

## 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  $\Delta H$  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

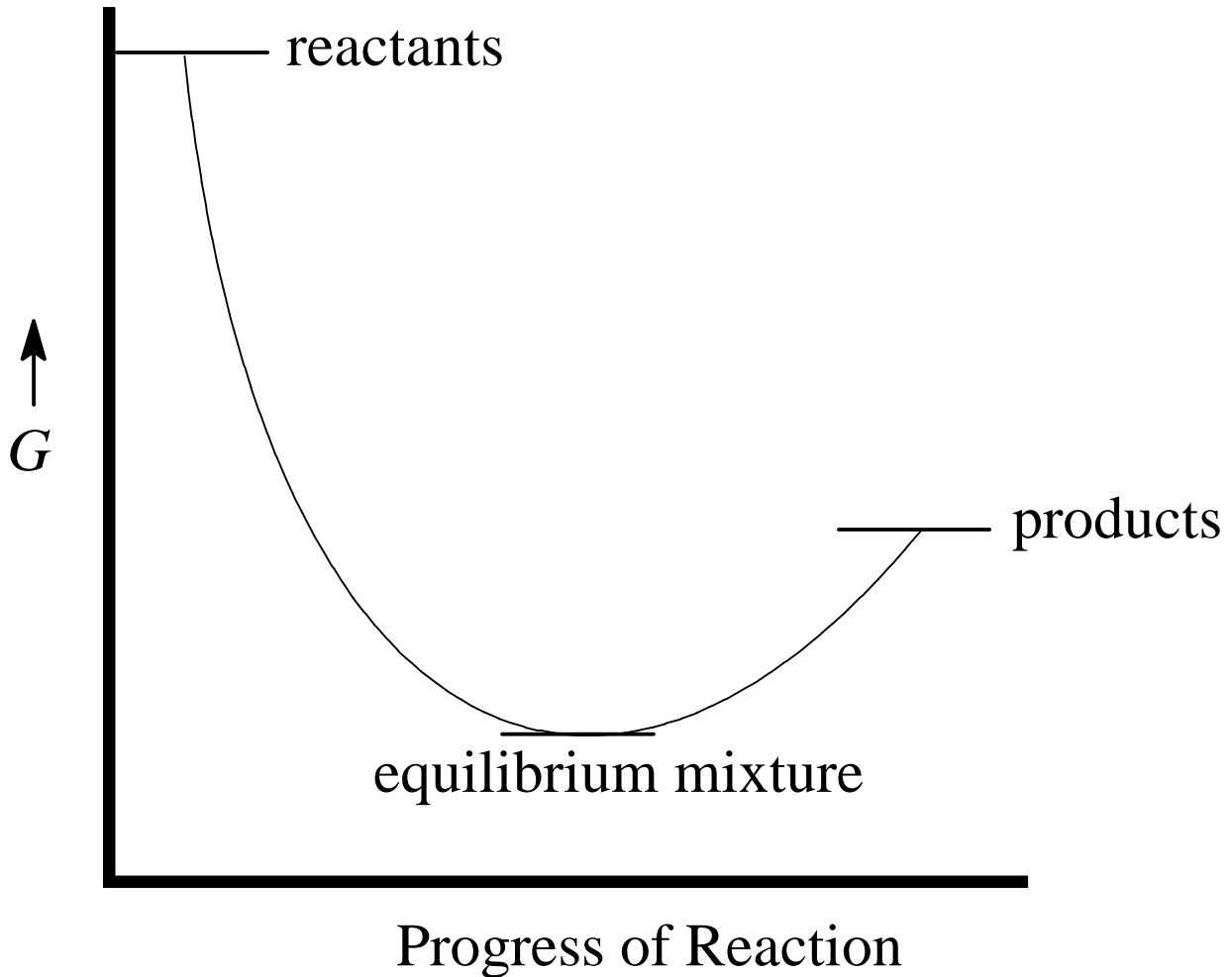
$$\Delta G = -T\Delta S_{\text{total}}$$

## **$\Delta G$ 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)	$\Delta H$ (kJ/mol)	$T\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)
$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$	-72.46	+34.00	-106.46
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$	-571.66	-97.25	-474.41
$2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}(\text{g})$	+163.2	-44.10	+207.30
$\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(\text{g})$	+51.88	+49.26	+2.62
$\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	+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  $\Delta S$  is not easily predicted if the sum of coefficients is the same on both sides.

## $\Delta G$ 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  $\Delta H$  and  $\Delta S$  with temperature, by  $\Delta G = \Delta H - T\Delta S$  we see that changing temperature affects the value of  $\Delta G$  and may affect the spontaneity of the reaction.

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

$\Delta H$	$\Delta S$	$\Delta G$	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,  $\Delta G^\circ$ , 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  $\Delta G^\circ$  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,  $\Delta G_f^\circ$ .

## Standard Enthalpy of Formation, $\Delta G_f^\circ$

- ☞  $\Delta G_f^\circ$  values are defined as the change in standard free energy when one mole of compound is formed from its elements in their standard state.
- ☞  $\Delta G_f^\circ = 0$  for any element in its standard state.
- ☞  $\Delta G^\circ$  for any reaction may be calculated as

$$\Delta G^\circ = \sum n \Delta G_f^\circ(\text{products}) - \sum m \Delta G_f^\circ(\text{reactants})$$

# 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<sup>1</sup>

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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<sup>1</sup>G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill, New York, 1923.

## Standard Absolute Entropy, $S^\circ$

- ☞ The **standard absolute entropy** of a substance,  $S^\circ$ , is the entropy of the substance in its standard state at 25 °C and 1 atm.
- ☞ The  $\Delta S^\circ$  for a reaction can be calculated from these data as

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

- ☞ 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  $\Delta H$  and  $S$  generally show only small changes with temperature.
- ✓ This allows us to use data for  $\Delta H^\circ$  and  $S^\circ$  to *estimate* values of  $\Delta G$  at other temperatures and to make predictions about spontaneity under those conditions.

## Gibbs Free Energy Under Non-Standard Conditions

- ☞ The value of  $\Delta G$  under non-standard conditions can be calculated from  $\Delta G^\circ$  by the equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

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

## $\Delta G$ and Equilibrium

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

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

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

☞  $K$  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 $\Delta G^\circ$ and $K$

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

## $\Delta G^\circ$ and $E^\circ_{\text{cell}}$

- ☞ Free energy and cell potential are related by the equation

$$\Delta G^\circ = -n\mathcal{F}E^\circ_{\text{cell}}$$

- ✓ In using this equation, recognize that

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

- ✓ Spontaneity is related to  $E^\circ_{\text{cell}}$  and  $\Delta G^\circ$  as follows:

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

- ✓ From  $\Delta G^\circ = -n\mathcal{F}E^\circ_{\text{cell}} = -RT \ln K$

$$\ln K = \frac{n\mathcal{F}E^\circ_{\text{cell}}}{RT} \quad \text{or} \quad \log K = \frac{nE^\circ_{\text{cell}}}{0.0592}$$