Outline

- Entropy
- Free Energy
- Chemical Changes
- Temperature and Concentration Dependence
- Coupled Reactions

Entropy

A spontaneous process is one that occurs by itself (no matter how fast)

All spontaneous processes increase in a property called <u>entropy</u>

Entropy (S) a measure of randomness or disorder

describes the number of arrangements available to a system in a given state

Probability that depends on number of arrangements is <u>positional</u> <u>probability</u>

Spontaneous processes proceed to the state with the highest positional probability (highest entropy)



We will find 2 molecules in each bulbs...

greatest # arrangements, highest positional probability, entropy is highest! Which has the higher entropy?

 $CO_{2}(s) \text{ or } CO_{2}(g)$ $CO_{2}(g) \qquad S_{solid} < S_{liquid} << S_{gas}$

Predict the sign of the entropy change for each:

sugar dissolves in water: ΔS is positive (increases entropy)

iodine vapor condenses: ΔS is negative (decreases entropy)

The Second Law of Thermodynamics

In any spontaneous process there is always an increase in the entropy of the universe

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur}$$
 for spontaneous process, $\Delta S_{univ} > 0$

 $H_2O(I) + energy \rightarrow H_2O(g)$

 $\begin{array}{ll} \Delta S^{o}{}_{sys} > 0 & \text{more disorder} \\ \Delta S^{o}{}_{sur} < 0 & \text{energy given to system} \\ \Delta S^{o}{}_{univ} < 0 & \text{below 100 °C} \\ \Delta S^{o}{}_{univ} > 0 & \text{above 100 °C} \end{array}$

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

$$q = heat transferred, J$$

$$T = temperature, K$$

$$\Delta S units of J/K$$

Entropy change depends on:

1. direction of heat flow q = +, energy in q = -, energy out

2. magnitude of temperature

Calculate ΔS_{sur} , ΔS_{sys} , ΔS_{univ} for $H_2O(I) \rightarrow H_2O(g) \quad \Delta H = 44 \text{ kJ/mol } H_2O(g)$

on a hot plate at 250. °C and 1 atm. Assume 1 mol of H₂O...

$$\Delta S_{sur} = \frac{q}{T} = \frac{-44 \text{ kJ}}{523 \text{ K}} = \frac{-84 \text{ J/K}}{523 \text{ K}}$$
$$\Delta S_{sys} = \frac{q}{T} = \frac{44 \text{ kJ}}{373 \text{ K}} = \frac{120 \text{ J/K}}{373 \text{ K}}$$
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} = 120 \text{ J/K} - 84 \text{ J/K} = \frac{36 \text{ J/K}}{36 \text{ J/K}}$$

Spontaneous! Can boil water with hot plate at 250 °C!

Calculate ΔS_{sur} , ΔS_{sys} , ΔS_{univ} for $H_2O(I) \rightarrow H_2O(g) \quad \Delta H = 44 \text{ kJ/mol } H_2O(g)$

on a hot plate at 25 °C and 1 atm. Assume 1 mol of $H_2O...$

$$\Delta S_{sur} = \frac{q}{T} = \frac{-44 \text{ kJ}}{298 \text{ K}} = \frac{-150 \text{ J/K}}{298 \text{ K}}$$
$$\Delta S_{sys} = \frac{q}{T} = \frac{44 \text{ kJ}}{373 \text{ K}} = \frac{120 \text{ J/K}}{373 \text{ K}}$$
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} = 120 \text{ J/K} - 150 \text{ J/K} = \frac{-30 \text{ J/K}}{200 \text{ J/K}}$$

Nonspontaneous! Can't boil water with hot plate at 25 °C!

Free Energy

Thermodynamic functions...

Another function that deals with spontaneity is...

Free Energy (G): G = H - TS

tells if a process is spontaneous or not

For a process at temperature T:



If $\Delta S_{univ} > 0$ for a spontaneous process, $\Delta G < 0$ for a spontaneous process!

For a process to be spontaneous, ΔG must be negative

 ΔH and ΔS contribute to spontaneity: $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG
(-) exothermic	(+) inc disorder	(-) spontaneous
(+) endothermic	(-) dec disorder	(+) nonspontaneous
(+) endothermic	(+) inc disorder	spont at high T
(-) exothermic	(-) dec disorder	spon at low T

Find ΔG° at -25 °C and 25 °C for the following process:

 $H_2O(s) \rightarrow H_2O(I) \quad \Delta H^\circ = 6030 \text{ J/mol and } \Delta S^\circ = 22.1 \text{ J/mol K}$

Determine if melting or freezing is spontaneous at each temperature.

 $\Delta G^{o} = \Delta H^{o} \text{ - } T \Delta S^{o}$

= 6030 J/mol - (248 K)(22.1 J/mol K)

= 550 J/mol

Forward rxn is nonspontaneous... reverse rxn (freezing) is spontaneous. <u>Water freezes at -25 °C!</u>

For 25 °C...

 $\Delta G^o = \Delta H^o \text{ - } T \Delta S^o$

= 6030 J/mol - (298 K)(22.1 J/mol K)

= **-** 560 J/mol

Forward rxn (melting) is spontaneous... Ice melts at 25 °C!

What does it mean if $\Delta G^{\circ} = 0$? Equilibrium

The temperature of a phase change (like melting) is the temperature that the 2 phases are in equilibrium...

Find the melting point of ice (freezing point of water) at 1 atm pressure.

$$H_2O(s) \rightleftharpoons H_2O(l)$$

Equilibrium at 1 atm pressure, $\Delta G^{\circ} = 0 \text{ kJ}$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$0 = \Delta H^{\circ} - T_{m}\Delta S^{\circ}$$

$$T_{m} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

$$= \frac{6030 \text{ J} / \text{mol}}{22.1 \text{ J} / \text{mol K}} = \underline{273 \text{ K}} \quad (0 \text{ °C})$$

Find the boiling point of water at 1 atm if $\Delta H^{\circ} = 44.0$ kJ/mol and $\Delta S^{\circ} = 118$ J/mol K.

$$H_2O(I) \rightleftharpoons H_2O(g)$$

Equilibrium at 1 atm pressure, $\Delta G^{\circ} = 0 \text{ kJ}$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$0 = \Delta H^{\circ} - T_{b}\Delta S^{\circ}$$

$$T_{b} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

$$= \frac{44000 \text{ J} / \text{mol}}{118 \text{ J} / \text{mol K}} = 373 \text{ K} \quad (100 \text{ }^{\circ}\text{C})$$

Chemical Changes

Predicting ΔS for Chemical Changes

1. ΔS is + (increase) when $s \rightarrow g$ or $I \rightarrow g$

2. ΔS is + when a solid dissolves

3. Δ S is – when a gas dissolves

For substances...

1. S is higher if delocalized systems exist (C_6H_6 , metals)

2. S increases as molar mass increases

The Third Law of Thermodynamics The entropy of a perfect crystal at 0 K is 0 J/K At 0 K At T > 0 KHCI HCI HCI HCL HCI HCI HC HCI HC HCI HCI HC HCI CIH HCI HC HCI HCI HCI HC HCI HCI HCI HCI S = 0 J/KS > 0 J/K

Absolute entropies of substances are listed in their standard states at 25 $^{\rm o}{\rm C}$



 $\Delta S_{rxn}^{o} = \sum n_{p} S^{o}(products) - \sum n_{r} S^{o}(reactants)$

Thermodynamic data is given for standard conditions

- 1. For gases, pressures are 1 atm
- 2. For solids and liquids, external pressure is 1 atm
- 3. For solutions, concentrations are 1 M

Standard thermodynamic data are identified as ΔH^{o} , ΔS^{o} , ΔG^{o}

Calculate ΔS° for $2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$ $S^{\circ}_{NiS} = 53 \text{ J/mol K}$ $S^{\circ}_{O2} = 205 \text{ J/mol K}$ $S^{\circ}_{SO2} = 248 \text{ J/mol K}$ $S^{\circ}_{NiO} = 38 \text{ J/mol K}$

 $\Delta S^{\circ} = [(2 \text{ mol x } 248 \text{ J/mol K}) + (2 \text{ mol x } 38 \text{ J/mol K})] - [(2 \text{ mol x } 53 \text{ J/mol K}) + (3 \text{ mol x } 205 \text{ J/mol K})]$

 $\Delta S^{\circ} = -149 \text{ J/K}$ The system is becoming more ordered!

Predicting ΔG for Chemical Changes

1. Standard Free Energies of Formation at 25 °C (ΔG^{o}_{f})

 $\Delta G_{rxn}^{o} = \sum n_{p}G_{f}^{o}(products) - \sum n_{r}G_{f}^{o}(reactants)$

2. $\Delta G = \Delta H - T\Delta S$ or (if standard states) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

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Calculate \Delta G^{\circ} for

2CH_{3}OH(g) + 3O_{2}(g) \rightarrow 2CO_{2}(g) + 4H_{2}O(g)

\Delta G^{\circ}_{CH_{3}OH} = -163 \text{ kJ/mol}

\Delta G^{\circ}_{O_{2}} = 0 \text{ kJ/mol}

\Delta G^{\circ}_{CO_{2}} = -394 \text{ kJ/mol}

\Delta G^{\circ}_{H_{2}O} = -229 \text{ kJ/mol}
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 $\Delta G^{\circ} = [(2 \text{ mol } x -394 \text{ kJ/mol}) + (4 \text{ mol } x -229 \text{ kJ/mol})]$ - [(2 mol x -163 kJ/mol) + (3 mol x 0 kJ/mol)]

 $\Delta G^{\circ} = -1378 \text{ kJ}$ This reaction is spontaneous! (at standard conditions) Calculate ΔH° , ΔS° , ΔG° at 25 °C for NH₄Cl(s) \rightarrow NH₃(g) + HCl(g)

 $\Delta H^{\circ} = [(1 \text{ mol } x - 46 \text{ kJ/mol}) + (1 \text{ mol } x - 92 \text{ kJ/mol})] \\ - [(1 \text{ mol } x - 314 \text{ kJ/mol})]$

 $\Delta \mathsf{H}^{\mathsf{o}} = \underline{\mathsf{176 kJ}}$

 $\Delta S^{\circ} = [(1 \text{ mol x } 193 \text{ J/mol K}) + (1 \text{ mol x } 187 \text{ J/mol K})] - [(1 \text{ mol x } 96 \text{ J/mol K})]$

 $\Delta S^{\circ} = 284 \text{ J/K} = 0.284 \text{ kJ/K}$

 $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} = (176 \text{ kJ}) - (298 \text{ K})(0.284 \text{ kJ/K}) = 91 \text{ kJ}$

At standard conditions, the reaction is nonspontaneous!

At what temperature is this process at equilibrium?

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
$$0 = \Delta H^{\circ} - T\Delta S^{\circ}$$
$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{176 \text{ kJ}}{0.284 \text{ kJ} / \text{ K}} = \underline{620. \text{ K}}$$

For temperatures greater than 620 K...

the process becomes spontaneous at standard conditions!

Calculate ΔH° , ΔS° , ΔG° at 25 °C for the following: $C(s) + 2H_{2}(g) \rightarrow CH_{4}(g)$

 $\Delta H^{\circ} = [(1 \text{ mol } x -75 \text{ kJ/mol})] - [(1 \text{ mol } x \text{ 0 kJ/mol}) + (2 \text{ mol } x \text{ 0 kJ/mol})]$

 $\Delta \mathsf{H}^{\mathsf{o}} = -75 \text{ kJ}$

 $\Delta S^{\circ} = [(1 \text{ mol x 186 J/mol K})] - [(1 \text{ mol x 6 J/mol K}) + (2 \text{ mol x 131 J/mol K})]$ $\Delta S^{\circ} = -82 \text{ J/K} = -\underline{0.082 \text{ kJ/K}}$ $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = (-75 \text{ kJ}) - (298 \text{ K})(-0.082 \text{ kJ/K}) = \underline{-51 \text{ kJ}}$

At standard conditions... the reaction is spontaneous!

$$T = \frac{\Delta H^{o}}{\Delta S^{o}} = \frac{-75 \text{ kJ}}{-0.082 \text{ kJ} / \text{ K}} = 910 \text{ K}$$

For temperatures greater than 910 K...

this process is nonspontaneous at standard conditions

Temperature Dependence

 ΔH° and ΔS° don't change much with temperature, but ΔG° does

 ΔG° determined at temperatures other than 25 °C:

$$\Delta G^{o}_{T} = \Delta H^{o}_{298} - T \Delta S^{o}_{298}$$

Determine ΔG° for the following reaction at 621 K: NH₄Cl(s) \rightarrow NH₃(g) + HCl(g) $\Delta H^{\circ} = 176$ kJ and $\Delta S^{\circ} = 0.284$ kJ/K

$$\Delta G_{621}^{\circ} = \Delta H_{298}^{\circ} - T \Delta S_{298}^{\circ}$$

 $\Delta G_{621}^{\circ} = (176 \text{ kJ}) - (621 \text{K})(0.284 \text{ kJ/K}) = -0.364 \text{ kJ} = 0 \text{ kJ}$

Determine ΔG° for the following reaction at 920 K: $C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H^{\circ} = -75$ kJ and $\Delta S^{\circ} = -0.082$ kJ/K

$$\Delta G^{o}_{920} = \Delta H^{o}_{298} - T \Delta S^{o}_{298}$$

$$\Delta G_{920}^{\circ} = (-75 \text{ kJ}) - (920\text{K})(-0.082 \text{ kJ/K})$$

 $\Delta G^{o}_{920} = \underline{0}.44 \text{ kJ} = \underline{0 \text{ kJ}}$

Concentration Dependence

 ΔG can determine if a reaction is spontaneous or not when reactants and products are not at standard conditions

 $\Delta G = \Delta G^{\circ} + RT Ln Q$ R = 8.314 J/mol K

Q is the reaction quotient...

gases represented with pressure units (atm) solutions represented with concentration units (M) solids and liquid are excluded

for
$$A(s) + B(g) \rightarrow C(I) + D(aq)$$
 $Q = \frac{[D]}{p_B}$

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What is \Delta G for the reaction

N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)
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in a container that is 0.10 atm N₂, 0.20 atm H₂, and 0.30 atm NH₃ at 25 °C. Δ G° is -33.3 kJ/mol for the above reaction.

$$\Delta \mathbf{G} = \Delta \mathbf{G}^{\mathsf{o}} + \mathsf{RT} \, \mathsf{Ln} \, \mathbf{Q}$$

$$Q = \frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3} = \frac{(0.30)^2}{(0.10)(0.20)^3} = 110$$

 $\Delta G = -33300 \text{ J/mol} + (8.314 \text{ J/mol K})(298 \text{ K}) \text{ Ln } 110$

= - 22000 J/mol

What is free energy change at equilibrium?

$$0 = \Delta G = \Delta G^{o} + RT Ln Q$$
$$0 = \Delta G^{o} + RT Ln K_{eq}$$

 $\Delta G^{o} = - RT Ln K_{eq}$

Relation between ΔG° and K_{eq}

$\Delta G^{o} = 0$	$K_{eq} = 1$
$\Delta G^{\circ} < 0$	$K_{eq} > 1$
$\Delta G^{\circ} > 0$	$K_{eq} < 1$

system at equilibrium system shifts to products system shifts to reactants

CH₃CO₂H(aq)
$$\rightleftharpoons$$
 H⁺(aq) + CH₃CO₂⁻(aq)
The K_{eq} (K_a) is 1.76 x 10⁻⁵ at 25 °C. Find ∆G°.
 Δ G^o = - RT Ln K_{eq}
 Δ G^o = - (8.314 J/mol K)(298 K) Ln 1.76 x 10⁻⁵
 Δ G^o = 27100 J/mol

The reaction is nonspontaneous at standard conditions!

$$\Delta G^{o} = - RT Ln K_{eq} \implies \frac{-\Delta G^{o}}{RT} = Ln K_{eq} \implies K_{eq} = e^{-\Delta G^{o}/RT}$$

$$H_2O(I) \rightleftharpoons H_2O(g) \quad \Delta G^\circ = 8 \text{ kJ/mol}$$

At standard conditions, the reaction is nonspontaneous at 25 °C!

For what pressure at 25 °C is this process at equilibrium?

$$\Delta G^{\circ} = -RT Ln K_{eq}$$

$$\Delta G^{\circ} = -RT Ln p_{H_2O}$$

 $p_{H_2O} = e^{-\Delta GO/RT}$

p_{H20} = exp -[(8000 J/mol)/(8.314 J/mol K)(298 K)]

 $p_{H_{20}} = 0.04 \text{ atm}$ (actual vapor pressure: 0.03 atm!)

Calculate the vapor pressure of bromine at 25 °C.

$$Br_2(I) \rightleftharpoons Br_2(g) \Delta G^\circ = 3 \text{ kJ/mol}$$

$$\Delta G^{\circ} = -RT Ln K_{eq}$$

$$\Delta G^{\circ} = -RT Ln p_{Br_2}$$

$$p_{Br_2} = e^{-\Delta GO/RT}$$

 $p_{Br_2} = exp -[(3000 J/mol)/(8.314 J/mol K)(298 K)]$

 $p_{Br_2} = 0.3 \text{ atm}$

Coupled Reactions

Free energy changes for reactions (like enthalpy and entropy changes) are additive

if:
$$rxn 3 = rxn 1 + rxn 2$$

then: $\Delta G_3 = \Delta G_1 + \Delta G_2$

$$\begin{array}{ll} 2 \mathrm{Fe}_2 \mathrm{O}_3(\mathrm{s}) \to 4 \mathrm{Fe}(\mathrm{s}) + 3 \mathrm{O}_2(\mathrm{g}) & \Delta \mathrm{G}^\circ = 1484 \ \mathrm{kJ} \\ \\ \underline{6 \mathrm{CO}(\mathrm{g}) + 3 \mathrm{O}_2(\mathrm{g}) \to 6 \mathrm{CO}_2(\mathrm{g})} & \Delta \mathrm{G}^\circ = -1543 \ \mathrm{kJ} \\ \\ 2 \mathrm{Fe}_2 \mathrm{O}_3(\mathrm{s}) + 6 \mathrm{CO}(\mathrm{g}) \to 4 \mathrm{Fe}(\mathrm{s}) + 6 \mathrm{CO}_2(\mathrm{g}) & \Delta \mathrm{G}^\circ = -59 \ \mathrm{kJ} \end{array}$$

Nonspontaneous reaction can occur if "coupled" to a spontaneous reaction

Coupled reactions common in human metabolism

Oxidation of glucose is a spontaneous process $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(I) \quad \Delta G^\circ = -2870 \text{ kJ}$ Reaction of glucose is coupled with conversion of ADP to ATP $ADP(aq) + HPO_4^{2-}(aq) + 2H^+(aq) \rightarrow ATP(aq) + H_2O(I) \quad \Delta G^\circ = 31 \text{ kJ}$