

Gibbs free energy

From second Law of thermodynamics

$$\Delta S_{\text{uni}} > 0$$

✗ In order to determine the sign of ΔS_{uni} for a reaction, however, we would need to calculate both ΔS_{sys} and ΔS_{surr} .

✗ We need another thermodynamic Function to help us determine whether a reaction will occur spontaneously.

✗ We Know that for a spontaneous process:

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\therefore \Delta S_{\text{uni}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$

✓ Multiplying both sides of the equation by T:

$$T\Delta S_{\text{uni}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$-T\Delta S_{\text{uni}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

- This equation says that for a process carried out at constant pressure and temperature T, if the changes in enthalpy and entropy of the system are such that $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$ is less than zero, the process must be **spontaneous**.
- Now, the spontaneous reaction is expressed only in terms of the properties of the system (ΔH_{sys} and ΔS_{sys}) and we can ignore the surroundings.

✓ Gibbs free energy:

$$G = H - TS$$

✓ The change in free energy (ΔG) of a system for a constant temperature process is:

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

Free energy \rightarrow is the energy available to do work.

Note that

$\Delta G < 0$ the reaction is spontaneous in the forward direction

$\Delta G > 0$ the reaction is non-spontaneous; the reaction is spontaneous in the opposite direction.

$\Delta G = 0$ the system is at equilibrium, There is no net change

Standard free energy change

Standard free energy of a reaction $\Delta G^\circ_{(rxn)} \rightarrow$ is the free energy change for a reaction when it occurs under standard-state conditions, when reactants are converted to products in their standard states.

✓ To calculate $\Delta G^\circ_{(rxn)}$

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

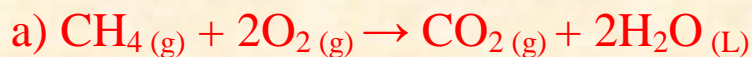
$\Delta G^\circ F \rightarrow$ standard free energy of formation

Standard free energy of formation \rightarrow is the free energy change that occurs when 1 mole of the compound is synthesized from its elements in their standard states.

✓ The standard free energy of formation of any element in its stable **allotropic** form at 1 atm and 25°C is **zero**.

Example 1:

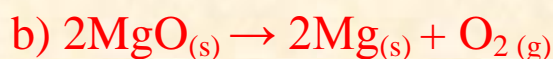
Calculate the standard free energy changes for the following reactions at 25°C.



Solution

$$\Delta G^\circ(\text{rxn}) = [\Delta G^\circ\text{F}(\text{CO}_2) + 2\Delta G^\circ\text{F}(\text{H}_2\text{O})] - [\Delta G^\circ\text{F}(\text{CH}_4) + 2\Delta G^\circ\text{F}(\text{O}_2)]$$

$$\Delta G^\circ(\text{rxn}) = [-394.4 + (2 * -237.2)] - [-50.8 + 2 * 0] = -818\text{KJ/mole}$$



$$G^\circ(\text{rxn}) = [2\Delta G^\circ\text{F}(\text{Mg}) + \Delta G^\circ\text{F}(\text{O}_2)] - [2\Delta G^\circ\text{F}(\text{MgO})]$$

$$G^\circ(\text{rxn}) = [2 * 0 + 0] - [(2) * -569.6] = 1139 \text{ KJ/mole}$$

Applications of ($\Delta G = \Delta H - T\Delta S$) equation☒ How to predict the sign of ΔG

1) If both ΔH and ΔS are positive, then ΔG will be negative only when the $T\Delta S$ term is greater in magnitude than ΔH .

→ This condition is met when T is large.

2) If ΔH is positive and ΔS is negative, ΔG will always be positive regardless of temperature.

3) If ΔH is negative and ΔS is positive, then ΔG will be negative regardless of temperature.

4) If ΔH is negative and ΔS is negative, then ΔG will be negative only when $T\Delta S$ is smaller in magnitude than ΔH .

→ This condition is met when T is small.

TABLE 18.3 Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$

| ΔH | ΔS | ΔG | Example |
|------------|------------|--|--|
| + | + | Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction. | $2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$ |
| + | - | ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures. | $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$ |
| - | + | ΔG is always negative. Reaction proceeds spontaneously at all temperatures. | $2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ |
| - | - | Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous. | $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$ |

Note that:

- ✘ The temperatures that will cause ΔG to be negative for the first and last cases depend on the actual values of ΔH and ΔS of the system.
- ✘ Under nonstandard state conditions, we must use the sign of ΔG rather than that of ΔG° to predict the direction of the reaction.
- ✘ The sign of ΔG° , tells us whether the products or the reactants are favored when the reacting system reaches equilibrium.
- ✘ A negative value of ΔG° , indicates that the reaction favors product formation.
- ✘ A positive value of ΔG° indicates that there will be more reactants than products at equilibrium.

Temperature and chemical reactions

☒ Preparation of calcium oxide "quick lime".

It's prepared by decomposing lime stone " CaCO_3 " in a kiln at a high Temperature.



→ the reaction is reversible and CaO readily combines with CO_2 to form CaCO_3

→ the pressure of CO_2 in equilibrium with CaCO_3 and CaO increases with temperature.

→ CO_2 is removed from the kiln to shift the equilibrium from left to right, promoting the formation of calcium oxide.

☒ We need to calculate the temperature at which the decomposition of CaCO_3 becomes appreciable.

1) we calculate ΔH° and ΔS° for the reaction at 25°C .

$$\Delta H^\circ = [\Delta H^\circ\text{F}(\text{CaO}) + \Delta H^\circ\text{F}(\text{CO}_2)] - [\Delta H^\circ\text{F}(\text{CaCO}_3)]$$

$$= [-635.6 + (-393.5)] - [-1206.9]$$

$$= 177.8 \text{ KJ/mol.}$$

$$\Delta S^\circ = [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - [S^\circ(\text{CaCO}_3)]$$

$$= [39.8 + 213.6] - [92.9]$$

$$= 160.5 \text{ J/K.mol.}$$

2) we calculate ΔG° for the reaction.

$$\therefore \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 177.8 - (298 * \frac{160.5}{1000}) = 130 \text{ KJ/mol}$$

Note that

Because ΔG° is a large positive, the reaction is not favored for product formation at 25°C .

- We need to make ΔG° negative.

We first have to find the temperature at which ΔG° is zero.

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{177.8 \times 1000}{160.5} = 1108\text{K}$$

$$T = 1103 - 273 = 835^\circ\text{C}$$

Note that

→ At temperature higher than 835°C , ΔG° becomes negative.

→ This indicating that the reaction now favors the formation of CaO and CO_2 .

→ The Fact that ΔG° is positive value at some temperature below 835°C does not mean that no CO_2 is produced, but rather that the pressure of the CO_2 gas formed at the temperature will be below 1 atm.

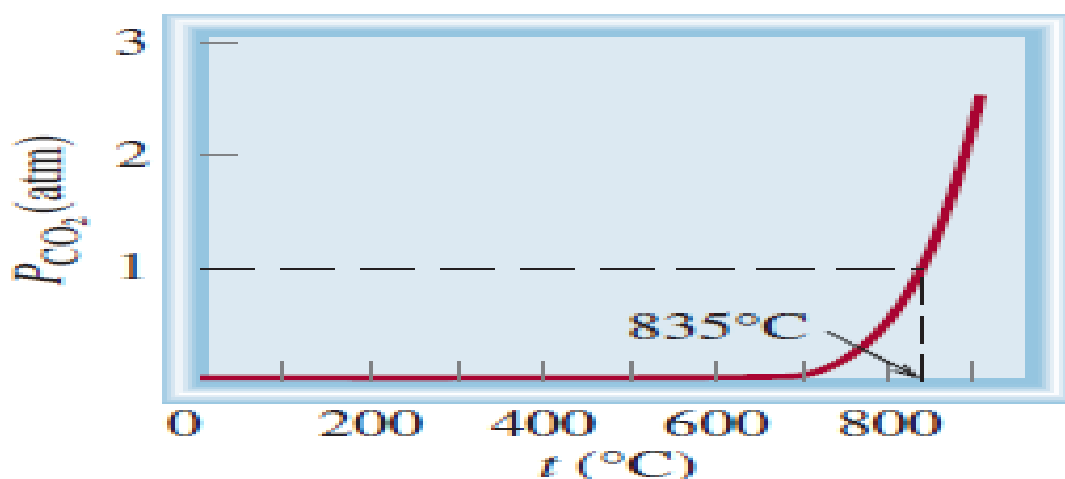


Figure show: Equilibrium pressure of CO₂ from the decomposition of CaCO₃, as a function of temperature. This curve is calculated by assuming that ΔH° and ΔS° of the reaction do not change with temperature.

Phase Transition

phase transition → as melting point or boiling point.

- At phase transition the system is at equilibrium.

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

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

$$\Delta S = \frac{\Delta H}{T}$$

For an (**ice** → **water**) transition

$$\Delta S_{\text{ice-water}} = \frac{\Delta H}{T}$$

ΔH → molar heat of fusion

T → the melting point

$$\Delta S_{\text{ice-water}} = \frac{6010\text{J/mol}}{273\text{K}} = \frac{22\text{J}}{\text{k.mol}}$$

- when 1 mole of ice melts at 0°C , there is an increase in entropy of 22J/K.mol.

For an (**water** → **ice**) transition

$$\Delta S_{\text{ice-water}} = \frac{\Delta H}{T}$$

$$\Delta S_{\text{ice-water}} = \frac{-6010\text{J/mol}}{273\text{K}} = \frac{-22\text{J}}{\text{k.mol}}$$

- when 1 mole of water change into ice , there is a decrease in entropy of -22J/K.mol

Example:

The molar heats of fusion and vaporization of benzene are 10.9 KJ/mol and 31KJ/mol respectively. Calculate the entropy changes for the(solid \rightarrow liquid) and(liquid \rightarrow vapor) transitions for benzene . at 1 atm pressure , benzene melts at 5.5°C and boils at 80.1°C.

Solution

$$\Delta S_{\text{solid-liquid}} = \frac{\Delta H_{\text{fus}}}{T_f} = \frac{10.9 \times 1000}{5.5 + 273} = \frac{39.1 \text{J}}{\text{K.mol}}$$

$$\Delta S_{\text{liquid-vapor}} = \frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} = \frac{31 \times 10^3}{80.1 + 273} = \frac{87.8 \text{J}}{\text{K.mol}}$$

Choose

1) From Second Law of thermodynamics

A) $\Delta S_{\text{uni}} \geq 0$

C) $\Delta S_{\text{uni}} < 0$

B) $S_{\text{sys}} = 0$

D) $\Delta S_{\text{uni}} = 0$

2) For a spontaneous process.

A) $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

C) $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} < 0$

B) $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} - \Delta S_{\text{surr}} > 0$

D) None of them

3) If the changes in enthalpy and entropy of the system are such that $\Delta S_{\text{sys}} - T\Delta S_{\text{sys}}$ is less than zero, the process must be.....

A) Spontaneous

C) Reversible

B) non-Spontaneous

D) irreversible

4) When the reaction is spontaneous in the forward direction, ΔG

A) $\Delta G > 0$

C) $\Delta G = 0$

B) $\Delta G < 0$

D) ΔG infinity

5) When $\Delta G < 0$, the reaction is..... in the forward direction.

- A) reversible
B) irreversible
C) non-spontaneous
D) spontaneous

6) When $\Delta G > 0$, the reaction is..... in the forward direction.

- A) spontaneous
B) non-spontaneous
C) reversible
D) irreversible

7) When $\Delta G > 0$, the reaction is..... in the opposite direction.

- A) spontaneous
B) non-spontaneous
C) reversible
D) irreversible

8) When the reaction is in equilibrium , ΔG

- A) $\Delta G > 0$
B) $\Delta G < 0$
C) $\Delta G = 0$
D) ΔG infinity

9) The change in free energy of a system for a constant temp. process is given by.....

- A) $\Delta G = \Delta H + T\Delta S$
B) $\Delta G = \Delta S + T\Delta H$
C) $\Delta G = \Delta H - T\Delta S$
D) $\Delta G = T\Delta S - \Delta H$

10) Is the free energy change for a reaction when it occurs under standard-state conditions.....

- A) ΔH° C) ΔG°
B) ΔG D) ΔH

11) Is the free energy change that occurs when 1 mole of the compound is synthesized from its elements in their standards state.....

- A) ΔG C) ΔG°_f
B) $\Delta G^\circ_{\text{rxn}}$ D) ΔH°

12) If ΔH is positive and ΔS is negative, ΔG will always be

- A) Zero C) negative
B) positive D) infinity

13) ΔG will always be positive if ΔH and ΔS

- A) negative - positive C) positive - positive
B) positive - negative D) negative - negative

14) If ΔH is negative and ΔS is positive, ΔG will always be

- A) positive C) zero
B) negative D) infinity

15) ΔG will always be negative if ΔH and ΔS

- A) positive - positive
B) positive - negative
C) negative - negative
D) negative - positive

16) If both ΔH and ΔS are positive , then ΔG will be..... only when $T\Delta S$ term is greater in magnitude than ΔH .

- A) Positive
B) Negative
C) infinity
D) zero

17) ΔG will be negative only when $T\Delta S$ term is greater in magnitude than ΔH if ΔH and ΔS

- A) positive - positive
B) positive - negative
C) negative - negative
D) negative - positive

18) under nonstandard state conditions, we must use the sign of to predict the direction of the reaction.

- A) ΔG
B) ΔG°
C) ΔH
D) ΔH°

24) Melting point or evaporation is called

- A) Phase difference
B) phase transition
C) transition state
D) none of them

25) Which species will have the greatest absolute entropy at 25°C?

- A) C₄H_{10(g)}
B) C₂H₅OH_(l)
C) H₂O_(l)
D) C₂H_{2(g)}

26) Which species will have the lowest absolute entropy at 25°C?

- A) C₂H₅OH_(l)
B) C₂H_{2(g)}
C) C₃H_{8(g)}
D) C₃H₇OH_(l)