

Chemical Thermodynamics

Chapter 16



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Chemistry 223
Professor Michael Russell

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4/28/24

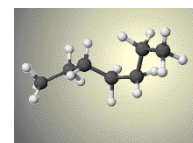
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Thermodynamics and Kinetics



How to predict if a reaction can occur, given enough time?

THERMODYNAMICS



How to predict if a reaction can occur at a reasonable rate?

KINETICS

First Law of Thermodynamics

First Law of Thermodynamics: "Energy cannot be created or destroyed" - conservation of energy

The total energy of the universe cannot change though you can transfer it from one place to another

$$\Delta E_{\text{universe}} = 0 = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}}$$

ΔE lost or gained through **heat (q) and/or work (w)**
Chemists focus on heat more than work; heat at constant pressure equals enthalpy (ΔH)



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Enthalpy - CH 221 flashback!

Enthalpy, ΔH , generally in kJ/mol

If products more stable than reactants, energy released
exothermic and $\Delta H = \text{negative}$

If reactants more stable than products, energy absorbed
endothermic and $\Delta H = \text{positive}$

Review Hess' Law, $\Delta H^{\circ}_{\text{rxn}} = \Sigma(\Delta H^{\circ}_{\text{prod}}) - \Sigma(\Delta H^{\circ}_{\text{react}})$,
bond enthalpies

Bond enthalpies (CH 222)

TABLE 8.4 Average Bond Enthalpies (kJ/mol)			
Single Bonds			
C-H	413	N-H	391
C-C	348	N-N	163
C-N	293	N-O	201
C-O	358	N-F	272
C-F	485	N-Cl	200
C-Cl	328	N-Br	243
C-Br	276		

Formation enthalpies (CH 221)

Standard Enthalpies of Formation, ΔH° , at 298 K			
Substance	Formula	ΔH° (kJ/mol)	Substance
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	-26.7	Hydrogen ch
Ammonia	$\text{NH}_3(\text{g})$	-46.19	Hydrogen flu
Benzene	$\text{C}_6\text{H}_6(\text{l})$	49.04	Hydrogen ox
Calcium carbonate	$\text{CaCO}_3(\text{s})$	-1207.1	Methane
Calcium oxide	$\text{CaO}(\text{s})$	-635.5	Methanol
Carbon dioxide	$\text{CO}_2(\text{g})$	-393.5	Propane

Spontaneous Reactions

Thermodynamics asks if a reaction will occur under the given conditions; if it does, system is favored to react - a **product-favored** system ($K > 1$) - called a **spontaneous** reaction

Most product-favored reactions are exothermic (ΔH)... but not all.

Nonspontaneous reactions require energy input to occur.

All reactions require **activation energy** (E_a) to take place

Spontaneity does not imply anything about **time** for the reaction to occur (i.e. **kinetics**). Spontaneity can be for fast and slow reactions!

The first law of thermodynamics does not predict if a reaction is spontaneous; the first law applies to all systems!

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Spontaneous Processes



Spontaneous



Non-spontaneous

Processes that are **spontaneous** in one direction are **nonspontaneous** in the reverse direction.

Thermodynamics and Kinetics

Diamond is **thermodynamically favored** to convert to graphite, but **not kinetically favored**.



Paper burns - a **product-favored** reaction. Also **kinetically favored** once reaction is begun.

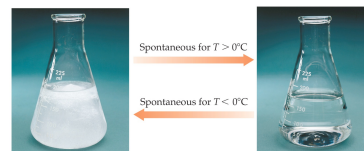


Both reactions are spontaneous!

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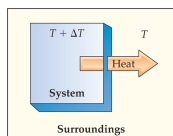
Spontaneous Processes

Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures. **Above 0 °C** it is spontaneous for ice to melt. **Below 0 °C** the reverse process is spontaneous.



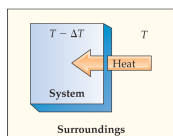
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Reversible Processes



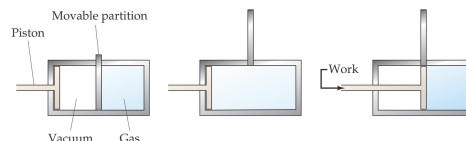
In a **reversible** process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

...quite rare in the "real world"...

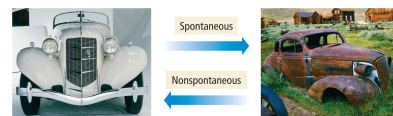


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Irreversible Processes



Irreversible processes cannot be undone by exactly reversing the change to the system. **Spontaneous** processes are **irreversible**



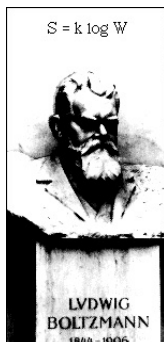
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Directionality of Reactions

How **probable** is it that reactant molecules will react (i.e. be **spontaneous**)?

PROBABILITY suggests that a product-favored reaction will result in the **dispersal**

- of **energy**
- of **matter**, or
- of **both energy and matter**



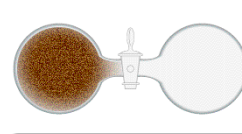
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Directionality of Reactions

Probability suggests that a product-favored reaction will result in the dispersal of energy or of matter or both.

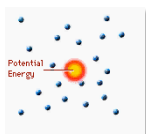
Matter Dispersal



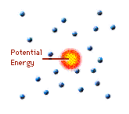
Directionality of Reactions

Probability suggests that a product-favored reaction will result in the dispersal of energy or of matter or both.

Energy Dispersal



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Directionality of Reactions Energy Dispersal

Exothermic reactions (*enthalpy! negative $\Delta H!$*) involve a release of stored chemical potential energy to the surroundings.

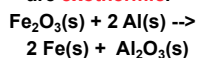
The stored potential energy starts out in a few molecules but is finally dispersed over a great many molecules.

The final state - with energy dispersed - is more probable and makes a reaction product-favored... *usually!*

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Product-Favored Reactions

In general, spontaneous or product-favored reactions are **exothermic**.



$$\Delta H = -848 \text{ kJ}$$

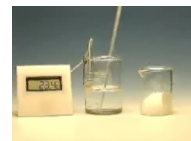


The Thermite Reaction

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Product-Favored Reactions

But many spontaneous reactions are endothermic! (*positive ΔH*)



We need more than just enthalpy (ΔH) to predict if a reaction is spontaneous!

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Entropy, S

One property common to product-favored processes is that the final state is more **disordered** or **random** than the original.

Spontaneity is related to an increase in randomness and the thermodynamic property related to randomness is **ENTROPY, S**.



Reaction of K with water

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Entropy and Microstates

The number of **microstates** (W) in a system is related to the **entropy** (S) of the system:

$$S = k \ln W$$

k = Boltzmann Constant = $1.38 \times 10^{-23} \text{ J/K}$ (*do not memorize!*)

A system with *fewer* microstates has *lower entropy*.
A system with *more* microstates has *higher entropy*.

All spontaneous endothermic processes exhibit an increase in entropy.

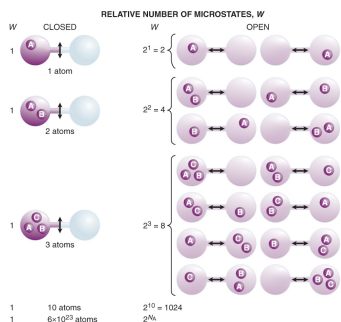
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Entropy and Microstates

$$S = k \ln W$$

When the stopcock opens, the number of microstates is 2^n , where n is the number of particles.

Punchline: the more atoms, the more entropy

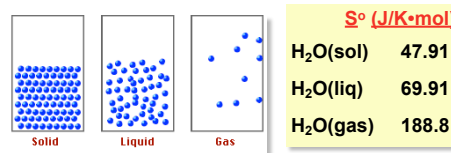


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Entropy, S

More disordered substances have higher entropy, so:
 $S(\text{solids}) < S(\text{liquids}) < S(\text{gases})$

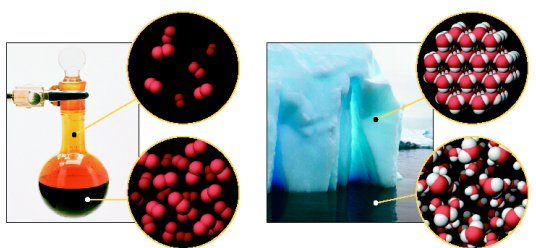


S° (J/K·mol)	
H ₂ O(sol)	47.91
H ₂ O(liq)	69.91
H ₂ O(gas)	188.8

Only pure (element), perfectly formed crystals at 0 K have zero entropy ($S = k \ln W$ where $W = 1$: the 3rd Law of Thermodynamics)

See the [Entropy Guide](#)

Entropy and States of Matter



$$S^\circ(\text{Br}_2 \text{ liq}) < S^\circ(\text{Br}_2 \text{ gas})$$

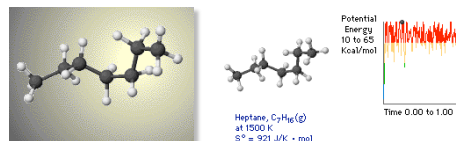
$$S^\circ(\text{H}_2\text{O sol}) < S^\circ(\text{H}_2\text{O liq})$$

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Entropy, S

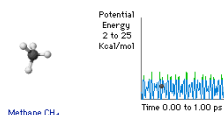
Entropy of a substance increases with temperature.



Molecular motions of heptane, C₇H₁₆

Molecular motions of heptane at different temps.
 $S(1500 \text{ K}) > S(200 \text{ K})$

Increases in molecular complexity and molar mass generally lead to increases in S.



S° (J/mol·K)	
He(g)	126.2
Ne(g)	146.1
Ar(g)	154.8
Kr(g)	163.8
Xe(g)	169.4

Entropy, S

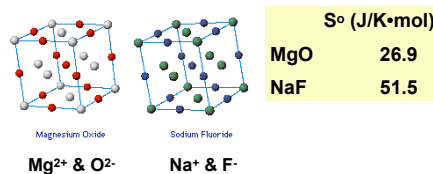
	S° (J/K·mol)
methane	186.3
ethane	229.6
propane	269.9

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Entropy, S

Entropies of ionic solids depend on coulombic attractions.



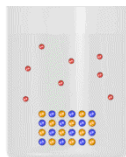
S° (J/K·mol)	
MgO	26.9
NaF	51.5

Mg²⁺ & O²⁻

Na⁺ & F⁻

Entropy, S

Entropy usually increases when a pure liquid or solid dissolves in a solvent.



See the [Entropy Guide](#)

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Standard Molar Entropies

Some Standard Molar Entropy Values at 298 K

Element	Entropy, S° (J/K · mol)	Compound	Entropy, S° (J/K · mol)
C(graphite)	5.6	CH ₄ (g)	186.3
C(diamond)	2.377	C ₂ H ₂ (g)	229.2
C(vapor)	158.1	C ₃ H ₈ (g)	270.3
Ca(s)	41.59	CH ₃ OH(l)	127.2
Ar(g)	154.9	CO(g)	197.7
H ₂ (g)	130.7	CO ₂ (g)	213.7
O ₂ (g)	205.1	H ₂ O(g)	188.84
N ₂ (g)	191.6	H ₂ O(l)	69.95
F ₂ (g)	202.8	HCl(g)	186.2
Cl ₂ (g)	223.1	NaCl(s)	72.11
Br ₂ (l)	152.2	MgO(s)	26.85
I ₂ (s)	116.1	CaCO ₃ (s)	91.7

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CH 221 / CH 222 “Enthalpy Flashback”

For a temperature change in the **same phase** (s, l, g) enthalpy (ΔH) equals the heat transferred (q) at constant pressure via:

$$\Delta H = q = mC\Delta T$$

m = mass (g), C = heat capacity (4.184 J g⁻¹ K⁻¹ for water!),
 ΔT = final temperature - initial temperature

For a **phase change**, the enthalpy change:

$$\Delta H = (\text{“mass”})(\text{“heat of something”})$$

“mass” = grams or moles, “heat of something” depends on phase change, i.e. 333 J/g = heat of fusion, 40.7 kJ/mol = heat of vaporization

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Entropy Changes for a Temperature Change in the Same Phase

For a temperature change in the same phase,

$$\Delta S = n C \ln \frac{T_2}{T_1}$$

where n = moles of substance

C = molar heat capacity (at const. P)

T = Kelvin Temperature

For 0.499 mol of H₂O heated from 281 K to 294 K:

$$C = 4.184 \text{ J g}^{-1} \text{ K}^{-1} * 18.02 \text{ g mol}^{-1} = 75.40 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S = 0.499 \text{ mol} * 75.40 \text{ J mol}^{-1} \text{ K}^{-1} * \ln(294/281)$$

$$\Delta S = 1.70 \text{ J K}^{-1}$$

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Entropy Changes for Phase Changes



For a phase change,

$$\Delta S = q/T$$

where q = heat transferred in phase change

For H₂O (liq) → H₂O(g),

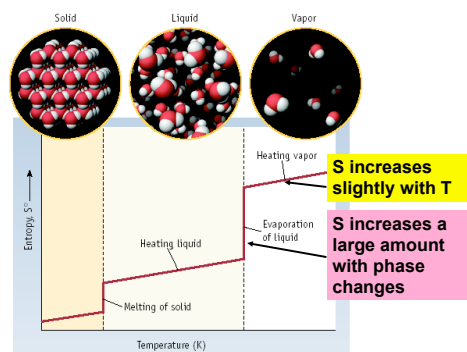
$$\Delta H = q = +40,700 \text{ J/mol}$$

40.7 kJ/mol is
 ΔH_{vap} for H₂O

$$\Delta S = \frac{q}{T} = \frac{40,700 \text{ J/mol}}{373.15 \text{ K}} = +109 \text{ J/K} \cdot \text{mol}$$

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Entropy and Temperature



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CH 221 / CH 222 "Enthalpy Flashback"

Also: the **system enthalpy** for a reaction can be calculated:

$$\Delta H_{\text{sys}}^{\circ} = \Sigma \Delta H^{\circ} (\text{products}) - \Sigma \Delta H^{\circ} (\text{reactants})$$

Find $\Delta H_{\text{sys}}^{\circ}$ for: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{liq})$

$$\Delta H^{\circ} = 2 \Delta H^{\circ} (\text{H}_2\text{O}(\text{l})) - [2 \Delta H^{\circ} (\text{H}_2) + \Delta H^{\circ} (\text{O}_2)]$$

$$\Delta H^{\circ} = 2 \text{ mol } (-285.85 \text{ kJ/mol}) - [2 \text{ mol } (0) + 1 \text{ mol } (0)]$$

$$\Delta H_{\text{sys}}^{\circ} = -571.70 \text{ kJ/mol}$$

ΔH for pure elements = 0. Values of ΔH found in tables
This reaction is **exothermic** due to negative ΔH value
(**endothermic** = positive ΔH). The "°" means "standard conditions" (298 K, 1 atm, 1 M, most common state)

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Calculating ΔS for a Reaction

$$\Delta S_{\text{sys}}^{\circ} = \Sigma S^{\circ} (\text{products}) - \Sigma S^{\circ} (\text{reactants})$$

$\Delta S_{\text{sys}}^{\circ}$ = "system entropy at standard conditions"

Calculate $\Delta S_{\text{sys}}^{\circ}$: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{liq})$

Use S° values in tables:

$$\Delta S^{\circ} = 2 S^{\circ} (\text{H}_2\text{O}(\text{l})) - [2 S^{\circ} (\text{H}_2(\text{g})) + S^{\circ} (\text{O}_2(\text{g}))]$$

$$\Delta S^{\circ} = 2 \text{ mol } (69.9 \text{ J/K}\cdot\text{mol}) - [2 \text{ mol } (130.7 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol } (205.3 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S_{\text{sys}}^{\circ} = -326.9 \text{ J/K}$$

Note that there is a **decrease in S** because 3 mol of gas give 2 mol of liquid.

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Calculating ΔS_f° for a Reaction

ΔS_f° is the "entropy of formation" or "formation entropy"
(which is similar to CH 221's "enthalpy of formation", ΔH_f°);
this means:

* only one mole of product will be formed

* all reactants are elements in their standard states

Example: Calculate ΔS_f° for: $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{liq})$

Must use fraction - only 1 mol of product! Use standard element states for reactants. Use S° values in tables:

$$\Delta S_f^{\circ} = S^{\circ} (\text{H}_2\text{O}(\text{l})) - [S^{\circ} (\text{H}_2(\text{g})) + 1/2 S^{\circ} (\text{O}_2(\text{g}))]$$

$$\Delta S_f^{\circ} = 69.9 \text{ J/K}\cdot\text{mol} - [130.7 \text{ J/K}\cdot\text{mol} + 1/2 (205.3 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S_f^{\circ} = -163.5 \text{ J/K}$$

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2nd Law of Thermodynamics

A reaction is spontaneous (product-favored) if ΔS for the universe is positive.

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

$\Delta S_{\text{universe}} > 0$ (positive) for all product-favored irreversible process

First calc. entropy created by matter dispersal

(ΔS_{system})

Next, calc. entropy created by energy dispersal

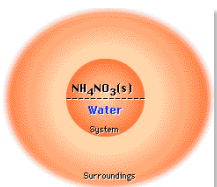
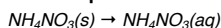
($\Delta S_{\text{surround}}$)

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2nd Law of Thermodynamics



Dissolving NH_4NO_3 in water - an entropy driven process:



$$\Delta S_{\text{universe}} =$$

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

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2nd Law of Thermodynamics

Calculate $\Delta S_{\text{universe}}^{\circ}$ for: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{liq})$

$$\Delta S_{\text{system}}^{\circ} = -326.9 \text{ J/K (earlier example for } \Delta S)$$

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

Can calculate that $\Delta H_{\text{system}}^{\circ} = -571.70 \text{ kJ}$

via $\Delta H^{\circ}(\text{system}) = \Sigma \Delta H^{\circ}(\text{prod}) - \Sigma \Delta H^{\circ}(\text{react})$

$$\Delta H^{\circ}(\text{system}) = 2^{\circ} \Delta H^{\circ}(\text{H}_2\text{O}) - (2^{\circ} \Delta H^{\circ}(\text{H}_2) + \Delta H^{\circ}(\text{O}_2))$$

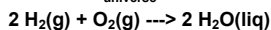
$$\Delta S_{\text{surroundings}}^{\circ} = \frac{-(-571.70 \text{ kJ})(1000 \text{ J/kJ})}{298.15 \text{ K}}$$

$$\Delta S_{\text{surroundings}}^{\circ} = +1917.5 \text{ J/K}$$

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2nd Law of Thermodynamics

Calculate $\Delta S^\circ_{\text{universe}}$ for:



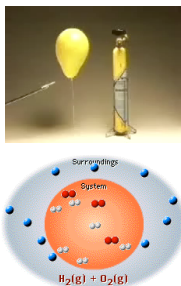
$$\Delta S^\circ_{\text{system}} = -326.9 \text{ J/K}$$

$$\Delta S^\circ_{\text{surroundings}} = +1917.5 \text{ J/K}$$

$$\Delta S^\circ_{\text{universe}} = \Delta S^\circ_{\text{system}} + \Delta S^\circ_{\text{surroundings}}$$

$$\Delta S^\circ_{\text{universe}} = -326.9 + 1917.5 = +1590.6 \text{ J/K}$$

The entropy of the universe is increasing, so the reaction is product-favored.



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Predicting if a Process Is Spontaneous

Type	$\Delta H^\circ_{\text{sys}}$	$\Delta S^\circ_{\text{sys}}$	Spontaneous Process?
1	Exothermic process $\Delta H^\circ_{\text{sys}} < 0$	Less order $\Delta S^\circ_{\text{sys}} > 0$	Spontaneous under all conditions $\Delta S^\circ_{\text{univ}} > 0$
2	Exothermic process $\Delta H^\circ_{\text{sys}} < 0$	More order $\Delta S^\circ_{\text{sys}} < 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at <i>lower</i> temperatures
3	Endothermic process $\Delta H^\circ_{\text{sys}} > 0$	Less order $\Delta S^\circ_{\text{sys}} > 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at <i>higher</i> temperatures
4	Endothermic process $\Delta H^\circ_{\text{sys}} > 0$	More order $\Delta S^\circ_{\text{sys}} < 0$	Not spontaneous under all conditions $\Delta S^\circ_{\text{univ}} < 0$

Spontaneous or Not?

Remember that $-\Delta H^\circ_{\text{sys}}$ is proportional to $\Delta S^\circ_{\text{surr}}$
An exothermic process has $\Delta S^\circ_{\text{surr}} > 0$.

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Gibbs Free Energy, G

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}$$

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

Multiply through by -T

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

$-T\Delta S_{\text{univ}}$ = change in Gibbs free energy for the system = ΔG_{system}

Under **standard conditions** -

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

See the *Gibbs Free Energy Guide*



Josiah Willard Gibbs

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

Gibbs **free energy** change =

total energy change for system

- energy lost in disordering the system

If reaction is

• **exothermic (negative ΔH°)** (energy dispersed)

• **and entropy increases (positive ΔS°)** (matter dispersed)

then ΔG° must be **NEGATIVE**

Reaction is **spontaneous** (and product-favored).

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

Gibbs **free energy** change =

total energy change for system

- energy lost in disordering the system

If reaction is

• **endothermic (positive ΔH°)**

• **and entropy decreases (negative ΔS°)**

then ΔG° must be **POSITIVE**

Reaction is **not spontaneous** (and is reactant-favored).

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Gibbs Free Energy, G

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

ΔH°	ΔS°	ΔG°	Reaction
exo(-)	increase(+)	-	Prod-favored
endo(+)	decrease(-)	+	React-favored
exo(-)	decrease(-)	?	T dependent
endo(+)	increase(+)	?	T dependent



spontaneous means product favored and implies a negative ΔG
non-spontaneous means reactant favored and implies a positive ΔG

Gibbs Free Energy, G

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

Two methods for calculating ΔG°

- Determine $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ and use Gibbs equation.
- Use tabulated values of free energies of formation, ΔG_f° .

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

See the Gibbs Free Energy Guide

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Free Energies of Formation

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

Standard Molar Free Energies of Formation of Some Substances at 298 K			
Element/Compound	$\Delta G_f^\circ (\text{kJ} \cdot \text{mol}^{-1})$	Element/Compound	$\Delta G_f^\circ (\text{kJ} \cdot \text{mol}^{-1})$
H ₂ (g)	0	CO ₂ (g)	-394.4
O ₂ (g)	0	CH ₄ (g)	-50.87
N ₂ (g)	0	H ₂ O(g)	-228.6
C (graphite)	0	H ₂ O(l)	-237.2
C (diamond)	2.900	NH ₃ (g)	-16.4
CO(g)	-137.2	Fe ₂ O ₃ (s)	-742.2

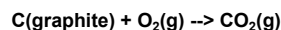
Note that ΔG_f° for an element = 0

MAR

Calculating $\Delta G^\circ_{\text{rxn}}$

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

Combustion of carbon



$$\Delta G^\circ_{\text{rxn}} = \Delta G_f^\circ(\text{CO}_2) - [\Delta G_f^\circ(\text{graph}) + \Delta G_f^\circ(\text{O}_2)]$$

$$\Delta G^\circ_{\text{rxn}} = -394.4 \text{ kJ} - [0 + 0]$$

$$\Delta G^\circ_{\text{rxn}} = -394.4 \text{ kJ}$$

Note that free energy of formation of an element in its standard state is 0.

Reaction is **product-favored** as expected - *green house gases!*

MAR

Calculating $\Delta G^\circ_{\text{rxn}}$

Some reactions occur spontaneously due to favorable $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ values.

These reactions are both "**enthalpy driven**" and "**entropy driven**"

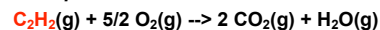


But not all reactions have favorable enthalpy and entropy values...

MAR

Calculating $\Delta G^\circ_{\text{rxn}}$

Example: Find $\Delta G^\circ_{\text{rxn}}$ for the combustion of **acetylene**:



* Use enthalpies of formation to calculate

$$\Delta H^\circ_{\text{rxn}} = -1238 \text{ kJ} \quad \Delta H^\circ(\text{rxn}) = \sum \Delta H^\circ(\text{prod}) - \sum \Delta H^\circ(\text{react})$$

* Use standard molar entropies to calculate

$$\Delta S^\circ_{\text{rxn}} = -97.4 \text{ J/K} \text{ or } -0.0974 \text{ kJ/K} \quad \textit{ditto for } \Delta S^\circ(\text{rxn})$$

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= -1238 \text{ kJ} - (298 \text{ K})(-0.0974 \text{ kJ/K}) \\ &= -1209 \text{ kJ} \end{aligned}$$

Reaction is **product-favored** despite negative $\Delta S^\circ_{\text{rxn}}$.
Reaction is "**enthalpy driven**"

MAR

Calculating $\Delta G^\circ_{\text{rxn}}$



Is the dissolution of ammonium nitrate product-favored?

If so, is it enthalpy- or entropy-driven?

MAR

Calculating $\Delta G^\circ_{\text{rxn}}$

Find $\Delta G^\circ_{\text{rxn}}$: $\text{NH}_4\text{NO}_3(\text{s}) + \text{heat} \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$

From tables of thermodynamic data we find

$$\Delta H^\circ_{\text{rxn}} = +25.7 \text{ kJ} \quad \Delta H^\circ(\text{rxn}) = \sum \Delta H^\circ(\text{prod}) - \sum \Delta H^\circ(\text{react})$$

$$\Delta S^\circ_{\text{rxn}} = +108.7 \text{ J/K or } +0.1087 \text{ kJ/K} \quad \text{ditto for } \Delta S^\circ(\text{rxn})$$

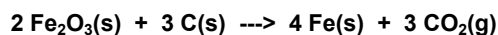
$$\Delta G^\circ_{\text{rxn}} = +25.7 \text{ kJ} - (298 \text{ K})(+0.1087 \text{ kJ/K}) \\ = -6.7 \text{ kJ}$$

Reaction is **product-favored** in spite of positive $\Delta H^\circ_{\text{rxn}}$.

Reaction is **"entropy driven"**

MAR

Free Energy and Threshold Temperature



$$\Delta H^\circ_{\text{rxn}} = +467.9 \text{ kJ} \quad \Delta S^\circ_{\text{rxn}} = +560.3 \text{ J/K}$$

$$\Delta G^\circ_{\text{rxn}} = +300.8 \text{ kJ}$$

Reaction is **reactant-favored** at 298 K

At what **Threshold Temperature** does $\Delta G^\circ_{\text{rxn}}$ just change from being (+) to being (-)?

$$\text{When } \Delta G^\circ_{\text{rxn}} = 0 = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$$

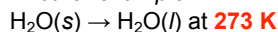
$$T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{467.9 \text{ kJ}}{0.5603 \text{ kJ/K}} = 835.1 \text{ K}$$

If ΔH and ΔS have the same sign, calculating the **Threshold Temperature** (between spontaneous and nonspontaneous reactions) can be important!

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Free Energy and Temperature

Another example:

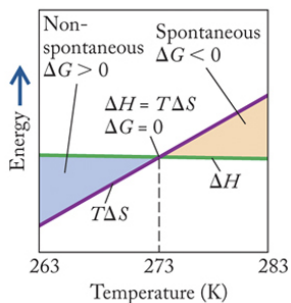


$$\Delta H = \text{positive}$$

$$\Delta S = \text{positive}$$

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

= negative above a certain temperature, when $T\Delta S > \Delta H$



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Free Energy and Equilibrium

K_{eq} is related to **reaction favorability** and $\Delta G^\circ_{\text{rxn}}$

The more negative the value of $\Delta G^\circ_{\text{rxn}}$ the larger the value of K .

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K$$

where $R = 8.3145 \text{ J/K}\cdot\text{mol}$

If not at standard states (i.e. ΔG_{rxn}) then:

$$\Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT \ln Q$$

Find $\Delta G^\circ_{\text{rxn}}$ with K first, then solve for ΔG_{rxn}

See the [Gibbs Free Energy Guide](#)

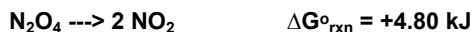


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Thermodynamics and K_{eq}

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K$$

Calculate K for the reaction:



$$\Delta G^\circ_{\text{rxn}} = +4800 \text{ J} = - (8.3145 \text{ J/K})(298 \text{ K}) \ln K$$

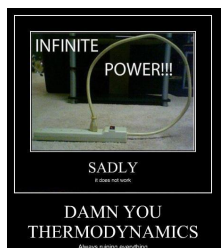
$$\ln K = -\frac{4800 \text{ J}}{(8.3145 \text{ J/K})(298 \text{ K})} = -1.94$$

$$K = e^{-1.94} = 0.14$$

When $\Delta G^\circ_{\text{rxn}} > 0$, then $K < 1$

and when $\Delta G^\circ_{\text{rxn}} < 0$, then $K > 1$

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See:

- [Chapter Sixteen Study Guide](#)
- [Chapter Sixteen Concept Guide](#)
- [Types of Equilibrium Constants](#)
- [Important Equations \(following this slide\)](#)
- [End of Chapter Problems \(following this slide\)](#)



The bankruptcy sale at the Entropy Institute was going to more difficult than Dave thought it'd be.

End of Chapter 16

MAR

**Important Equations, Constants, and Handouts
from this Chapter:**

$$\Delta H_{\text{sys}}^{\circ} = \Sigma \Delta H^{\circ} (\text{products}) - \Sigma \Delta H^{\circ} (\text{reactants})$$

$$\Delta S_{\text{sys}}^{\circ} = \Sigma S^{\circ} (\text{products}) - \Sigma S^{\circ} (\text{reactants})$$

$$\Delta G_{\text{sys}}^{\circ} = \Sigma \Delta G^{\circ} (\text{products}) - \Sigma \Delta G^{\circ} (\text{reactants})$$

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

$$\Delta G^{\circ}_{\text{rxn}} = -RT \ln K$$

$$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln Q$$

Handouts:

- Types of Equilibrium Constants
- Thermodynamic Values (Problem Set #5)

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- **know the three laws of thermodynamics!**
- **know the difference between enthalpy and entropy and how they relate to Gibbs free energy**
- **know how to calculate enthalpy (CH 221) entropy and Gibbs energy (this chapter)**
- **know how the sign of ΔG relates to spontaneity (and also $\Delta S_{\text{universe}}$)**

End of Chapter Problems: Test Yourself

You will need a table of thermodynamic values found in problem set #5

1. Use S° values to calculate the entropy change, ΔS° , for the following process: $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
2. Calculate ΔH° and ΔS° for the reaction: $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ Is the reaction predicted to be spontaneous at room temperature? higher temperatures?
3. Using values of ΔG°_f , calculate $\Delta G^{\circ}_{\text{rxn}}$ for: $2 \text{ K}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{ KCl}(\text{s})$
4. Estimate the temperature required to decompose $\text{HgS}(\text{s, red})$ into $\text{Hg}(\text{l})$ and $\text{S}(\text{g})$.
5. Calculate ΔG° and K_p at 25 °C for the reaction: $2 \text{ HBr}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{ HCl}(\text{g}) + \text{Br}_2(\text{l})$ Is the reaction predicted to be product-favored under standard conditions?

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End of Chapter Problems: Answers

1. 93.3 J/K
2. $\Delta H^{\circ} = 191.59 \text{ kJ}$, $\Delta S^{\circ} = 141.9 \text{ J/K}$, $\Delta G^{\circ} = 149.3 \text{ kJ}$ (298 K), not spontaneous, but reaction should be spontaneous at higher temperatures (entropy driven)
3. $\Delta G^{\circ}_{\text{rxn}} = -817.0 \text{ kJ}$, spontaneous
4. $T = 2089 \text{ K}$ and greater
5. $\Delta G^{\circ} = -83.74 \text{ kJ}$, and $K_p = 4.8 \times 10^{14}$ product favored

You will need a table of thermodynamic values found in problem set #5

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