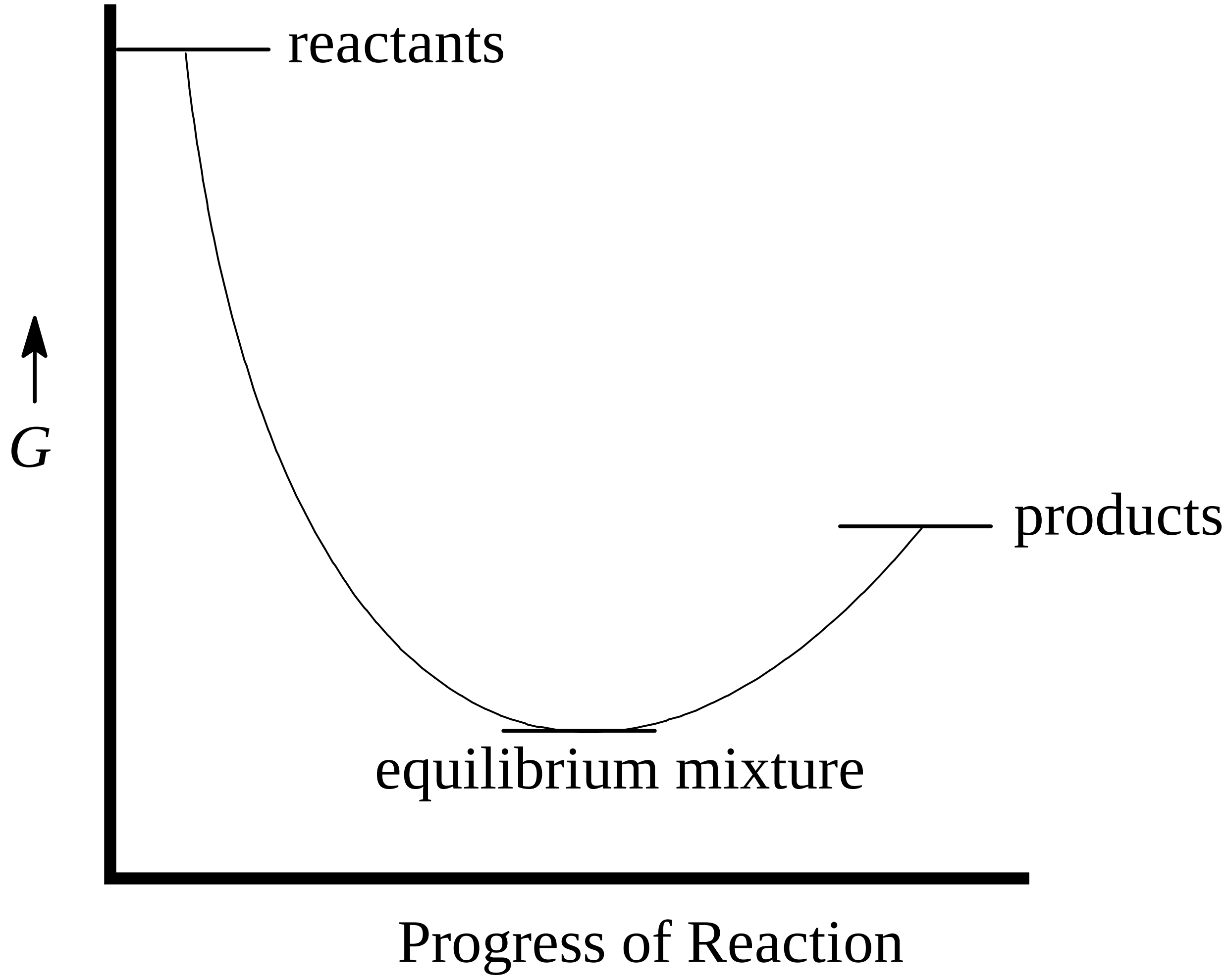
$$\Delta G = -T\Delta S_{\text{total}}$$

ΔG and Spontaneity

- ✔ If $\Delta G < 0$, the reaction is spontaneous as written.
- ✔ If $\Delta G > 0$, the reaction is non-spontaneous as written, but is spontaneous in the reverse direction.
- ✔ If $\Delta G = 0$, the reaction is at equilibrium.

Free Energy Through a Reaction

☞ As a spontaneous reaction proceeds, it releases free energy until it reaches a minimum at equilibrium, at which point $\Delta G = 0$.



Factors that Favor a Spontaneous Reaction

✔ Reactions with $\Delta H < 0$ favor spontaneity.

✔ Reactions that increase randomness ($\Delta S > 0$) favor spontaneity.

Reaction (at 298 K)	ΔH (kJ/mol)	$T\Delta S$ (kJ/mol)	ΔG (kJ/mol)
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	–72.46	+34.00	–106.46
$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$	–571.66	–97.25	–474.41
$2N_2(g) + O_2(g) \rightarrow 2N_2O(g)$	+163.2	–44.10	+207.30
$H_2(g) + I_2(s) \rightarrow 2HI(g)$	+51.88	+49.26	+2.62
$N_2O_4(g) \rightarrow 2NO_2(g)$	+58.02	+52.63	+5.4

✔ Gas-phase reactions in which the sum of coefficients is higher for products than reactants have $\Delta S > 0$, favoring a spontaneous reaction.

✔ Gas-phase reactions in which the sum of coefficients is lower for products than reactants have $\Delta S < 0$, favoring a non-spontaneous reaction.

✔ The sign on ΔS is not easily predicted if the sum of coefficients is the same on both sides.

ΔG and Temperature

☞ Since $\Delta G = -T\Delta S_{\text{total}}$, higher temperatures, which result in greater randomness, favor spontaneity, and lower temperatures, which foster greater order, disfavor spontaneity.

☞ Assuming little change in ΔH and ΔS with temperature, by $\Delta G = \Delta H - T\Delta S$ we see that changing temperature affects the value of ΔG and may affect the spontaneity of the reaction.

Interplay of ΔH, ΔS, and T in $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG	Spontaneity
–	+	–	Spontaneous at all temperatures
+	–	+	Non-spontaneous at all temperatures
–	–	– at low T + at high T	Spontaneous at low temperatures Non-spontaneous at high temperatures
+	+	+ at low T – at high T	Non-spontaneous at low temperatures Spontaneous at high temperatures

Standard Free Energies

- ☞ The standard free energy change of a process, ΔG^o, is defined under conditions of 25 °C and 1 atm with all reactants and products in their standard states.

- ☞ We can apply the Law of Hess to obtain the ΔG^o value for a reaction from values of the standard free energies of any set of reactions that add to give the overall reaction of interest.

- ☞ The most useful set of tabulated data is the standard free energies of formation, ΔG^o_f.

Standard Enthalpy of Formation, ΔG^{o}_{f}

- ΔG^{o}_{f} values are defined as the change in standard free energy when one mole of compound is formed from its elements in their standard state.

- $\Delta G^{o}_{f} = 0$ for any element in its standard state.

- ΔG^{o} for any reaction may be calculated as

$$\Delta G^{o} = \sum n\Delta G^{o}_{f}(\text{products}) - \sum m\Delta G^{o}_{f}(\text{reactants})$$

Absolute Entropies and the Third Law

Walther Nernst, 1906

☞ At the absolute zero of temperature, a perfect crystal would have $S = 0$.

☞ There are no perfect crystals, and absolute zero is unattainable; therefore, all substances have positive absolute entropies at all real temperatures.

Lewis and Randall’s Classic Statement of the Third Law[1]

> If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

✔ Absolute entropies can be calculated from the temperature variation of heat capacities

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[1] G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill, New York, 1923.

Standard Absolute Entropy, S^o

☞ The **standard absolute entropy** of a substance, S^o, is the entropy of the substance in its standard state at 25 ^{o}C and 1 atm.

☞ The ΔS^o for a reaction can be calculated from these data as

$$\Delta S^o = \sum nS^o(\text{products}) - \sum mS^o(\text{reactants})$$

☛ Note that the absolute entropy of an element is *not* zero, and the absolute entropy of a compound *cannot* be calculated from the absolute entropies of its elements.

Non-Standard Conditions

- ☞ Values for ΔH and S generally show only small changes with temperature.
  - ✔ This allows us to use data for ΔH^{o} and S^{o} to *estimate* values of ΔG at other temperatures and to make predictions about spontaneity under those conditions.

Gibbs Free Energy Under Non-Standard Conditions

- The value of ΔG under non-standard conditions can be calculated from ΔG^{o} by the equation

$$\Delta G = \Delta G^{o} + RT \ln Q$$

- Under standard conditions, all species have unit activity (effective concentrations or pressures of 1). Therefore under standard conditions, $Q = 1$, $\ln Q = 0$, and $\Delta G = \Delta G^{o}$.

ΔG and Equilibrium

☞ At equilibrium, $\Delta G = 0$ and $Q = K$; therefore,

$$\Delta G^o = -RT \ln K$$

$$K = \exp(-\Delta G^o/RT)$$

☞ K in this equation is the *thermodynamic* equilibrium constant, defined in terms of the *activities* of participants in their standard states.

- K is inherently unitless.
- For gas-phase reactions, K is approximately K_p.

Relationship Between ΔG^o and K

$\Delta G^o > 0$	$K < 1$
$\Delta G^o = 0$	$K = 1$
$\Delta G^o < 0$	$K > 1$

ΔG^o and E^o_{cell}

☞ Free energy and cell potential are related by the equation

$$\Delta G^o = -n\mathscr{F}E^o_{\text{cell}}$$

✔ In using this equation, recognize that

$$1\ \mathscr{F} = 96{,}500\ \text{C/mol} = 96{,}500\ \text{J/V·mol}$$

✔ Spontaneity is related to E^o_{cell} and ΔG^o as follows:

$E^o_{\text{cell}} > 0$	$\Delta G^o < 0$	spontaneous
$E^o_{\text{cell}} = 0$	$\Delta G^o = 0$	equilibrium
$E^o_{\text{cell}} < 0$	$\Delta G^o > 0$	non-spontaneous

✔ From $\Delta G^o = -n\mathscr{F}E^o_{\text{cell}} = -RT\ln K$

$$\ln K = \frac{n\mathscr{F}E^o_{\text{cell}}}{RT} \qquad \text{or} \qquad \log K = \frac{nE^o_{\text{cell}}}{0.0592}$$