Section 20.1
Entropy and the Three Laws of Thermodynamics

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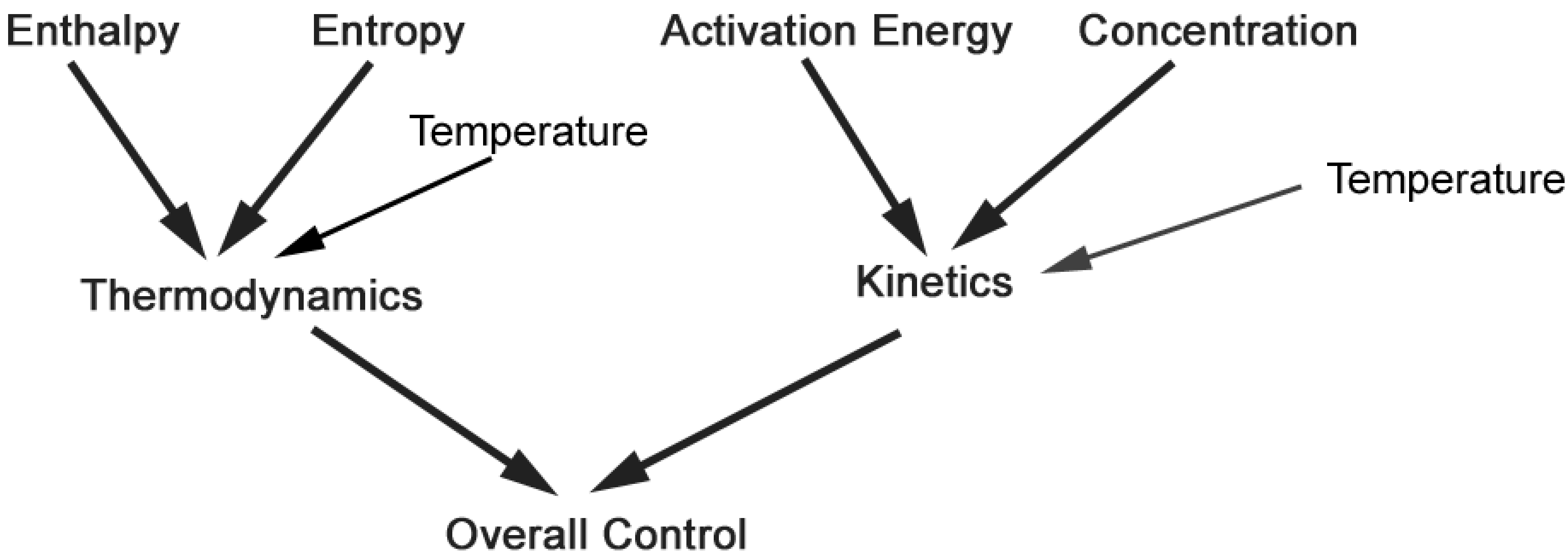
Control of Chemical Reactions



Thermodynamic Control of Reactions

<u>Enthalpy</u>

Bond Energies

– Forming stronger bonds favors reactions.

– Molecules with strong bonds are more stable.

<u>Entropy</u>

Randomness

– Reactions that increase random-ness are favored.

– Forming gases favors reactions.

The Laws of Thermodynamics

1st Law of Thermodynamics: Energy is Conserved

2nd Law of Thermodynamics: All physical and chemical changes occur such that

- at least some energy *disperses,*
- the total concentrated or organized energy of the universe *decreases,* and
- the total diffuse or *dis*organized energy of the universe *increases.*

Any process leads to an increase in total entropy.

In chemical systems entropy is viewed as the freedom of movement of molecules and atoms.

Entropy

A measure of dissipated energy within a system.

Symbol: S
Units: J/K

2nd Law of Thermodynamics:

All physical and chemical changes occur such that the total entropy of the universe increases.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$ = a "spontaneous" system

Standard Molar Entropy

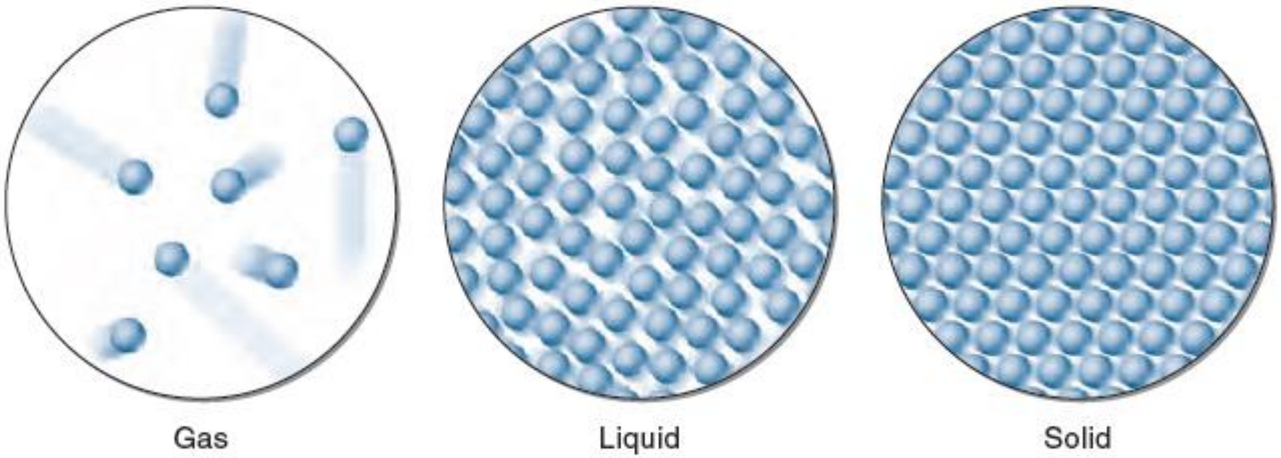
Symbol: S
Units: J/K

Table 19.1.2 Standard Molar Entropies for Some Common Substances at 25 °C

Solids	S^o (J/mol K)	Liquids	S^o (J/mol K)	Gases	S^o (J/mol K)
C(diamond)	2.4	Hg	75.9	He	126.2
C(graphite)	5.7	H_2O	69.9	Ne	146.3
Fe	27.8	CH_3OH	126.8	H_2	130.7
Al	28.3	Br_2	152.2	O_2	205.1
Cu	33.2	H_2SO_4	156.9	H_2O	188.8
CaS	56.5	CH_3CH_2OH	160.7	CO	197.7
KI	106.3	C_6H_6	172.8	CO_2	213.7

Trends in Entropy

State



$Br_2(g)$ = 245.5 J/K vs. $Br_2(\ell)$ = 152.2 J/K

Temperature

As temperature increases, molecular motions increase (even without a phase change). Therefore, S increases with increasing temperature.

Trends in Entropy

Molecular Size: Larger molecules have more vibrational modes and greater freedom of movement

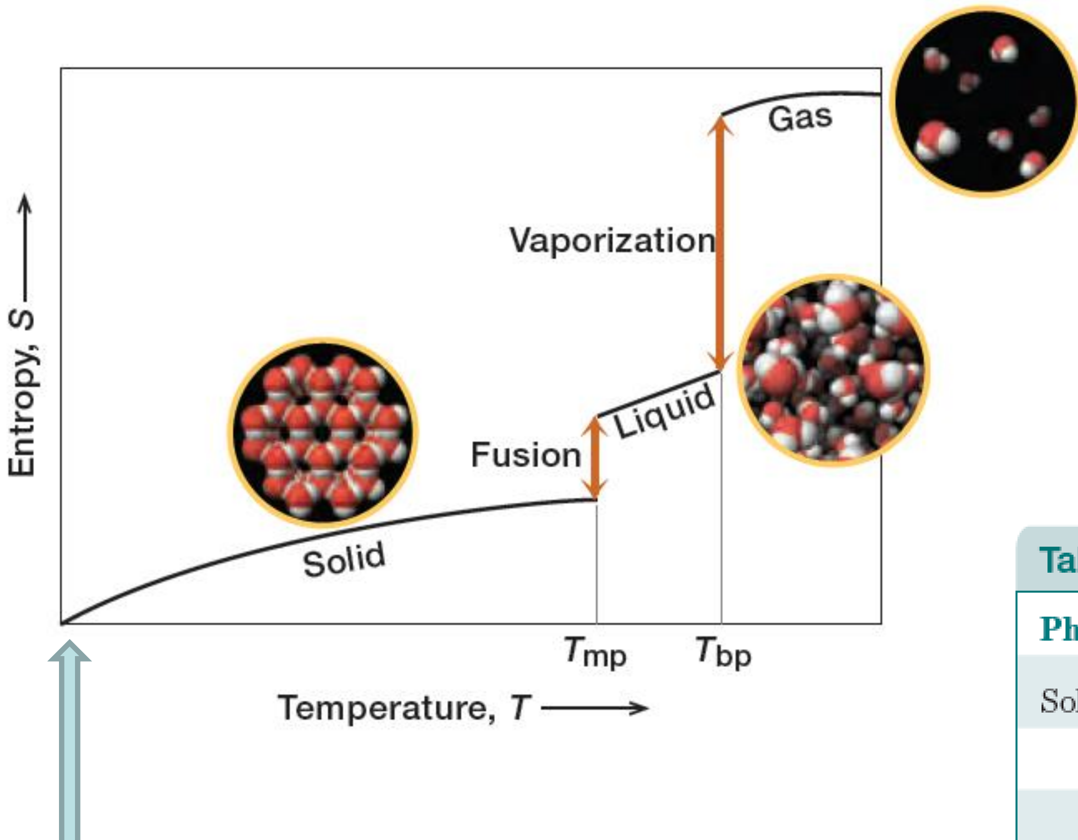
$CH_4(g)$ = 186.3 J/K $CH_3CH_3(g)$ = 229.6 J/K $CH_3CH_2CH_3(g)$ = 269.9 J/K

Forces Between Particles:

Stronger bonding in a solid results in less freedom of movement.

NaF = 51.2 J/K MgO = 26.9 J/K

Where does standard entropy come from?



Entropy of perfect solid at 0 K = 0 J/K

Table 19.1.1 Entropy of H_2O from 2 K to 373 K

Phase	Temperature (K)	$S°$ (J/mol K)
Solid	2	0.00049
	12	0.14
	38	3.1
Liquid	273	64
	300	70
	373	87
Gas	373	197

Section 20.2
Calculating Entropy Change

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Calculating Entropy Change

For the System, in general:

$$\Delta S^o = \sum S^o(products) - \sum S^o(reactants)$$

If the system gets **more random**, ΔS is **positive**. (Favors the reaction)

If the system gets **more ordered**, ΔS is **negative**. (Disfavors the reaction)

Calculating ΔS
Special Case: Phase Changes

$$\Delta S = \frac{q_{rev}}{T} \qquad \Delta S = \frac{\Delta H_{phase\,change}}{T}$$

Heat of fusion (melting) of ice is 6000 J/mol. What is the entropy change for melting ice at 0 ^{o}C?

Calculating ΔS: All other reactions

$$\Delta S^o = \sum S^o(products) - \sum S^o(reactants)$$

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(\ell)$

	S^o(J/K)
$C_3H_8(g)$	= 269.9
$O_2(g)$	= 205.1
$CO_2(g)$	= 213.7
$H_2O(\ell)$	= 69.9

Predicting the sign of entropy change:

What types of reactions lead to increased entropy?

Effect of moles of gas:

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

$$H_2CO(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$$

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

$$2CO_2(g) + N_2(g) \longrightarrow 2CO(g) + 2NO(g)$$

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

What types of reactions lead to increased entropy?

Effect of dissolution:

$NaCl(s) \rightarrow NaCl(aq)$

$S^o(NaCl(s)) = 72.1$ J/K

$S^o(NaCl(aq)) = 115.5$ J/K

$NaOH(s) \rightarrow NaOH(aq)$

$S^o(NaOH(s)) = 64.5$ J/K

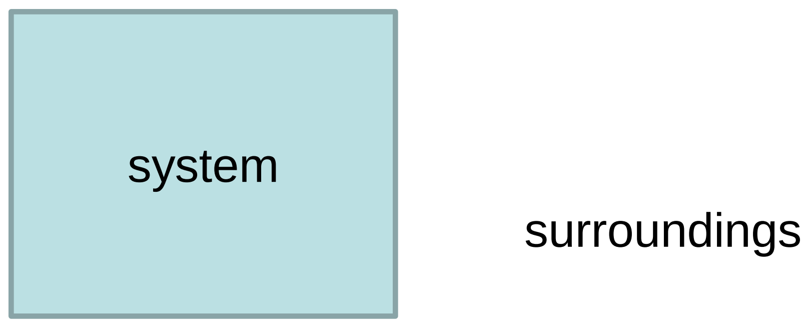
$S^o(NaOH(aq)) = 48.1$ J/K

Entropy vs. Enthalpy Control of Reactions

Second law of thermodynamics: system and surroundings

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

exothermic system:



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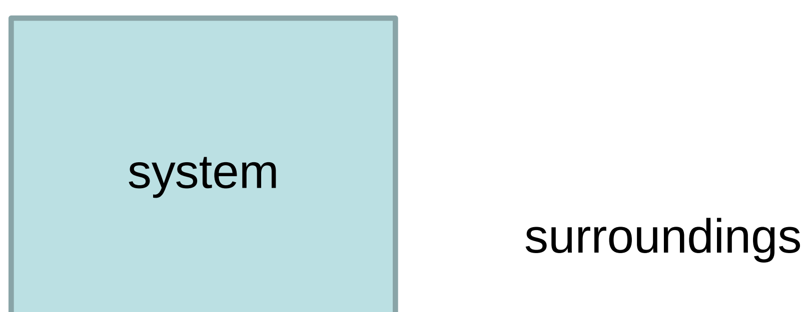
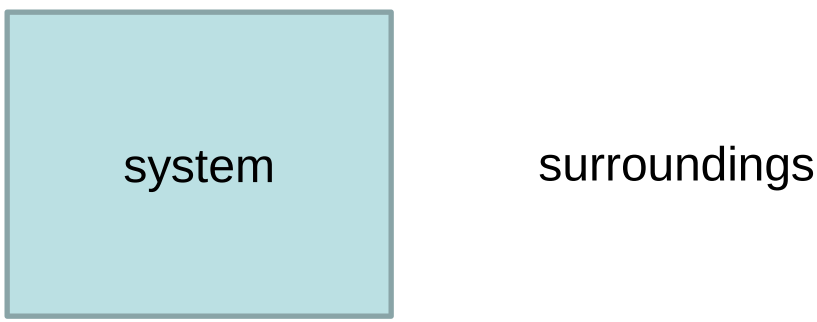
endothermic system:



Entropy vs. Enthalpy Control of Reactions

Second law of thermodynamics: system and surroundings

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$



$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T}$$

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Calculate the entropy change for the universe for the reaction:

$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$

$\Delta H^o = -752.2$ kJ and $\Delta S^o = -351.6$ J/K

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T}$$

Calculate the entropy change for the universe for the reaction:

$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$

$\Delta H^o = -752.2$ kJ and $\Delta S^o = -351.6$ J/K

$\Delta S^o_{universe} = +2171.3$ J/K

The reaction is: _______________ favored.

The reaction ________ favored by entropy.

The reaction ________ favored by enthalpy.

At this temperature, the reaction is controlled by _________________.

Section 20.3
Free Energy

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Putting ΔS, ΔH and Temperature Together

Gibb's Free Energy: $\Delta G = \Delta H - T\Delta S$

When ΔG is *negative*, reaction is *favored*.

When ΔG is *positive*, reaction is *disfavored*.

$2\ Fe_2O_3(s) + 3\ C(s) \rightarrow 4\ Fe(s) + 3\ CO_2(g)$

$\Delta H = +468$ kJ

$\Delta S = +561$ J/K

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

What is ΔG at 25 ^oC and at 1000 ^oC?

Enthalpy vs. Entropy Control of Reactions

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

At high temperatures:

At low temperatures:

Temperature Domains and Reaction Favorability

ΔS \ ΔH	+	-
+		
-		

$2\ Fe_2O_3(s) + 3\ C(s) \rightarrow 4\ Fe(s) + 3\ CO_2(g)$

$\Delta H = +468$ kJ

$\Delta S = +561$ J/K

In what temperature range
will this reaction be favored?

High or low?

What temperature?

Free Energy vs. Temperature Curves

Catalytic Converters

Nitrogen oxides cause smog.

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$ $\Delta H = +180\ kJ$

$\Delta S = +25\ J/K$

Free Energy of Formation: *Only used at 25 °C*

ΔG^o_f*(compound) =* ΔG^o *for reaction to make 1 mol from elements in their natural states*

Table 19.3.2 Selected Standard Free Energies of Formation for Pure Substances at 25 °C

Substance	ΔG_f^o (kJ/mol)	Substance	ΔG_f^o (kJ/mol)
C(diamond)	2.9	Hg(ℓ)	0
C(graphite)	0	HCl(g)	−95.3
CO(g)	−137.2	HCl(aq)	−131.2
CO_2(g)	−394.4	$FeCl_2$(s)	−302.3
CH_3OH(ℓ)	−166.3	Cu(s)	0
CH_3CH_2OH(ℓ)	−174.8	H_2O(g)	−228.6
C_6H_6(ℓ)	124.5	H_2O(ℓ)	−273.1
H_2(g)	0		

Free Energy of Formation: *Only used at 25 °C*

$$\Delta G^o = \sum \Delta G_f^o(products) - \sum \Delta G_f^o(reactants)$$

$CH_3CH_2OH(\ell) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(\ell)$

Table 19.3.2 Selected Standard Free Energies of Formation for Pure Substances at 25 °C

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C(diamond)	2.9	$Hg(\ell)$	0
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$CH_3OH(\ell)$	−166.3	Cu(s)	0
$CH_3CH_2OH(\ell)$	−174.8	$H_2O(g)$	−228.6
$C_6H_6(\ell)$	124.5	$H_2O(\ell)$	−273.1
$H_2(g)$	0		