Predicting Relative S° Values

See Appendix B for tables of standard molar entropies (S°) at 298 K (25 °C)

--Using the ideas of disorder and W.

(1) As temperature increases, entropy increases

Increase in T increases the heat energy, so increases the average kinetic energy of the atoms or molecules, i.e. greater positional disorder, i.e. greater entropy. Fig 20.6

For Cu (s):	T (K):	273	295	298	
	S°:	31.0	32.9	33.2	J/mol.K

(2) When more ordered phase → more disordered phase, $\Delta S > 0$

$Na(s) \rightarrow Na(g)$

S°: 51.4 153.6 $\Delta S° = 102.2\ J.mol^{-1}K^{-1}$ Fig 20.7

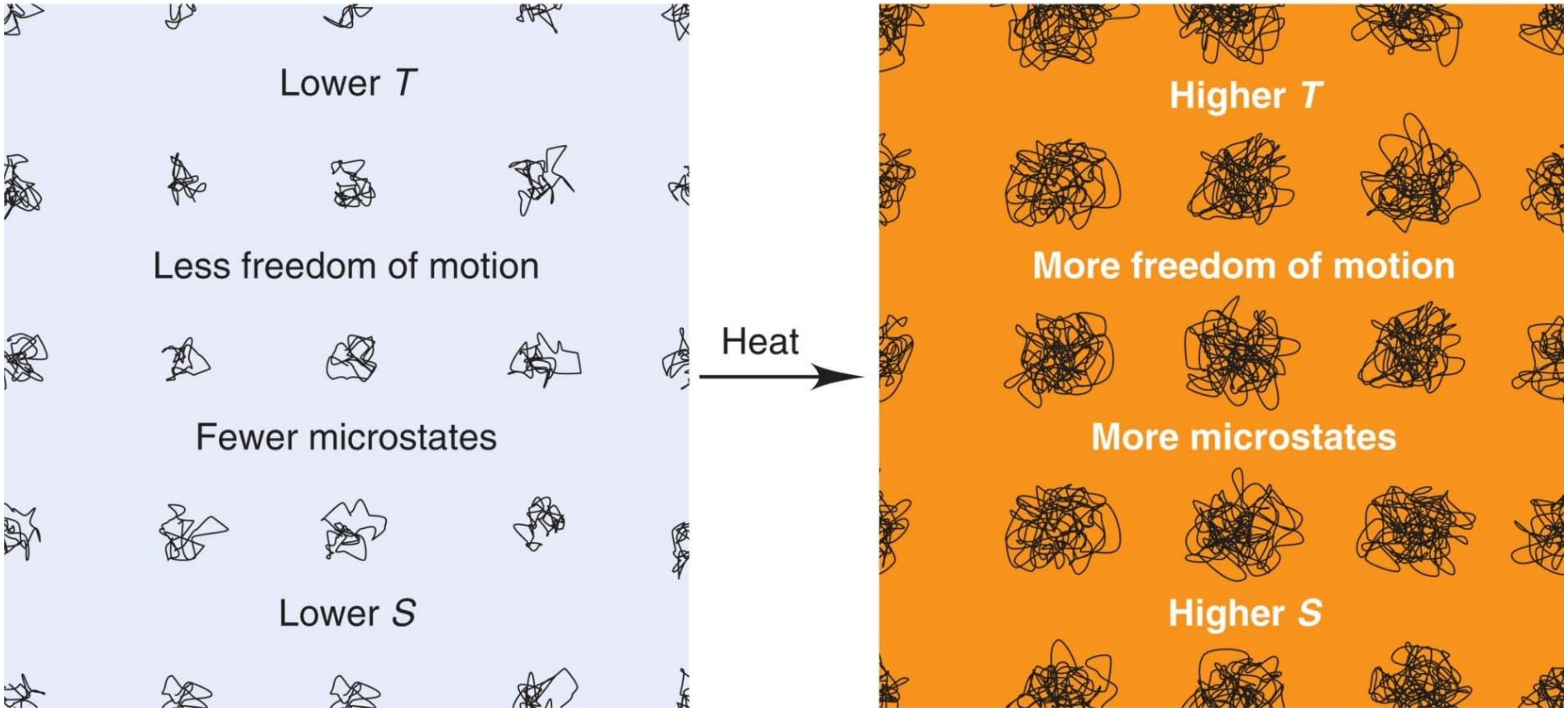
(3) Dissolution of solid or liquid increases its entropy but we must be careful to also consider the entropy of the solvent.

NaCl (s) = 72.1	but	$AlCl_3$ (s) = 110.7	J/mol.K
NaCl (aq) = 115.1		$AlCl_3$ (aq) = -148	J/mol.K

$\Delta S°$ for dissolution of NaCl > 0 <u>but</u> $\Delta S°$ for dissolution of $AlCl_3$ < 0 Fig 20.8

Why? Because although $AlCl_3$ breaks up into more disordered Al^{3+} and 3 Cl^-, the water molecules become highly ordered around small, highly charged Al^{3+}. So, usually, $\Delta S°$ for dissolution > 0 (positive): occasionally, $\Delta S < 0$ if it involves small, highly charged ions such as Al^{3+}.

Figure 20.6A Visualizing the effect of temperature on entropy.



Computer simulations show each particle in a crystal moving about its lattice position. Adding heat increases *T* and the total energy, so the particles have greater freedom of motion, and their energy is more dispersed. *S* therefore increases.

Figure 20.7 The increase in entropy during phase changes from solid to liquid to gas.

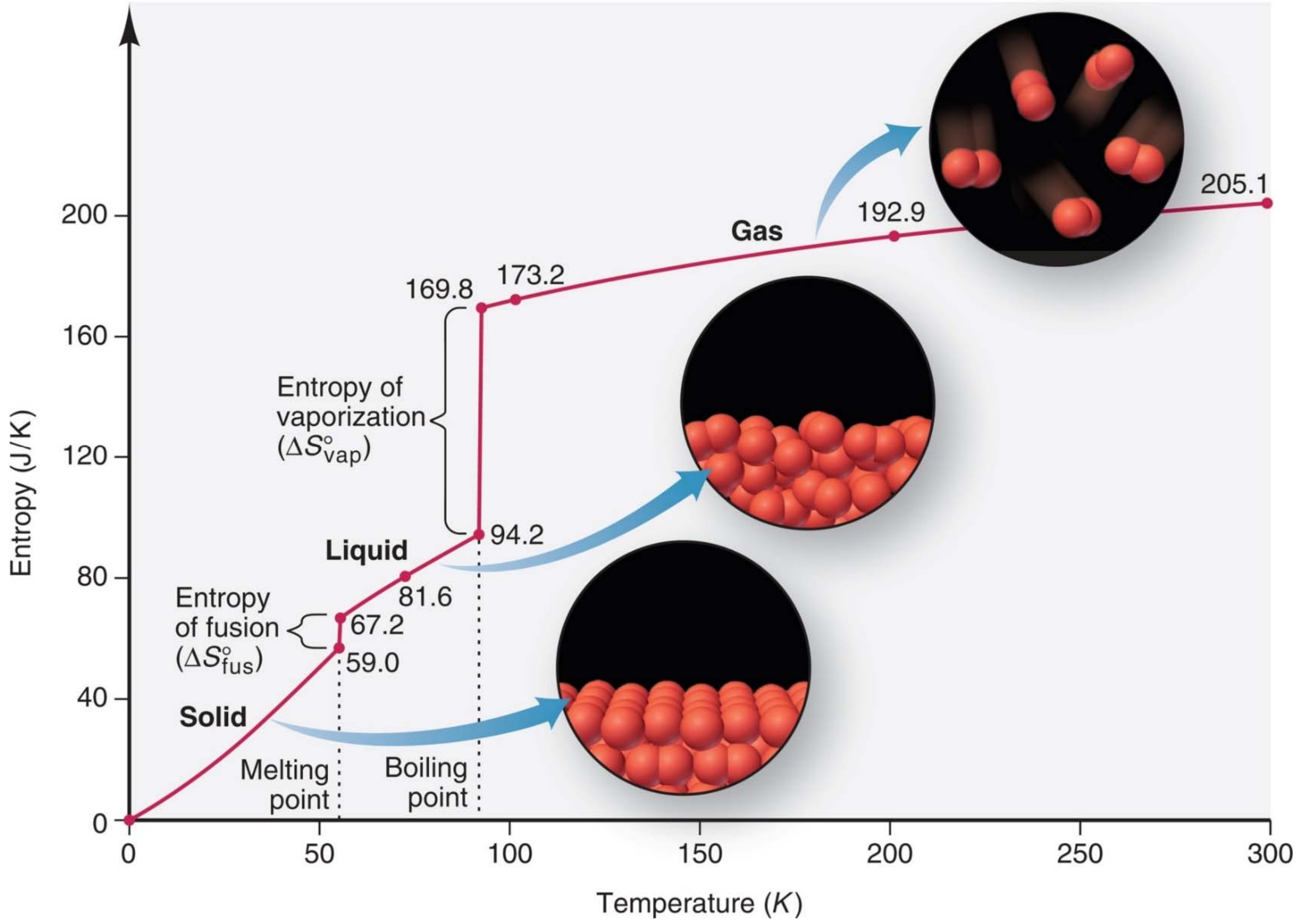
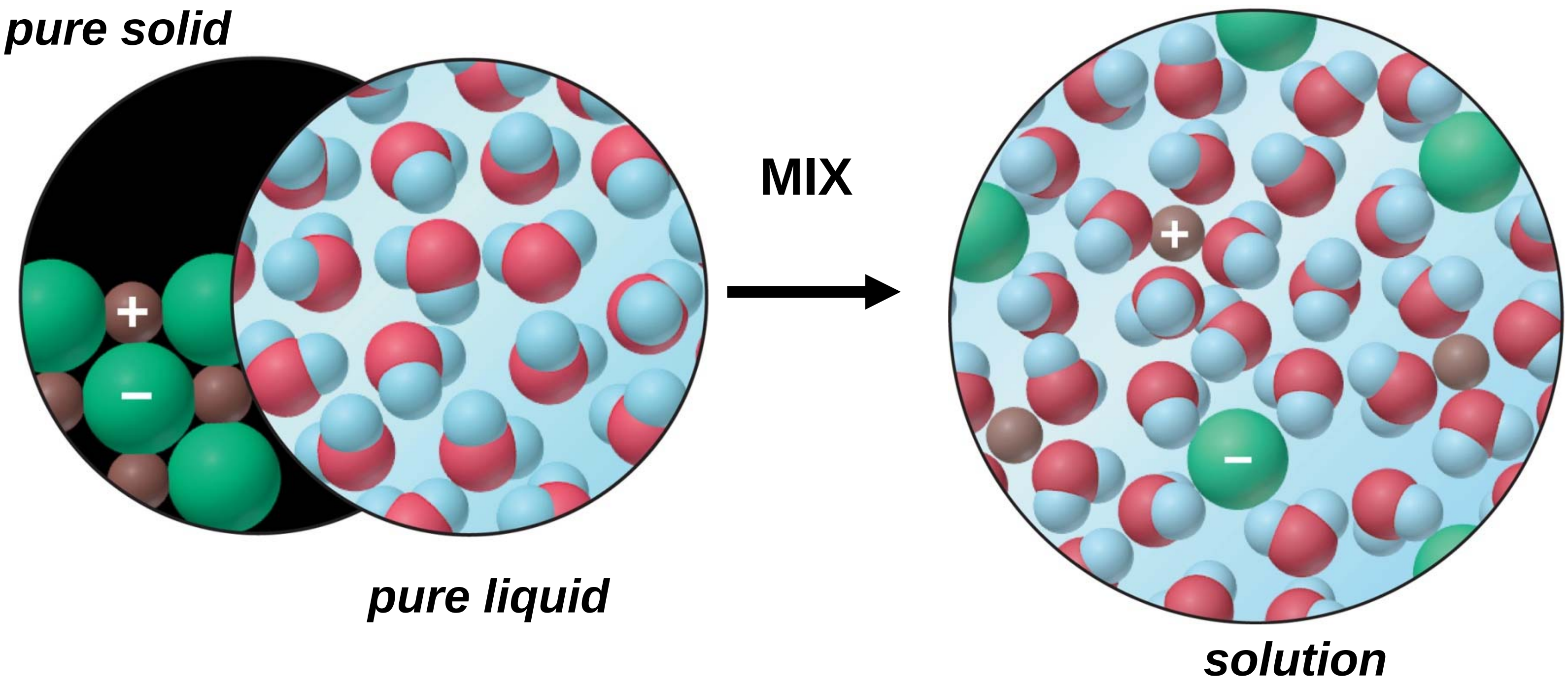


Figure 20.8 The entropy change accompanying the dissolution of a salt.



Usually, ∆S° > 0 (positive) for dissolution of solid in liquid, unless a small highly charged ion such as Al^{3+} is involved.

For non-ionic substances: ΔS much smaller, due to no separation into ions. For mixing H_2O and MeOH (or EtOH), there is little change to H-bonding interactions $\therefore$ ΔS small

Pure MeOH (l): $S^\circ = 127$ $\therefore$ $\Delta S^\circ = 5$ $J.mol^{-1}.K^{-1}$. Fig. 20.9
MeOH (aq) $S^\circ = 132$ small !

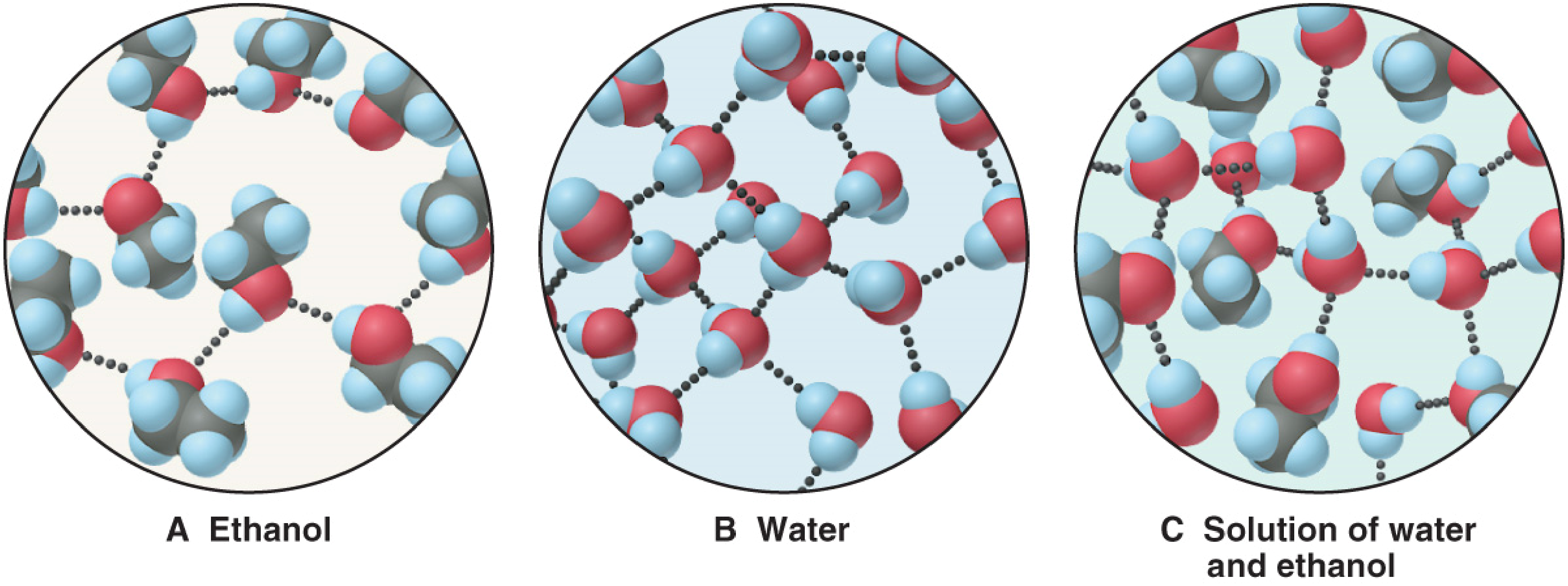
(4) Dissolution of a gas decreases entropy: Gases are very disordered, so dissolution gives a more ordered solution $\therefore$ entropy always decreases on dissolution. Fig. 20.10
However, mixing one gas into another increases entropy.

(5) Complexity of the substance: For a given phase, S° depends on atomic size and molecular complexity.

e.g.,	Li →	Na →	K →	Rb →	Cs	(down a group)
S°(s)	29.1	51.4	64.7	69.5	85.2	$J.mol^{-1}K^{-1}$

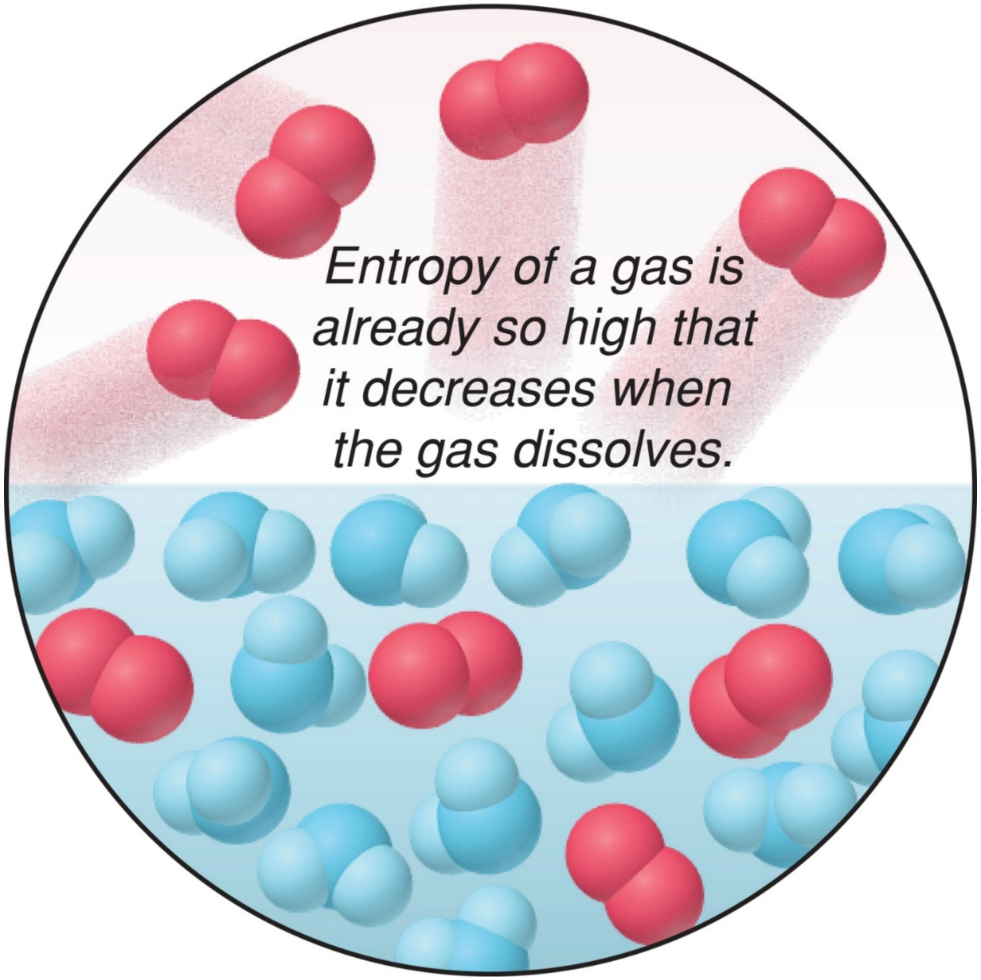
Also, CF_4 (g) (261.5) < CCl_4 (g) (309.7) $J.mol^{-1}.K^{-1}$.

Figure 20.9 The small increase in entropy when ethanol dissolves in water.



Ethanol (A) and water (B) each have many H bonds between their own molecules. In solution (C) they form H bonds to each other, so their freedom of motion does not change significantly.

Figure 20.10 The entropy of a gas dissolved in a liquid.



For different forms of an element, S° less for form with stronger, more directional bonds, *e.g.* C (diamond) *vs* C (graphite). S° (diamond) < S° (graphite)

For compounds (ionic or molecular), S° greater for greater complexity (number of atoms/ions involved) (IF phase is the same!) Fig 20.11

e.g.,	$Cl\ (g)$	<	$Cl_2\ (g)$		$O\ (g)$	<	$O_2\ (g)$	<	$O_3\ (g)$	
	165.1		223.0		16		205		239	$J.mol^{-1}.K^{-1}$

$CH_4\ (g)$	<	$C_2H_6\ (g)$	<	$C_3H_8\ (g)$	<	$C_4H_{10}\ (g)$	
186.1		229.5		269.9		310	$J.mol^{-1}.K^{-1}$

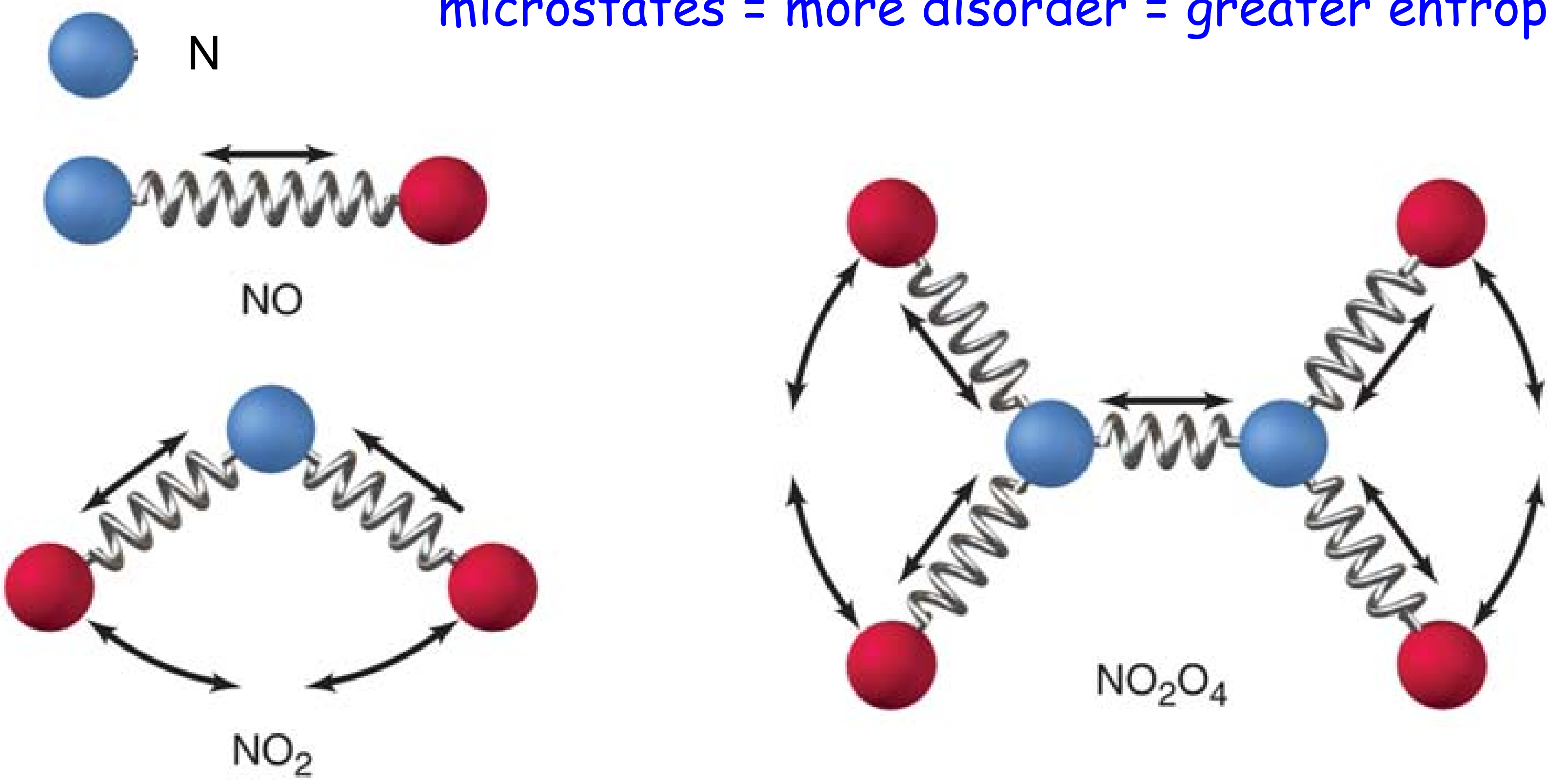
e.g.,	HF	<	HCl	<	HBr	<	HI	
	173.7		186.8		198.6		206.3	$J.mol^{-1}.K^{-1}$

Note:	$CH_4\ (g)$	<	$CH_3OH\ (g)$
	186.1		238
but	$CH_4\ (g)$	>	$CH_3OH\ (l)$
	186.1		127

Must compare same phase (e.g., gas with gas) otherwise complexity rule doesn't hold.

Figure 20.11 Molecular complexity, vibrational motion, and entropy

More atoms = more ways of vibrating = more microstates = more disorder = greater entropy



	N	NO	NO_2	N_2O_4
S^0	153.2	211	240	304

J/mol.K

Sample Problem 20.1 Predicting Relative Entropy Values

PROBLEM: Choose the member with the higher entropy in each of the following pairs, and justify your choice [assume constant temperature, except in part (e)]:

(a) 1 mol of $SO_2(g)$ or 1 mol of $SO_3(g)$

(b) 1 mol of $CO_2(s)$ or 1 mol of $CO_2(g)$

(c) 3 mol of $O_2(g)$ or 2 mol of $O_3(g)$

(d) 1 mol of KBr(*s*) or 1 mol of KBr(*aq*)

(e) seawater at 2°C or at 23°C

(f) 1 mol of $CF_4(g)$ or 1 mol of $CCl_4(g)$

For c), number of moles is more important than complexity difference

20.2 Calculating Entropy Changes (ΔS°)

-- it is very useful to be able to predict sign of ΔS°

Consider $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

Change in entropy (ΔS°) = S° (products) – S° (reactants)

Prediction: 4 moles of gas → 2 moles of gas
(greater disorder → less disorder)
(less order → more order)

$\therefore$ we predict change in entropy (ΔS°) will be < 0 (negative)

Calculation: $\boxed{\Delta S^\circ_{rxn} = \Delta S^\circ = \sum mS^\circ_{prod} - \sum nS^\circ_{reacts}}$

ΔS°_{rxn} = standard entropy of reaction
m and n are coefficients in balanced eqn

$\therefore\ \Delta S^\circ = [2\text{mol.}S^\circ(NH_3) - 1\text{mol.}S^\circ(N_2) - 3\text{mol.}S^\circ(H_2)]$

$\therefore\ \Delta S^\circ = [2(193) - 1(91.5) - 3(130.6)]$ J/K

= -197 J/K (note units: this is ΔS° for the reaction as written above)

$\therefore\ \Delta S^\circ < 0$, as predicted)

Further Examples

(1) Na (s) → Na (g)

prediction: solid → gas, $\Delta S^\circ_{rxn} > 0$

calculation: $\Delta S^\circ_{rxn} = S^\circ_{prod} - S^\circ_{react} = (153.61 - 51.446)$ J/K

$\therefore \Delta S^\circ_{rxn} = 102.16$ J/K (> 0, as predicted)

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

prediction: 6 moles gas → 3 moles gas

Decrease in disorder $\therefore$ predict $\Delta S^\circ_{rxn} < 0$

Note: in a reaction with gases and liquids or solids, gases are so much more disordered than liquids or solids that they dominate what happens to ΔS°_{rxn}

calculation: $\Delta S^\circ_{rxn} = S^\circ_{prods} - S^\circ_{reacts}$

$\Delta S^\circ_{rxn} = [3(213.7) + 4(69.9) - 1(269.9) - 5(205.0)]$ J/K

$\therefore \Delta S^\circ_{rxn} = -374.2$ J/K (< 0, as predicted)

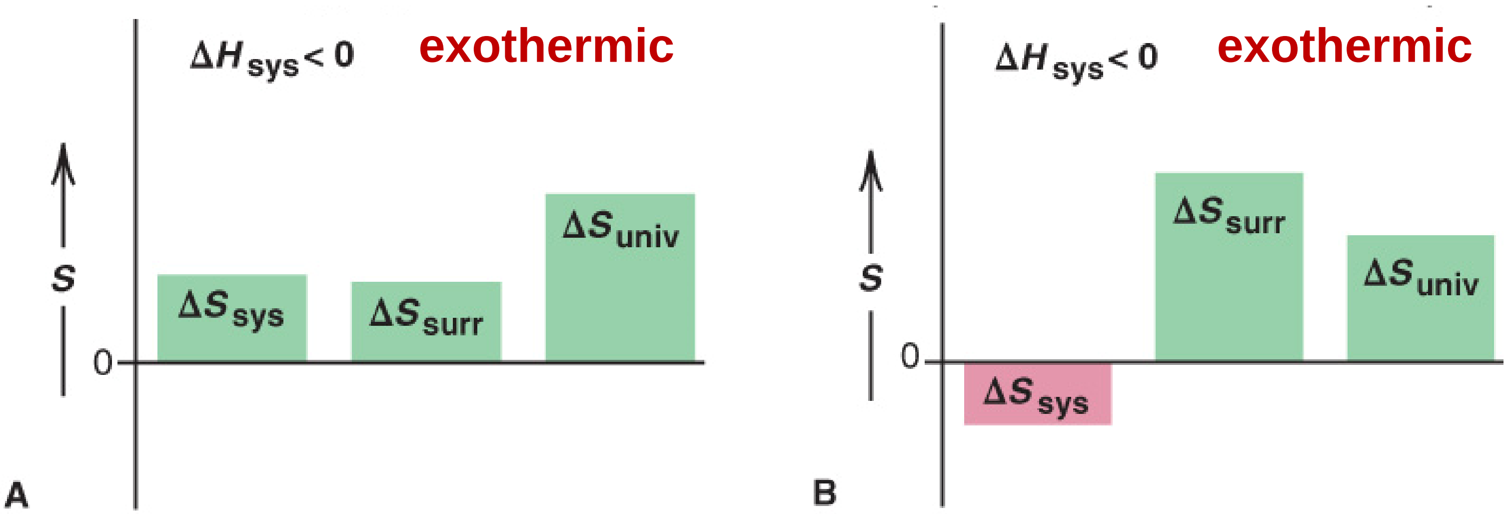
Now, let's look at ΔS_{surr} for the last reaction above:

Burning of propane is a spontaneous rxn, as we all know:

So, since $\Delta S_{univ} > 0$, and $\Delta S_{rxn} < 0$, See Fig. 20.13

$\therefore$ it must be that $\Delta S_{surr} \gg 0$ (remember: $\Delta S_{univ} = \Delta S_{rxn} + \Delta S_{surr}$)

Figure 20.13AB Components of ΔS°_{univ} for spontaneous reactions.



For an exothermic reaction in which $\Delta S_{sys} > 0$, the size of ΔS_{surr} is not important since $\Delta S_{surr} > 0$ for all exothermic reactions. The reaction will always be spontaneous.

For an exothermic reaction in which $\Delta S_{sys} < 0$, ΔS_{surr} must be ***larger*** than ΔS_{sys} for the reaction to be spontaneous.

ΔS_{surr} is always > 0 for exothermic reactions.

Let's now think about ΔS_{surr} more:

It turns out that ΔS_{surr} is related to ΔH_{rxn} !!

Why? Think about it:

ΔH_{rxn} gives heat (q) to, or takes heat from surroundings $\therefore$ the entropy ΔS_{surr} of the surroundings will be changed

(A) If $\Delta H_{rxn} < 0$ (exothermic), $q_{sys} < 0$, $q_{surr} > 0$ $\therefore$ $\Delta S_{surr} > 0$
(B) If $\Delta H_{rxn} > 0$ (endothermic), $q_{sys} > 0$, $q_{surr} < 0$ $\therefore$ $\Delta S_{surr} < 0$

Thus, heat/enthalpy changes in system cause S_{surr} to change, and therefore $\Delta S_{surr} \neq 0$.

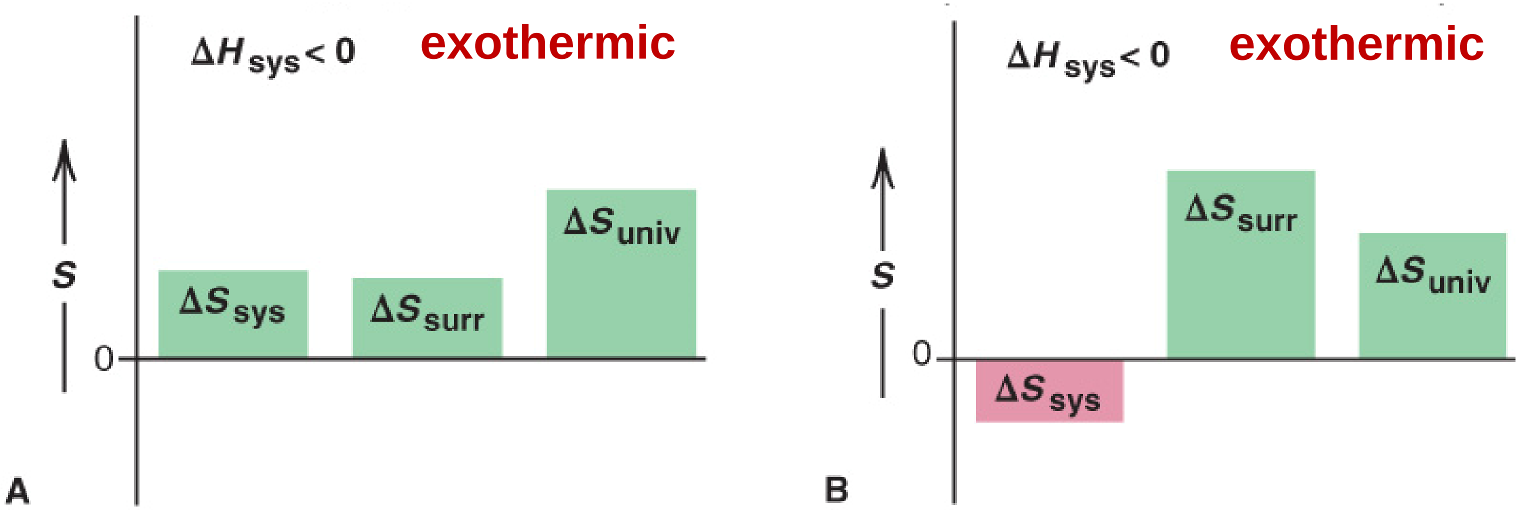
$\therefore$ ΔS_{surr} is proportional to $-q_{sys}$ and temperature (T) of surroundings

The relationship is: $\Delta S_{surr} = -\frac{q_{sys}}{T}$ $\therefore$ $\boxed{\Delta S_{surr} = -\frac{\Delta H_{rxn}}{T}}$ Fig 20.13

** So, ΔS_{surr} is given by ΔH_{rxn} (= ΔH_{sys}) and the T at which the reaction takes place **

Let's look at this figure again – it will make more sense now

Figure 20.13AB **Components of $\Delta S°_{univ}$ for spontaneous reactions.**



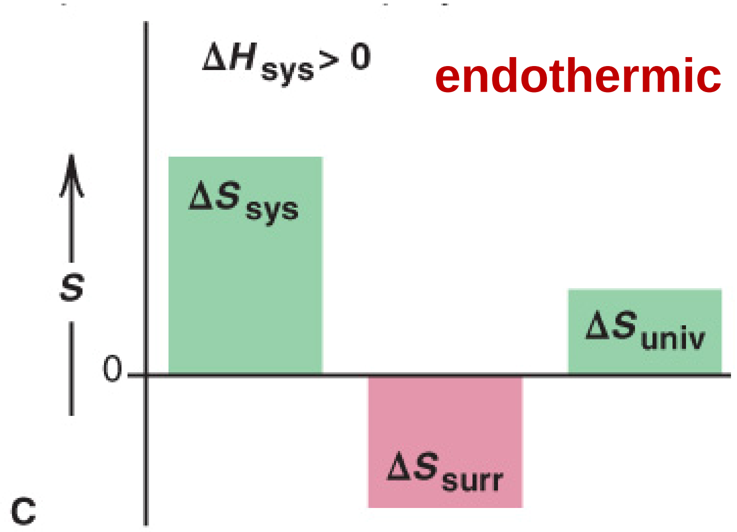
For an exothermic reaction in which $\Delta S_{sys} > 0$, the size of ΔS_{surr} is not important since $\Delta S_{surr} > 0$ for all exothermic reactions. The reaction will always be spontaneous.

For an exothermic reaction in which $\Delta S_{sys} < 0$, ΔS_{surr} must be ***larger*** than ΔS_{sys} for the reaction to be spontaneous.

**** ΔS_{surr} is always > 0 for exothermic reactions ****

Also for endothermic reactions – what can we deduce?

Figure 20.13C **Components of ΔS°_{univ} for spontaneous reactions.**



For an endothermic reaction: $\Delta S_{surr} < 0$
$\therefore$ ΔS_{sys} must be **positive and *greater*** than ΔS_{surr} for the reaction to be spontaneous.

**** ΔS_{surr} is always < 0 for endothermic reactions ****

So, consider again: $N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$

ΔS°_{rxn} = -197 J/K (as we calculated)

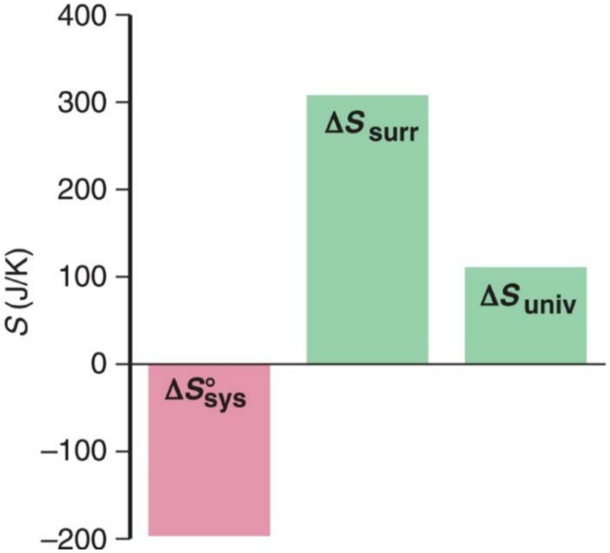
ΔH°_{rxn} = 2mol(-45.9 kJ/mol)-[1mol(0 kJ/mol) + 3mol(0 kJ/mol)]

= -91.8 kJ = -91800 J

$$\Delta S^\circ_{surr} = -\frac{\Delta H_{rxn}}{T} = -\frac{(-91800\text{J})}{298\text{K}} = 308\ \text{J/K}$$

$\Delta S^\circ_{univ} = \Delta S^\circ_{sys} + \Delta S^\circ_{surr}$ = -197 J/K + 308 J/K = 111 J/K

$\therefore \Delta S^\circ_{univ} > 0$ $\therefore$ **the reaction is spontaneous at 298 K (but <u>very</u> slow!)**



Although the entropy of the system decreases, this is outweighed by the increase in the entropy of the surroundings.

Entropy Changes at Equilibrium

At equilibrium, no net change to the reaction $\therefore \Delta S_{univ} = 0$

$\therefore \Delta S_{sys} = -\Delta S_{surr}$ (because $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$)

Example: $H_2O\ (l) \rightleftharpoons H_2O\ (g)$ $\Delta H_{vaporization} = +40.7$ kJ/mol)

- this is an equilibrium at 100 °C (373 K)

$$\Delta S^\circ_{sys} = \Delta S^\circ_{prod} - \Delta S^\circ_{react} = (195.9 - 86.8)\ J/K = 109\ J/K$$

$$\Delta S^\circ_{surr} = \frac{-\Delta H^\circ_{sys}}{T} = \frac{-\Delta H^\circ_{vap}}{T} = -109\ J/K$$

$$\therefore \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

This is true for both forward and reverse directions $\therefore$ at equilibrium, no movement away from equilibrium in either direction is spontaneous, *i.e.,* no change.

** Summary:

A reaction is spontaneous if $\Delta S_{univ} > 0$ i.e. $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

For a spontaneous reaction:

if $\Delta H < 0$ (exothermic), $\Delta S_{surr} > 0$ and ΔS_{sys} can be >0 or <0

if $\Delta H > 0$ (endothermic), $\Delta S_{surr} < 0$ and ΔS_{sys} must be >0

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

At equilibrium, no movement from equilibrium position is spontaneous:

$\Delta S_{sys} = -\Delta S_{surr}$ **

20.3. Free Energy (G) and Work

To avoid considering ΔS_{surr} and only consider the system/reaction, define a new thermodynamic quantity called FREE ENERGY (G).

$$G = H - TS \quad \text{and} \quad \Delta G = \Delta H - T\Delta S$$

Remember: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ and $\Delta S_{surr} = \dfrac{-\Delta H_{sys}}{T}$

$$\therefore \quad \Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

$$\therefore \quad T\Delta S_{univ} = T\Delta S_{sys} - \Delta H_{sys}$$

$$\therefore \quad -T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys} \qquad (\therefore\ \Delta G_{sys} = -T\Delta S_{univ})$$

$$\boxed{\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}} \quad \text{or usually just} \quad \boxed{\Delta G = \Delta H - T\Delta S}$$

Since $\Delta G_{sys} = -T\Delta S_{univ}$ and $\Delta S_{univ} > 0$ for a spontaneous reaction:

** $\Delta G < 0$ (*i.e.,* negative) for spontaneous reaction
$\Delta G > 0$ (*i.e.,* positive) for non-spontaneous reaction
$\Delta G = 0$ for process at equilibrium **

This is the most convenient form of the 2nd Law of Thermodynamics
i.e. saying $\Delta G_{sys} < 0$ for a spontaneous reaction **<u>is the same</u>** as saying $\Delta S_{univ} > 0$

Note: Free Energy is a state function and $\Delta G°$ = standard free energy change (kJ/mol)

Sample problem 20.4. Calculate ΔG°_{rxn} for

$$4\ KClO_3\ (s) \rightarrow 3\ KClO_4\ (s) + KCl\ (s)$$

Method 1: **Calculate ΔH°_{rxn} and ΔS°_{rxn}, use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$**

ΔH°_{rxn} = [3mol(-432.8 kJ/mol) + 1mol(-436.7 kJ/mol)-4mol(-397.7 kJ/mol)]

$\therefore$ ΔH°_{rxn} = -144.3 kJ (exothermic)

ΔS°_{rxn} = [3mol(151.0 J/mol.K) + 1mol(82.6 J/mol.K) – 4mol(143.1 J/mol.K)]

$\therefore$ ΔS°_{rxn} = -36.8 J/K = -36.8×10^{-3} kJ/K

$\therefore$ $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ = -144.3 kJ –[(298K)(-36.8×10^{-3} kJ/K)]

$\therefore$ ΔG°_{rxn} = -133 kJ (spontaneous)

Method 2: **Use ΔG°_f values of products and reactants**

ΔG°_f = standard free energy of formation

= free energy change to make substance from its component elements

Like ΔH°_f, ΔG°_f = 0 for an element in its standard state.

$\therefore$ $\Delta G^\circ_{rxn} = \sum m\Delta G^\circ_f$ (products) - $\sum n\Delta G^\circ_f$ (reactants)

$\therefore$ ΔG°_{rxn} = 1 mol (-409.2 kJ/mol) + 3 mol (-303.2 kJ/mol) - 4 mol (-296.3 kJ/mol)

$\therefore$ ΔG°_{rxn} = -133.6 kJ (same as Method 1)

Slight discrepancy due to sig. figs/errors in ΔH°_f, S°, and ΔG°_f values in Appendix B.

The Meaning of ΔG

For a spontaneous process, ΔG = maximum work (w) the system can do.
For a non-spontaneous process, ΔG = the minimum work that must be done to the system to make the change happen.

$$\therefore \Delta G = w_{max}$$

Since $\Delta G = \Delta H - T\Delta S$ $\quad \therefore \Delta H = \Delta G + T\Delta S$ $\quad \therefore \Delta H = w_{max} + T\Delta S$

ΔH = heat/energy released by the exothermic reaction
$\Delta G = w_{max}$ = portion usable to do work
$T\Delta S$ = portion lost as entropy change

i.e., part of the energy released (ΔH) goes into an entropy change and is not available to do work.

Consider burning of octane in a car engine:

$$C_8H_{18}\ (l) + 12\tfrac{1}{2}\ O_2\ (g) \rightarrow 8\ CO_2\ (g) + 9\ H_2O\ (g)$$

Very exothermic ($\Delta H < 0$), and $\Delta S > 0$ ($12\frac{1}{2}$ moles gas → 17 moles gas)

$$\Delta H = \Delta G + T\Delta S = w_{max} + T\Delta S$$

ΔG is portion of ΔH usable to do work (drive car wheels). $T\Delta S$ portion lost as increased entropy of car engine (temperature) and surrounding air $\therefore$ not usable for work.

Also: $\Delta G = w_{max}$: in practice, we cannot get maximum amount, because of further losses to *e.g.*, friction. Fraction of ΔG used determines the efficiency of the process: **no process is 100% efficient**.

Effect of Temperature on Reaction Spontaneity

Most exothermic reactions are also spontaneous because the ΔH contribution to ΔG >> than the entropy contribution ($T\Delta S$), *i.e.,* the negative ΔH helps make ΔG negative. However, in many cases the T can change the importance of the $T\Delta S$ term.

Let's look at the possibilities (and assume ΔH and ΔS are approximately independent of T, which is true if no phase change (e.g., s to g) occurs.

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

ΔH°	ΔS°	$-T\Delta S^\circ$	ΔG°	**Conclusion**
-	+	-	-	reaction spont. at all T $\Delta G^\circ < 0$ at all T
+	-	+	+	$\Delta G > 0$ at all T reaction non-spont. at all T
-	-	+	+ or -	$\Delta G < 0$ at low T ∴ spont. at low T $\Delta G > 0$ at high T ∴ non-spont. at high T
+	+	-	+ or -	$\Delta G > 0$ at low T ∴ non-spont. at low T $\Delta G < 0$ at high T ∴ spont. at high T

Examples:

(a) $2\ H_2O_2\ (l) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$ $\Delta H < 0, \Delta S > 0$

$\therefore$ Spontaneous at all T

(b) $3\ O_2\ (g) \rightarrow 2\ O_3\ (g)$ $\Delta H > 0, \Delta S < 0$

$\therefore$ non-spontaneous at all T

(c) $2\ H_2O\ (g) \rightarrow 2\ H_2\ (g) + O_2\ (g)$ $\Delta H > 0, \Delta S > 0$

$\therefore$ non-spontaneous at lower T, spontaneous at higher T

(d) $Na\ (s) + Cl_2\ (g) \rightarrow 2\ NaCl\ (s)$ $\Delta H < 0, \Delta S < 0$

$\therefore$ spontaneous at lower T, non-spontaneous at higher T

Example Calculation: $2\ SO_2\ (g) + O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$

at 298 K, $\Delta G° = -141.6$ kJ, $\Delta H° = -198.4$ kJ, $\Delta S° = -187.9$ J/K

$\Delta G° < 0$ at 298 K $\therefore$ reaction is spontaneous

But $\Delta H° < 0$ and $\Delta S° < 0$ $\therefore$ expect non-spont. at high enough T

So, is it spontaneous at 900 °C? (i.e. at T = 1173 K?)

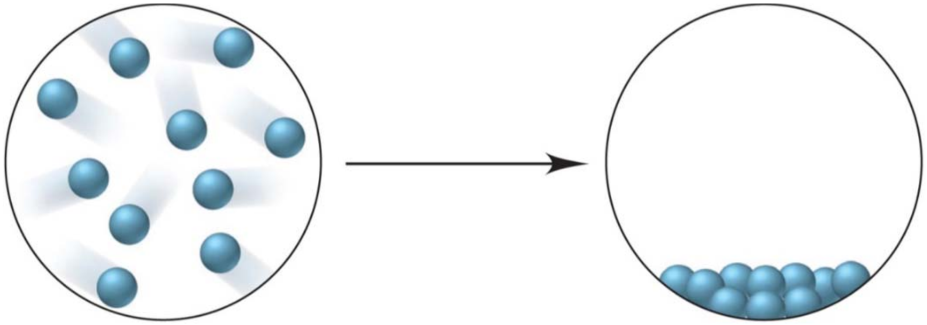
$$\Delta G° = \Delta H° - T\Delta S°$$

$$= -198.4 \text{ kJ} - (1173 \text{ K})(-187.9 \text{ J/K})(10^{-3} \text{ kJ/J})$$

$\therefore \Delta G° = 22.0$ kJ $\therefore$ non-spontaneous at 900 °C

Sample Problem 20.6 **Using Molecular Scenes to Determine the Signs of Δ*H*, Δ*S*, and Δ*G***

PROBLEM: The following scenes represent $H_2O\ (g) \rightarrow H_2O\ (l)$



(a) What are the signs of Δ*H* and Δ*S* for this process? Explain.

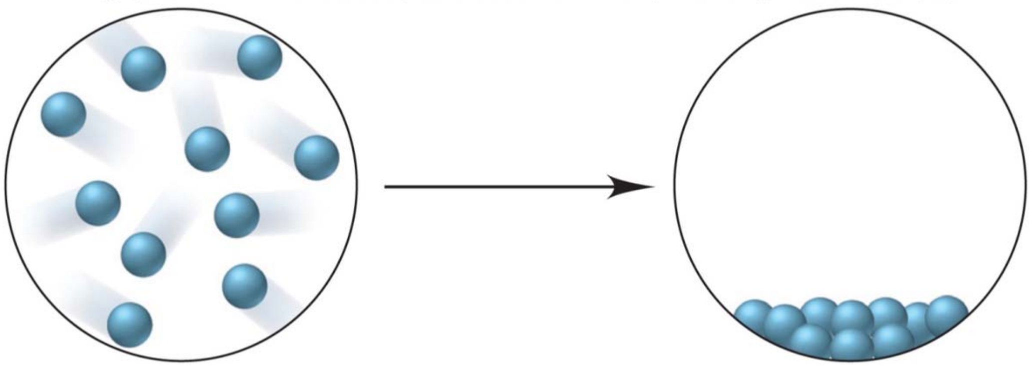
(b) Is the process spontaneous at all *T*, no *T*, low *T*, or high *T*? Explain.

PLAN: **(a)** From the scenes, we determine any change in the amount of gas, which indicates the sign of Δ*S*, and any change in the freedom of motion of the particles, which indicates whether heat is absorbed or released.

(b) To determine reaction spontaneity we need to consider the sign of Δ*G* at different temperatures.

Sample Problem 20.6

SOLUTION:



(a) The scene represents the condensation of water vapor, so the amount of gas decreases dramatically, and the separated molecules give up energy as they come closer together.

$\Delta S < 0$ and $\Delta H < 0$

(b) Since ΔS is negative and ΔH is negative, the $-T\Delta S$ term is positive. In order for ΔG to be < 0, the temperature must be high.

The process is spontaneous at low temperatures

Temperature at which Reaction becomes Spontaneous

When signs of ΔH and ΔS are the same, the sign of ΔG changes with T. At which T will this happen??

Crossover from $\Delta G < 0$ to $\Delta G > 0$ (or vice-versa) occurs when
$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$.
$\therefore$ when $\Delta H^\circ = T\Delta S^\circ$ i.e. crossover is at $\boxed{T = \frac{\Delta H^\circ}{\Delta S^\circ}}$ Fig. 20.15

Example: $Cu_2O\ (s) + C\ (s) \rightarrow 2\ Cu\ (s) + CO\ (g)$

$\Delta H^\circ = 58.1$ kJ $\Delta S^\circ = 165$ J/K

At room temperature (298 K):

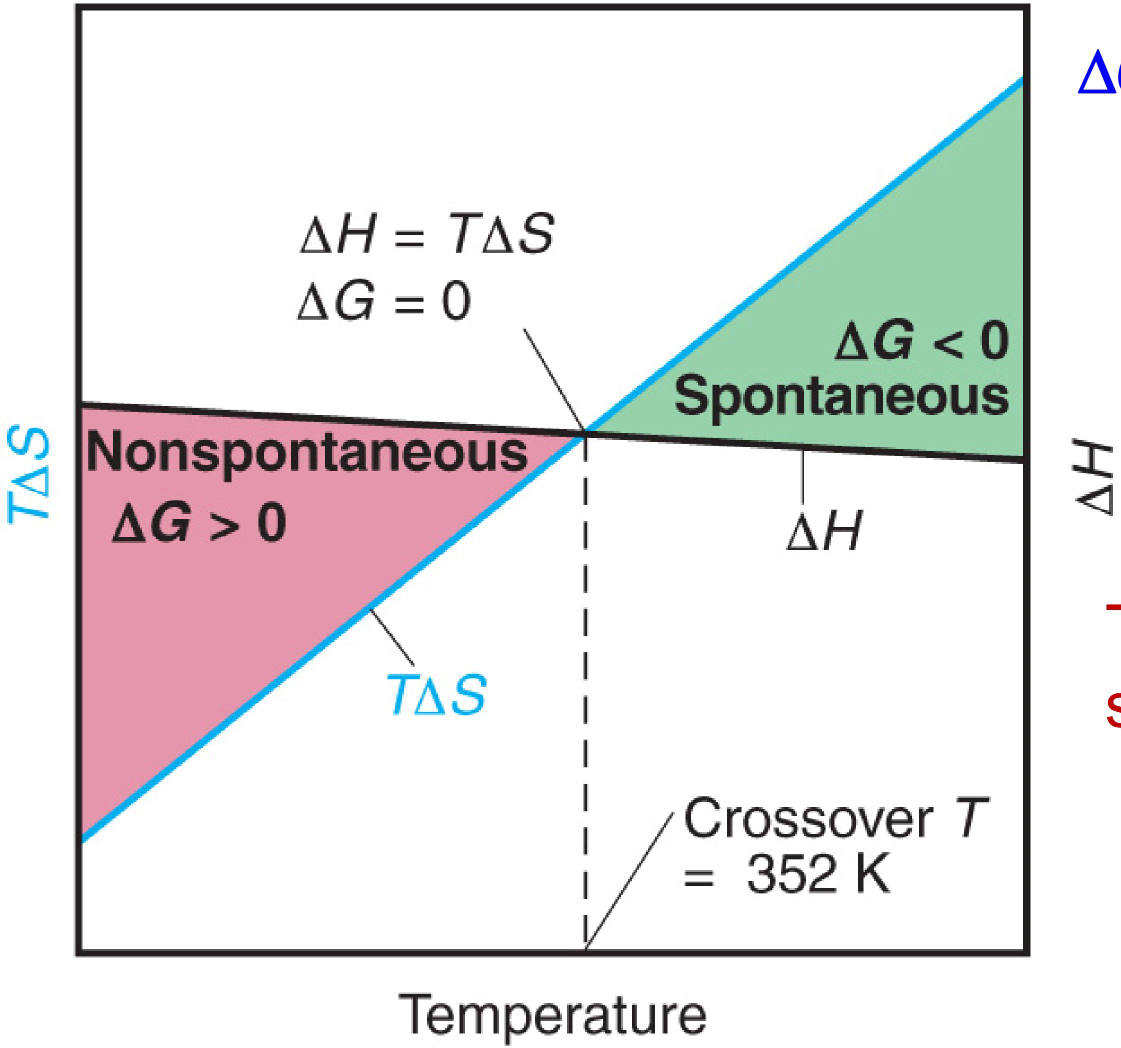
$$\Delta G = 58.1 \text{ kJ} - (298 \text{ K})(165 \text{ J/K})(10^{-3} \text{ kJ/J})$$

$\therefore$ $\Delta G = 8.9$ kJ $\therefore$ non-spontaneous

At what T does it become spontaneous?
Spontaneous when $\Delta G = 0$, *i.e.*, $\Delta H^\circ = T\Delta S^\circ$

$$\therefore T = \frac{\Delta H^\circ}{\Delta S} = \frac{58.1\text{kJ}}{(165\text{J}/\text{K})(10^{-3}\text{kJ}/\text{J})} = 352 \text{ K } (79\ ^\circ\text{C})$$

Figure 20.15 The effect of temperature on reaction spontaneity.



$\Delta G° = \Delta H° - T\Delta S°$

$\Delta H° = 58.1$ kJ
$\Delta S° = 165$ J/K

The sign of ΔG switches at

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

Coupling Reactions to Drive a Non-Spontaneous Reaction

The negative ΔG of a spontaneous reaction can be used to drive another reaction in its non-spontaneous direction.

Example 1: Making copper metal from Cu_2O.

(1) $Cu_2O\ (s) \rightarrow 2\ Cu\ (s) + \frac{1}{2}\ O_2\ (g)$ At 375 K, $\Delta G_{375} = 140$ kJ ∴ non-spontaneous

Also at 375 K
(2) $C\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$ $\Delta G_{375} = -143.8$ kJ ∴ spontaneous

Combine reactions (1) and (2); *i.e.*, add together and cancel O_2

$Cu_2O\ (s) + C\ (s) \rightarrow 2\ Cu\ (s) + CO\ (g)$ $\Delta G_{375} = -3.8$ kJ ∴ spontaneous

Thus, mixing C (s) with Cu_2O (s) allows reaction (2) to drive reaction (1).

∴ We can drive a non-spontaneous reaction by combining it with a sufficiently spontaneous one.

Note: the strategy is to find a very exothermic reaction of the O_2 that would be liberated if the non-spont reaction (1) occurs,

Example 2: reversing the rusting of Fe to get Fe (s).

Let's assume rust is Fe_2O_3 (it is actually a mixture of hydrated Fe^{3+} oxides ($Fe_2O_3 \cdot nH_2O$, $FeO(OH)$ and $Fe(OH)_3$).

(1) $2\ Fe_2O_3\ (s) \rightarrow 4\ Fe\ (s) + 3\ O_2\ (g)$ $\Delta G° = +1487$ kJ (<u>very non-spont</u>)

(2) $2\ CO\ (g) + O_2\ (g) \rightarrow 2\ CO_2\ (g)$ $\Delta G° = -514.4$ kJ

(2′) $6\ CO\ (g) + 3\ O_2\ (g) \rightarrow 6\ CO_2\ (g)$ $\Delta G° = -1543$ kJ

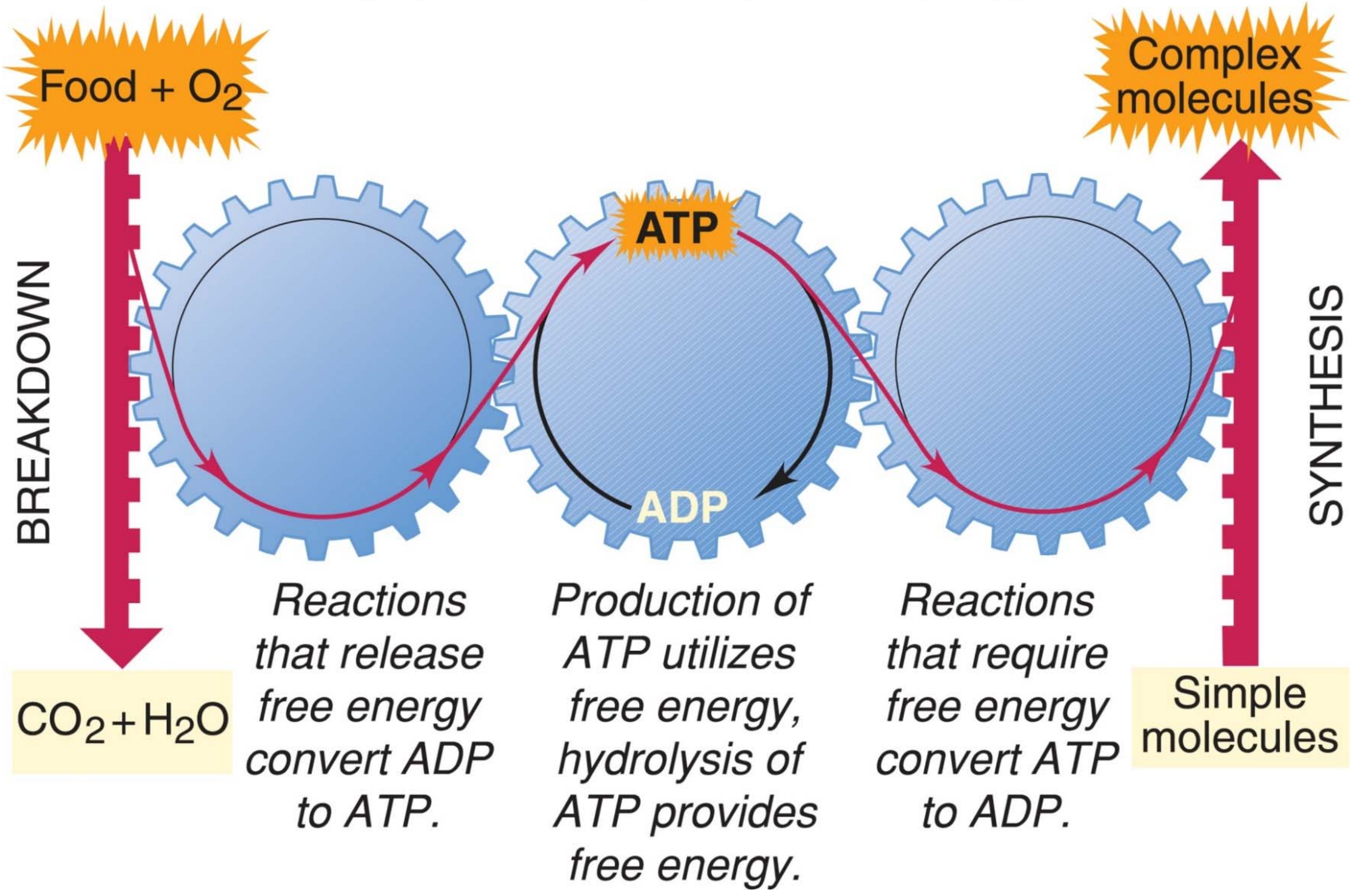
Use (2) to drive (1) i.e., add 1 and 2′

$$2\ Fe_2O_3\ (s) + 6\ CO\ (g) \rightarrow 4\ Fe\ (s) + 6\ CO_2\ (g)$$

$\Delta G° = -56$ kJ $\therefore$ <u>spontaneous</u>

Chemical Connections

Figure B20.2 The cycling of metabolic free energy.



Reactions that release free energy convert ADP to ATP.

Production of ATP utilizes free energy, hydrolysis of ATP provides free energy.

Reactions that require free energy convert ATP to ADP.

20.4. Free Energy and Equilibrium

Consider $A \rightarrow B$ $\quad Q = [B]/[A]$

In Chapter 20, we said $A \rightarrow B$ is the spontaneous direction if $\Delta G < 0$.
$\therefore B \rightarrow A$ is the non-spontaneous direction.

In Chapter 17, $Q < K$ is the spontaneous direction for left-to-right, where Q = mass-action expression.

How are the two rules related?

$$\left.\begin{array}{l} Q < K \quad \text{i.e.,} \quad \dfrac{Q}{K} < 1, \text{ spontaneous, } \Delta G < 0 \\ Q > K \quad \text{i.e.,} \quad \dfrac{Q}{K} > 1, \text{ non-spontaneous, } \Delta G > 0 \\ Q = K \quad \text{i.e.,} \quad \dfrac{Q}{K} = 1, \text{ equilibrium, } \Delta G = 0 \end{array}\right\} \begin{array}{l} \text{for rxn. left} \longrightarrow \text{right} \\ \text{i.e., } A \longrightarrow B \end{array}$$

How are Q/K and ΔG mathematically related?

$$\Delta G = RT \ln (Q/K) \qquad (\therefore \ln 1 = 0 \text{ and } \Delta G = 0 \text{ at equil})$$

$$\therefore \boxed{\Delta G = RT \ln Q - RT \ln K}$$

This relationship tells us that the ΔG is the difference in free energy between the initial state and final (equilibrium) state. At equilibrium, $Q = K \therefore \Delta G = 0$. Thus, ΔG depends on the difference in size between Q and K.

When all initial concns. are 1 M (or all gas pressures 1 atm), we have standard conditions.

$\therefore$ Q = 1, ln Q = 0 and $\Delta G = \Delta G°$

$\therefore$ $\boxed{\Delta G° = -RT \ln K}$ Very important equation! Table 20.2

Extremely useful relationship between $\Delta G°$ and K !!!

Note: Small change in ΔG can give big change in K.

Since most reactions do not begin with reactants in standard conditions, we can calculate equation relating ΔG to $\Delta G°$.

$$\boxed{\Delta G = \Delta G° + RT \ln Q}$$

Note: This allows us to calculate ΔG for any initial concn's if we know $\Delta G°$ (which we can calculate from Appendix B, for example).

Table 20.2 The Relationship Between $\Delta G°$ and K at 298 K

$\Delta G°$ (kJ)	K	Significance
200	9×10^{-36}	Essentially no forward reaction; reverse reaction goes to completion
100	3×10^{-18}	
50	2×10^{-9}	
10	2×10^{-2}	
1	7×10^{-1}	
0	1	Forward and reverse reactions proceed to same extent
-1	1.5	
-10	5×10^{1}	
-50	6×10^{8}	
-100	3×10^{17}	Forward reaction goes to completion; essentially no reverse reaction
-200	1×10^{35}	

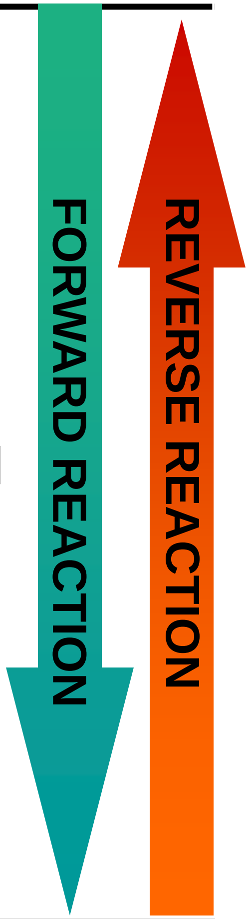
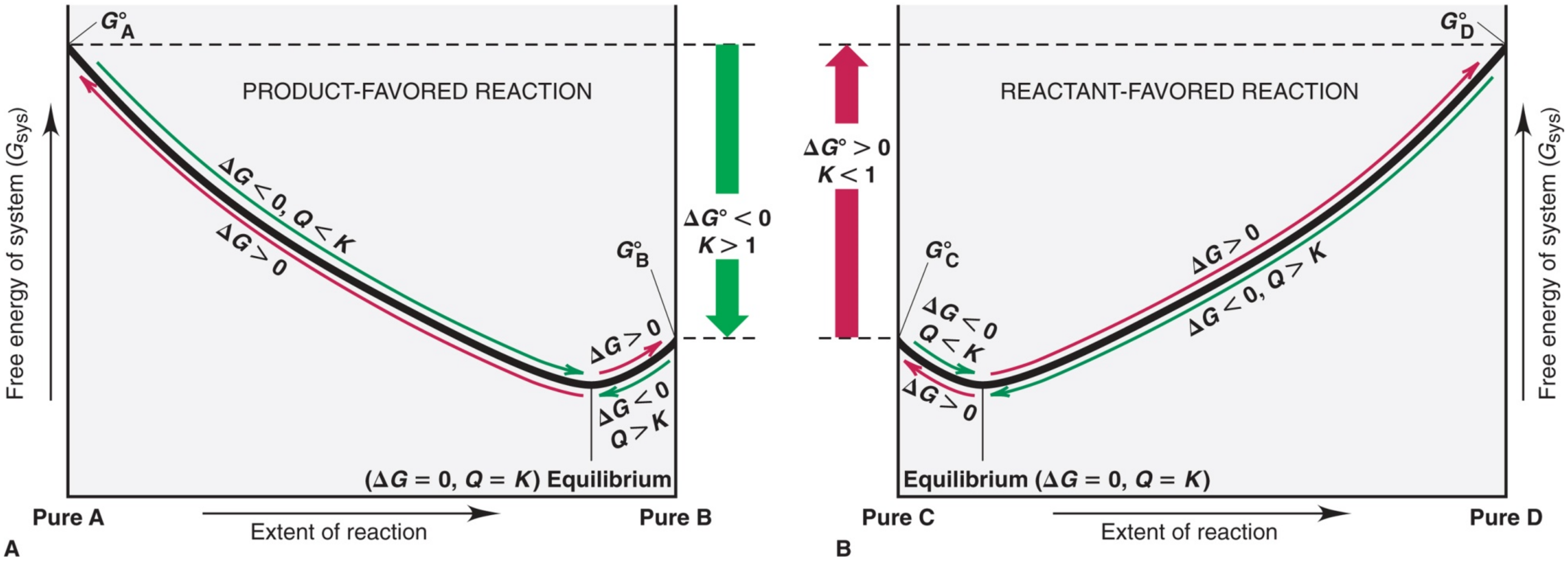


Figure 20.16 Free energy and the extent of reaction.



Each reaction proceeds spontaneously (*green curved arrows*) from reactants or products to the equilibrium mixture, at which point $\Delta G = 0$. After that, the reaction is nonspontaneous in either direction (*red curved arrows*). Free energy reaches a minimum at equilibrium.

Sample Problem 19.7

Oxidation of $SO_2(g)$ is too slow at 298 K to be useful for making sulfuric acid. But is it useful (thermodynamically) to run this reaction at a higher T (*i.e.,* does equilibrium lie more to right) ?

$$2\ SO_2\ (g) + O_2 \rightleftharpoons 2\ SO_3\ (g)$$

Let's compare the reactions at 298 K and 973 K

ΔG^o_{298} = -141.6 kJ/mol (obtained using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$)

ΔG^o_{973} = -12.12 kJ/mol

What is K at 298 and 973 K?

At 298 K: $\Delta G^o = -RT \ln K \therefore \ln K = -(\Delta G^o/RT)$ $\therefore K = e^{-(\Delta G^o/RT)}$

$$\therefore -(\Delta G^o/RT) = -\left(\frac{-141.6kJ/mol x 1000J/KJ}{(8.31J/mol.K)(298K)}\right) = 57.2$$

$\therefore K = e^{57.2} = 7 \times 10^{24}$ very big !

At 973 K: $$-\Delta G^o/RT = -\left(\frac{-12.12kJ/mol x 1000J/kJ}{(8.31J/mol.K)(973K)}\right) = 1.50$$

$\therefore K = e^{1.50} = 4.5$ not big

$\therefore$ Reaction much more to the right at lower T, *i.e.,* more product SO_3 at lower T ! So need to use T between 298 and 973 to get significant amount of SO_3 at a reasonable rate.

Question: If we have two vessels each containing 0.50 atm SO_2 / 0.010 atm O_2 / 0.10 atm SO_3, but one vessel is at 298 K and the other at 973 K, in which direction will the reaction proceed to reach equilibrium at each T?

Answer: Calculate Q and compare to K.

$$Q = \frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}} = \frac{(0.10)^2}{(0.50)^2(0.010)} = 4.0$$

At 298 K: $Q \ll K$ $(K = 7 \times 10^{24})$, ∴ rxn. spontaneously shifts to the right.

At 973 K: $Q \leq K$ $(K = 4.5)$, ∴ rxn. moves only very slightly to the right.

Finally, calculate ΔG at each T.

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

At 298 K: $\Delta G_{298} = \Delta G^\circ_{298} + RT \ln Q$

$= (-141.6\times10^{-3} J/mol)+(8.314\ J/K.mol)(298K)\ln 4.0$

$= -138.2\ kJ/mol$

At 973 K: $\Delta G_{973} = \Delta G^\circ_{973} + RT \ln Q$

$= (-12.12\times10^{-3} J/mol)+(8.314 J/K.mol)(973K)\ln 4.0$

$= -0.91\ kJ/mol$