

# Chemistry 2000 Slide Set 10: Free energy

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# Gibbs free energy

- Suppose that we have a thermodynamically allowed process at constant  $T$  and  $p$ .
- The entropy change of the universe is positive, so

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

- The heat transferred to the system is  $\Delta H_{\text{system}}$  (constant  $p$ ), so the heat transferred to the surroundings is  $-\Delta H_{\text{system}}$ .
- The surroundings are assumed to be sufficiently large that this heat transfer has a negligible effect on them, i.e. is reversible:

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{rev}}}{T} = \frac{-\Delta H_{\text{system}}}{T}$$

$$\therefore \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T} > 0$$

- All of the quantities in the inequality now refer to the system, so we drop the subscripts:

$$\Delta S - \frac{\Delta H}{T} > 0$$

or

$$T\Delta S - \Delta H > 0$$

or

$$\Delta H - T\Delta S < 0$$

- Define the Gibbs free energy

$$G = H - TS$$

- At constant  $T$ ,

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

- For a thermodynamically allowed process at constant  $T$  and  $p$ , we just saw that

$$\Delta H - T\Delta S < 0$$

$\Delta G < 0$  for a thermodynamically allowed process at constant  $T$  and  $p$ .

# The standard state

- The Gibbs free energy change is very sensitive to the reaction conditions.
- We therefore define a **standard state** we will use as a reference.

Standard temperature and pressure (STP):

25 °C and 1 bar (100 000 Pa)

**Gas:** at STP and ideally behaving

**Solid:** at STP

**Liquid:** pure, at STP

**Solute:** 1 mol/L concentration at STP and ideally behaving

# Standard molar Gibbs energy of formation

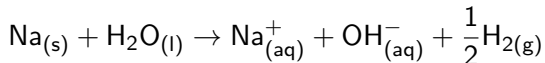
- We use exactly the same device for tables of free energies as we do for enthalpy, namely the **standard (molar) Gibbs free energy of formation**.
- This is the change in Gibbs free energy in making a compound from its elements when all reactants and products are under standard conditions.
- We can write the standard free energy change for a reaction as a difference of standard free energies of formation for products and reactants.

# Notes on the standard free energies of formation

- 1 By definition,  $\Delta_f G^\circ = 0$  for an element in its most stable form.
- 2 Only one allotrope of an element will have  $\Delta_f G^\circ = 0$ .  
For example,  $\Delta_f G^\circ(\text{C, diamond}) = 2.9 \text{ kJ/mol}$ .
- 3 Due to experimental difficulties, we cheat a little with phosphorus and use white phosphorus ( $\text{P}_4$ ) as the reference state of the element rather than the more stable amorphous black phosphorus.
- 4 The state of matter matters (if you'll pardon the pun).  
Example:  $\Delta_f G^\circ(\text{O}_2, \text{g}) = 0$ , but  $\Delta_f G^\circ(\text{O}_2, \text{aq}) = 16.35 \text{ kJ/mol}$ .
- 5 Our inability to make aqueous ions without an accompanying counterion forces us to add a reference state for ions in solution.  
By convention,  $\Delta_f G^\circ(\text{H}^+, \text{aq}) = 0$ .

## Example: Reaction of sodium with water

- Let's start with a reaction we know to be spontaneous:



$$\begin{aligned} \Delta_r G^\circ &= \Delta_f G^\circ(\text{Na}^+, \text{aq}) + \Delta_f G^\circ(\text{OH}^-, \text{aq}) + \frac{1}{2}\Delta_f G^\circ(\text{H}_2, \text{g}) \\ &\quad - [\Delta_f G^\circ(\text{Na}, \text{s}) + \Delta_f G^\circ(\text{H}_2\text{O}, \text{l})] \\ &= \Delta_f G^\circ(\text{Na}^+, \text{aq}) + \Delta_f G^\circ(\text{OH}^-, \text{aq}) + \frac{1}{2}(0) \\ &\quad - [0 + \Delta_f G^\circ(\text{H}_2\text{O}, \text{l})] \\ &= -261.87 + (-157.30) - (-237.192) \text{ kJ/mol} \\ &= -181.98 \text{ kJ/mol} \end{aligned}$$



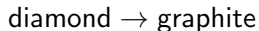
- $\Delta_r G^\circ = -181.98 \text{ kJ/mol} < 0$  therefore this reaction is thermodynamically allowed **under standard conditions** (25 °C, 1 bar, each solute at 1 mol/L).

## Example: Conversion of graphite to diamond

- The diamond industry has used the line “a diamond is forever” since the mid-1940s.

Is it true?

If so, the reaction



should **not** be thermodynamically allowed.

- $\Delta_r G^\circ = \Delta_f G^\circ(\text{graphite}) - \Delta_f G^\circ(\text{diamond})$   
 $= -2.9 \text{ kJ/mol} < 0$
- From this calculation, we conclude that the conversion of diamond to graphite **is** thermodynamically allowed.
- It would seem that the diamond industry's claim that diamonds are forever is fallacious.

## Example: Conversion of graphite to diamond

- At ambient temperature and pressure, diamond is **metastable**, which is to say that it is not in true thermodynamic equilibrium with its surroundings, but that it is trapped, at least temporarily, in a non-equilibrium state.
- The structural rearrangement required to make graphite from diamond is so unlikely as to be essentially impossible at room temperature, so for most practical purposes, diamonds are, if not forever, exceedingly long lived.
- **Thermodynamics tells us what *can* happen, not what *will* happen.**
- However, if we provide a little heat. . .  
<http://www.youtube.com/watch?v=7L7BV3IBfFA>

## Activity: Measuring the deviation from standard conditions

- It is rare that we run a reaction under standard conditions.
- The **activity** ( $a$ ) of a substance measures its deviation from the standard state.
- $a = 1$  for a substance in the standard state.
- The activity is a **dimensionless** quantity.

# Activities of ideal substances

**Ideal gas:** Defined by negligible intermolecular forces, always true at sufficiently low pressures

$$a = p/p^\circ, p^\circ = 1 \text{ bar}$$

**Solid:**  $a = 1$

**Ideal solvent:** Intermolecular forces experienced by solvent essentially identical to those in the pure solvent, true if the solvent and solute are chemically similar **or** if the solute is at a sufficiently low concentration

$$a = X \text{ (mole fraction} = n_{\text{solvent}} / \sum n_i)$$

(But usually,  $X \approx 1$  for the solvent.)

**Ideal solute:** Negligible intermolecular forces between solute molecules, always true at sufficiently low concentrations

$$a = c/c^\circ, c^\circ = 1 \text{ mol/L}$$

## Aside: What about nonideal substances?

- For nonideal substances, we modify the activity by an activity coefficient  $\gamma$ .
- For example,  $a = \gamma c / c^\circ$  for a solute.
- The activity coefficient tends to 1 in situations where a substance behaves ideally, e.g.  $\gamma \rightarrow 1$  when  $c / c^\circ \rightarrow 0$  since all solutes behave ideally in this limit.

# Free energy change under nonstandard conditions

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$

$\Delta_r G_m$  is the molar free energy change under given conditions.

$R$  is the ideal gas constant.

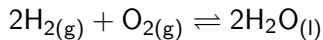
$T$  is the absolute temperature.

$Q$  is the **reaction quotient**:

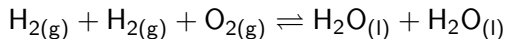
$$Q = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$

# The reaction quotient

- When forming the reaction quotient, we have to take the stoichiometric coefficients into account.
- Example: Think of the reaction



as



so

$$Q = \frac{(a_{\text{H}_2\text{O}})(a_{\text{H}_2\text{O}})}{(a_{\text{H}_2})(a_{\text{H}_2})(a_{\text{O}_2})} = \frac{(a_{\text{H}_2\text{O}})^2}{(a_{\text{H}_2})^2(a_{\text{O}_2})}$$

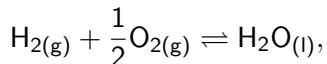


# The reaction quotient

(continued)

- The stoichiometric coefficients become exponents, even if the reaction is written with fractional coefficients.

Example: For the reaction



$$Q = \frac{a_{\text{H}_2\text{O}}}{(a_{\text{H}_2})(a_{\text{O}_2})^{1/2}}$$

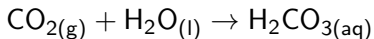
## Example: Rusting of iron under atmospheric conditions

**Question:** Based on thermodynamic considerations alone, would you expect iron to rust under atmospheric conditions?

**Data:**  $p_{\text{O}_2} = 0.21 \text{ bar}$

$$\Delta_f G^\circ(\text{Fe}_2\text{O}_3, \text{s}) = -743.6 \text{ kJ/mol}$$

# Example: Soft drink carbonation



Species	$\Delta_f G^\circ / \text{kJ mol}^{-1}$
$\text{CO}_{2(\text{g})}$	-394.37
$\text{H}_2\text{CO}_{3(\text{aq})}$	-623.1
$\text{H}_2\text{O}_{(\text{l})}$	-237.140

Data: Atmospheric  $\text{CO}_2 = 0.038 \text{ bar}$ ,  $[\text{H}_2\text{CO}_3]$  in soft drink =  $0.1 \text{ mol/L}$ ,  
 $[\text{sugar}] = 0.6 \text{ mol/L}$ ,  $1 \text{ L H}_2\text{O} = 55.33 \text{ mol}$

What happens to the carbonic acid in an open soft drink at  $25^\circ\text{C}$ ?

What if  $p_{\text{CO}_2} = 5 \text{ bar}$ ?

## Reaction of lead(II) nitrate with ammonium sulfate

- 20 mL of a 0.040 mol/L solution of lead(II) nitrate is mixed with 15 mL of a 0.0031 mol/L solution of ammonium sulfate at 25 °C. Does a precipitate form?

Species	$\Delta_f G^\circ / \text{kJ mol}^{-1}$
$\text{Pb}_{(\text{aq})}^{2+}$	-24.24
$\text{PbSO}_{4(\text{s})}$	-813.04
$\text{SO}_{4(\text{aq})}^{2-}$	-744.00

**Answer:**  $\Delta_r G_m = -19.01 \text{ kJ/mol} < 0$  therefore a precipitate forms.

# Summary

- The **standard** free energy change,  $\Delta_r G_m^\circ$ , doesn't tell us much by itself because reactions are almost never run under standard conditions. Often, the standard conditions are not even experimentally realizable!
- To decide if a reaction is thermodynamically allowed, calculate

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$