Chapter 19
Chemical Thermodynamics

Kinetics

How fast a rxn. proceeds

Equilibrium

How far a rxn proceeds
towards completion

Thermodynamics

Study of energy relationships & changes which occur during chemical & physical processes

A) First Law of Thermodynamics

Law of Conservation of Energy :

Energy can be neither created nor destroyed but may be converted from one form to another.

Energy lost by system	=	Energy gained by surroundings

1) Internal Energy, E

E = total energy of the system

Actual value of E cannot be determined

Only ΔE

2) Relating ΔE to Heat & Work

2 types of energy exchanges occur between system & surroundings

Heat & Work

+ q : heat absorbed, endothermic

– q : heat evolved, exothermic

+ w : work done on the system

– w : work done by the system

a) First Law

$$\boxed{\Delta E = q + w}$$

3) System and Surroundings

System = portion we single
out for study

- focus attention on changes which occur w/in definite boundaries

Surroundings = everything else

System : Contents of rx. flask

Surround. : Flask & everything outside it

Agueous soln. rx :

System : dissolved ions & molecules
Surround : H_2O that forms the soln.

B) Thermodynamic State & State Functions

Thermodynamic State of a System

defined by completely specifying
ALL properites of the system

- P, V, T, composition, physical st.

1) State Function

prop. of a system determined
by specifying its state.

depends only on its present
conditions & NOT how it got there

$$\Delta E = E_{\textbf{final}} - E_{\textbf{initial}}$$

independent of path taken
to carry out the change

- Also is an extensive prop.

C) Enthalpy

In ordinary chem. rx., work generally arises as a result of pressure-volume changes

Inc. vol. & system does work against pressure of the atmosphere

Constant Pressure

$$w = -P\Delta V$$

Negative because work done by system

$$\Delta E = q - P\,\Delta V$$

1) ΔE at Constant Volume

$$\boxed{\Delta E = q_v}$$

2) ΔE at Constant Pressure :

$$\Delta E = q_p - P\,\Delta V$$

$$q_p = \Delta E + P\Delta V$$

3) Enthalpy, H

$$H = E + PV$$

Change in enthalpy at constant P is:

$$\boxed{\Delta H = \Delta E + P\,\Delta V}$$

&

$$\boxed{\Delta H = q_p}$$

Can think of as heat content

state fnc. & is extensive

D) Enthalpies of Reaction

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(\ell) \quad \Delta H = -572\ \text{kJ}$$

Thermochemical eqn.

Physical states are given and energy associated w. rx. written to right

- MUST give physical states

If product is $H_2O(\mathbf{g})$, $\Delta H = -484$kJ

ΔH corresponds to molar quantities given in eqn. as written

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow H_2O(\ell) \quad \Delta H = -286\ \text{kJ}$$

1) Guidelines

a) Enthalpy is extensive

Multiply a rxn by some factor the ΔH is multiplied by that factor

b) $\Delta H_{\mathbf{reverse}} = -\,\Delta H_{\mathbf{forward}}$

c) Enthalpy is a state function

ΔH depends on the states of reactants and products.

E) Hess's Law

ΔH is a state fnc.

Same whether the process occurs as a single step or as a series of steps

The ΔH_{rxn} is the sum of the ΔH's for the individual steps.

$$\Delta H_{rx} = \sum_{\text{Steps}} \Delta H_{steps}$$

* Add chem. eqn's for steps to get overall rxn.

* Add $\Delta H_{steps} \Rightarrow \Delta H_{rxn}$

1) Note:

In using Hess's Law:

a) If an eqn. is multiplied by a factor, ΔH is multiplied by the same factor.

b) If an eqn. is reversed, sign of ΔH changes

c) All substances NOT appearing in desired eqn. MUST cancel

F) Enthalpy of Formation

Enthalpy change for the formation of a compound from its elements

ΔH_f

1) Standard enthalpy change

Enthalpy change when all reactants and and products are in their standard states

$\Delta H°$

2) Standard State

Most stable state of a substance in its pure form under standard pressure (1 atm) (& some specified temp. of interest - usually 25 °C)

3) Thermochemical Standard States

a) solid or liquid

Pure substance at 1 atm

b) gas

partial pressure of 1 atm

c) species in solution

Conc. of 1 M

4) Standard Enthalpy of Formation

ΔH for the rxn in which 1 mole of a cmpd. is formed from its elements with ALL substances in their standard states (in kJ/mol)

$$\Delta H_f°$$

Note: $\Delta H_f° = \mathbf{0}$ for an element in its standard state

	$\Delta H_f°$
$\frac{1}{2}$ $N_2(g)$ + $\frac{3}{2}$ $H_2(g) \rightarrow NH_3(g)$	− 46.2
$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$	− 411.0
C(graphite) → C(diamond)	+ 1.897

THERMODYNAMIC QUANTITIES FOR SELECTED SUBSTANCES AT 298.15 K (25 °C)

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
Aluminum			
$Al(s)$	0	0	28.32
$AlCl_3(s)$	−705.6	−630.0	109.3
$Al_2O_3(s)$	−1669.8	−1576.5	51.00
Barium			
$Ba(s)$	0	0	63.2
$BaCO_3(s)$	−1216.3	−1137.6	112.1
$BaO(s)$	−553.5	−525.1	70.42
Beryllium			
$Be(s)$	0	0	9.44
$BeO(s)$	−608.4	−579.1	13.77
$Be(OH)_2(s)$	−905.8	−817.9	50.21
Bromine			
$Br(g)$	111.8	82.38	174.9
$Br^-(aq)$	−120.9	−102.8	80.71
$Br_2(g)$	30.71	3.14	245.3
$Br_2(l)$	0	0	152.3
$HBr(g)$	−36.23	−53.22	198.49
Calcium			
$Ca(g)$	179.3	145.5	154.8
$Ca(s)$	0	0	41.4
$CaCO_3(s, \text{calcite})$	−1207.1	−1128.76	92.88
$CaCl_2(s)$	−795.8	−748.1	104.6
$CaF_2(s)$	−1219.6	−1167.3	68.87
$CaO(s)$	−635.5	−604.17	39.75
$Ca(OH)_2(s)$	−986.2	−898.5	83.4
$CaSO_4(s)$	−1434.0	−1321.8	106.7
Carbon			
$C(g)$	718.4	672.9	158.0
$C(s, \text{diamond})$	1.88	2.84	2.43
$C(s, \text{graphite})$	0	0	5.69
$CCl_4(g)$	−106.7	−64.0	309.4
$CCl_4(l)$	−139.3	−68.6	214.4
$CF_4(g)$	−679.9	−635.1	262.3
$CH_4(g)$	−74.8	−50.8	186.3
$C_2H_2(g)$	226.77	209.2	200.8
$C_2H_4(g)$	52.30	68.11	219.4
$C_2H_6(g)$	−84.68	−32.89	229.5
$C_3H_8(g)$	−103.85	−23.47	269.9
$C_4H_{10}(g)$	−124.73	−15.71	310.0
$C_4H_{10}(l)$	−147.6	−15.0	231.0
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_6(l)$	49.0	124.5	172.8
$CH_3OH(g)$	−201.2	−161.9	237.6
$CH_3OH(l)$	−238.6	−166.23	126.8
$C_2H_5OH(g)$	−235.1	−168.5	282.7
$C_2H_5OH(l)$	−277.7	−174.76	160.7
$C_6H_{12}O_6(s)$	−1273.02	−910.4	212.1
$CO(g)$	−110.5	−137.2	197.9
$CO_2(g)$	−393.5	−394.4	213.6
$CH_3COOH(l)$	−487.0	−392.4	159.8
Cesium			
$Cs(g)$	76.50	49.53	175.6
$Cs(l)$	2.09	0.03	92.07
$Cs(s)$	0	0	85.15
$CsCl(s)$	−442.8	−414.4	101.2
Chlorine			
$Cl(g)$	121.7	105.7	165.2
$Cl(aq)$	−167.2	−131.2	56.5
$Cl_2(g)$	0	0	222.96
$HCl(aq)$	−167.2	−131.2	56.5
$HCl(g)$	−92.30	−95.27	186.69
Chromium			
$Cr(g)$	397.5	352.6	174.2
$Cr(s)$	0	0	23.6
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
Cobalt			
$Co(g)$	439	393	179
$Co(s)$	0	0	28.4
Copper			
$Cu(g)$	338.4	298.6	166.3
$Cu(s)$	0	0	33.30

C) Determine ΔH°_{rxn} from ΔH_f°

$$\Delta H^\circ_{rxn} = \sum_{\text{prod.}} n\,\Delta H_f^\circ - \sum_{\text{react.}} m\,\Delta H_f^\circ$$

n = coef. in bal. eqn. for each **product**

m = coef. in bal. eqn. for each **reactant**

I) Spontaneous Processes

Spontaneous Process

Process which proceeds on own without outside assistance

- occurs in one direction only

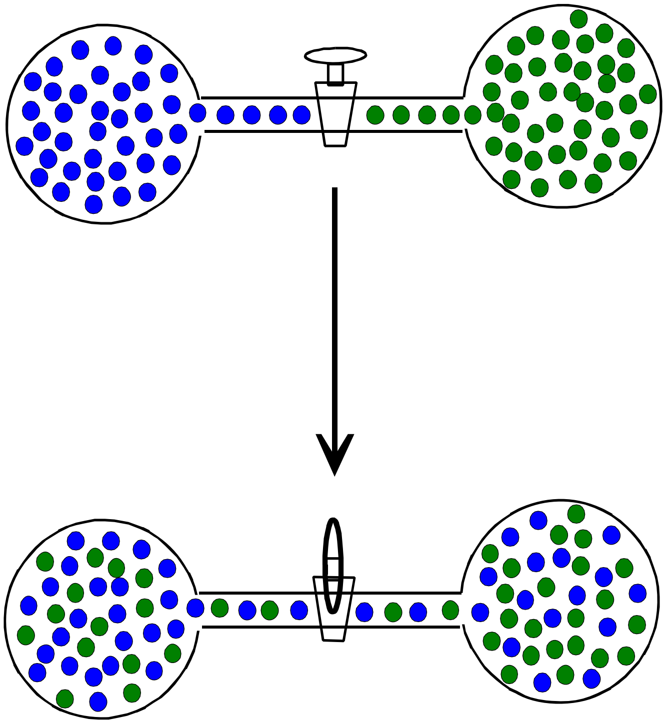
NONspontaneous Process

Can NOT proceed w/o outside assistance

- reverse of spont. process

Processes which are spont. in
one direction are nonspont. in
the reverse direction.

Mix 2 ideal gases



Open stopcock

Spontaneously mix

Reverse process is NOT spont.

Will all spont. rxns. be exothermic or vice versa?

Will all nonspont. rxns. be endothermic or vice versa?

NO!

Spontaneity can depend on temp. & pressure

For H_2O:

T > 0 °C : melting spont.

T < 0 °C : freezing spont.

T = 0 °C : equilibrium and neither conversion occurs spont.

A) Reversible & IRreversible Processes

1) Reversible Process

Change made in a way that system & surroundings can be restored to their original states by exactly reversing chg

NO net chg. to system or its surr.

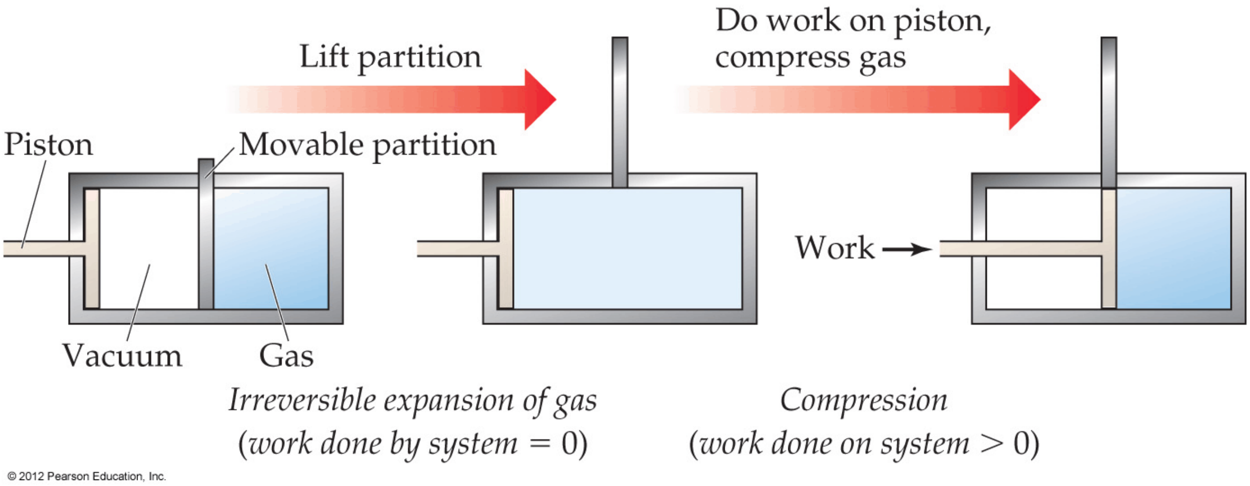
2) IRreversible Process

Can NOT simply be reversed to restore system & surroundings to their original states

A reversible change produces the max. amt. of work which can be done by a system on its surroundings.

3) Isothermal Expansion of a Gas

Expansion of ideal gas at
constant temperature.



Irreversible expansion of gas
(*work done by system* = 0)

Compression
(*work done on system* > 0)

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Remove partition - gas spont. expands to fill the whole cylinder. No work is done by the system.

Compressing the gas back to the original state requires surroundings to do work on the system.

Process is IRreversible

Can be done reversibly by doing the expansion and compression infinitely slowly so the external and internal pressures are always in equilibrium.

- can not actually be done in real processes

- ALL real processes are IRreversible

4) Conclusions

a) A spont. process is an IRreversible process

b) Driving force is tendency to go to a less ordered state or state of higher probability.

II) Entropy, S & 2nd Law of Thermodynamics

Measure of randomness or
disorder in a system

or

Extent to which energy is distributed among the various motions of the molecules in the system.

State Fnc: $\Delta S = S_{final} - S_{initial}$

$\Delta S > 0$ $S_f > S_i$ inc. in disorder

$\Delta S < 0$ $S_f < S_i$ dec. in disorder

A) Isothermal Process

Constant temp. process

$$\Delta S = \frac{q_{rev}}{T}$$

q_{rev} = heat which would be transferred if process were reversible

S is a state function

- Thus this eqn. can be used to calc. ΔS for any isothermal process (whether reversible or irreversible).

1) ΔS and Phase Changes

Phase changes occur at constant T

$$q_{rev} = \Delta H_{\text{phase change}}$$

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{phase change}}}{T}$$

a) Ex: boiling water at 100 °C

$$\Delta H_{vap} = 44.01 \text{ kJ/mol}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{44.01 \text{ kJ/mol}}{373.15 \text{ K}}$$

$$= 0.1178 \text{ kJ/mol}\bullet\text{K}$$

$$= +\ 117.8 \text{ J/mol}\bullet\text{K}$$

B) 2nd Law of Thermodynamics and S

Irreversible Process

Results in inc. in S_{total} ($\Delta S > 0$)

Reversible Process

Results in no change in S_{total} ($\Delta S = 0$)

2nd Law of Thermodynamics

Total entropy of a system & its surroundings always inc. for a spont. process

Irreversible (Spont.) Process

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

Reversible Process

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

1) Ex: 1 mole of Liquid water is left outside where it's -10.0 °C and it freezes. Calc. ΔS_{sys} & ΔS_{surr}. Will it spontaneously freeze?

$\Delta H_{fus} = + 6.01$ kJ/mol

$\Delta H_{freezing} = - \Delta H_{fus} = - 6.01$ kJ/mol

$$\Delta S_{sys} = \frac{\Delta H_{frz}}{T} = \frac{(1\ \text{mol})(-\ 6.01\ \text{kJ/mol})}{273\ \text{K}}$$

$$= -\ 0.0220\ \text{kJ/mol}\bullet\text{K} = -\ 22.0\ \text{J/mol}\bullet\text{K}$$

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{(1\ \text{mol})(+\ 6.01\ \text{kJ/mol})}{263\ \text{K}}$$

$$= +\ 0.0229\ \text{kJ/mol}\bullet\text{K} = +\ 22.9\ \text{J/mol}\bullet\text{K}$$

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

$$= (-\ 22.0\ \text{J/mol}\bullet\text{K}) + (+\ 22.9\ \text{J/mol}\bullet\text{K})$$

$$= +\ 0.9\ \text{J/mol}\bullet\text{K}$$ Spont.

This shows that even though the entropy of the system DEC. the process was still spont. because the entropy of the surroundings increased more.

$$\Delta S_{univ} > 0$$

Spont. processes occur w. an overall INC. in ΔS_{univ}

Practically speaking we can't always easily determine ΔS_{univ}.

Want to focus on the system. Will see how to determine spontaneity based on ΔS_{sys}.

Simplify notation and refer to ΔS_{sys} simply as ΔS

III) Molecular Inerpretation of Entropy

A) Expansion of Gas at Molecular Level

Have the following system:

(a)

The two molecules are colored red and blue to keep track of them.

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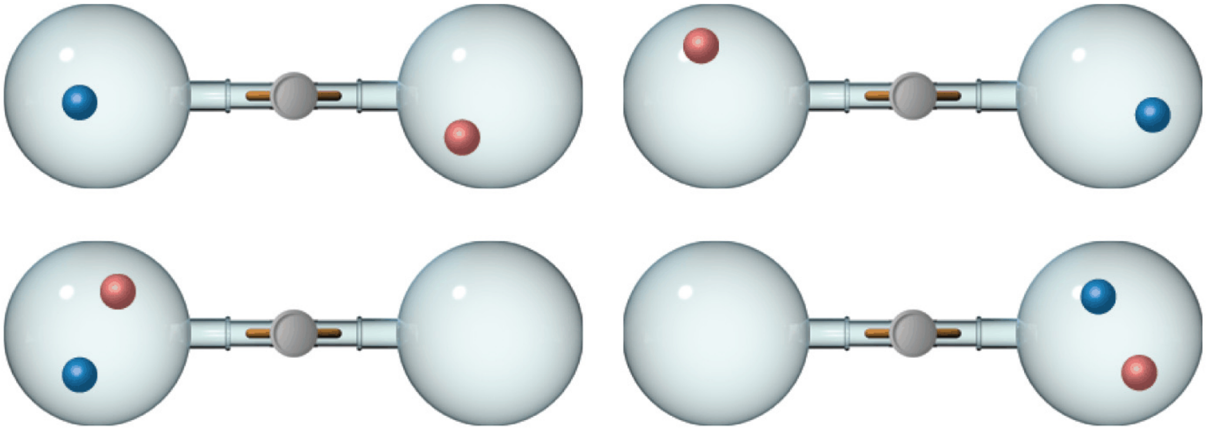
Open stopcock:

We know gas expands spont.

Why?

Look at possible arrangements of the particles



(b)
Four possible arrangements (microstates)
once the stopcock is opened.

Probability that blue molecule is in left flask is ½. Same for the red particle.

Probability that both molecules remain in the left flask is:

$$(1/2)^2 = 1/4$$

For 3 particles it would be

$$(1/2)^3 = 1/8$$

Consider a mole of gas:

Prob. all the molecules are in the left flask at the same time is:

$(1/2)^N$ where $N = 6.02 \times 10^{23}$

Infinitesimally small!!!

Essentially ZERO prob.
of all molecules in left
flask at same time.

- Gas SPONT. expands to fill both flasks

- Does NOT spont. go back to left flask

Most probable arrangements are those with essentially equal numbers of particles in both flasks.

Gas spreads out and the arrangement of gas particles is more disordered than when confined to one flask

Greater entropy

Just seen disorder on the molecular level

B) Boltzmann's Eqn. & Microstates

Statistical Thermodynamics

Uses statistics and probability to link microscopic & macroscopic worlds.

Microstate

Single possible arrangement of the positions and kinetic energies of the molecules - snapshot

Exceptionally LARGE # microstates

Can use probability and statistics to determine total # microstates for a thermodynamic state

W = # microstates

Very Large # for a mole of particles

Related to Entropy

Boltzmann Eqn.

$S = k \bullet \ln W$

k = Boltzmann's constant

$= 1.38 \times 10^{-23}$ J/K

S is a measure of # microstates associated w. a particular macroscopic state

$$\Delta S = k \bullet \ln W_{final} - k \bullet \ln W_{initial}$$

$$= k \bullet \ln \frac{W_f}{W_i}$$

When $W_f > W_i$ $\Delta S > 0$

Entropy inc. w. # microstates

Ex: Inc volume of a gas

greater vol - greater # of positions available to the particles and greater # microstates

∴ Entropy inc. as vol. inc.

C) Molecular Motions and Energy

Ideal gas particles are idealized points w. no vol. and no bonds

- translational motion only

Real molecules

- translational motion
- rotational motions

  spin about an axis

  Linear: 2 axes of spin

  Nonlinear: 3 axes of spin

- vibrational motions

Atoms periodically move toward & away from each other

Linear: 3N - 5
Nonlinear: 3N - 6

N = # atoms in molecule (N > 2)

microstates inc. as complexity of molecule inc.

- there are many more vibrational motions

D) Predicting Sign of ΔS

1) Phase changes

Solid ----> Liquid ----> Gas

$\Delta S > 0$ $\Delta S > 0$

2) Number of Molecules Inc.

$F_2(g) \longrightarrow 2\,F(g)$

$\Delta S > 0$

3) Inc. # Atoms in a Molecule

Inc. degrees of freedom

$\Delta S > 0$

4) Mixing of Substances

Generally, $\Delta S_{soln} > 0$

5) Temp. Changes

Inc. Temp., KE inc.

- molecules move faster
- broadens distribution of speeds

$\Delta S > 0$

6) Vol. Inc.

Vol. inc. - greater # positions available to atoms

$\Delta S > 0$

E) Ex: The ΔH_f° of liquid acetone is - 247.6 kJ/mol at 25 °C. The ΔH_f° for the vapor is -216.6 kJ/mol at 25 °C. What is the entropy change when 1.00 mol of liquid acetone vaporizes at 25 °C?

F) Ex: A sample of 2.00 mol of an ideal gas expands from a vol. of 1.0 L to 10.0 L at constant temperature. What is the entropy change, ΔS? Is the sign of ΔS consistent w. your expectations?

IV) Third Law & Standard Entropy

A) 3rd Law

A perfectly crystalline substance at 0 K has entropy of zero

Can measure Absolute entropy, also called standard entropy, S^o

- entropy value for standard state of species

Standard State

Pure substance: 1 atm pressure

Species in Soln: 1 M

Can calculate from heat capacities

$$S^\circ_T = \int_0^T \frac{C_p(T)\,dT}{T}$$

1) Values for compounds do NOT correspond to formation from the elements

2) Absolute entropy of an element in its solid state ≠ 0

3) Values on order of 10's of joules (not kJ like enthalpy)

Ebbing, GENERAL CHEMISTRY, Third Edition
Table 18.1 Standard entropies (Part 1)

Formula	$S°$, J/(mol · K)	Formula	$S°$, J/(mol · K)	Formula	$S°$, J/(mol · K)
Hydrogen		***Carbon***		***Carbon (continued)***	
$H^+(aq)$	0	C(graphite)	5.7	$HCN(l)$	112.8
$H_2(g)$	130.6	C(diamond)	2.4	$CCl_4(g)$	309.7
Sodium		$CO(g)$	197.5	$CCl_4(l)$	214.4
$Na^+(aq)$	60.2	$CO_2(g)$	213.7	$CH_3CHO(g)$	266
$Na(s)$	51.4	$HCO_3^-(aq)$	95.0	$C_2H_5OH(l)$	161
$NaCl(s)$	72.1	$CH_4(g)$	186.1	***Silicon***	
$NaHCO_3(s)$	102	$C_2H_4(g)$	219.2	$Si(s)$	18.0
$Na_2CO_3(s)$	139	$C_2H_6(g)$	229.5	$SiO_2(s)$	41.5
Calcium		$C_6H_6(l)$	172.8	$SiF_4(g)$	285
$Ca^{2+}(aq)$	−55.2	$HCHO(g)$	219	***Lead***	
$Ca(s)$	41.6	$CH_3OH(l)$	127	$Pb(s)$	64.8
$CaO(s)$	38.2	$CS_2(g)$	237.8	$PbO(s)$	66.3
$CaCO_3(s)$	92.9	$CS_2(l)$	151.0	$PbS(s)$	91.3
		$HCN(g)$	201.7		

B) Entropy Change for a Rxn.

$$\boxed{\Delta S^\circ_{rxn} = \sum_{\text{prod.}} \mathbf{n}\, S^\circ - \sum_{\text{react.}} \mathbf{m}\, S^\circ}$$

n = coef. in bal. eqn. for each **product**

m = coef. in bal. eqn. for each **reactant**

1) Ex: Calculate the entropy change for the formation of H_2O from its elements at 25 °C.

$S^o_{(H2)} = 130.58$ J/mol•K

$S^o_{(O2)} = 205.0$ J/mol•K

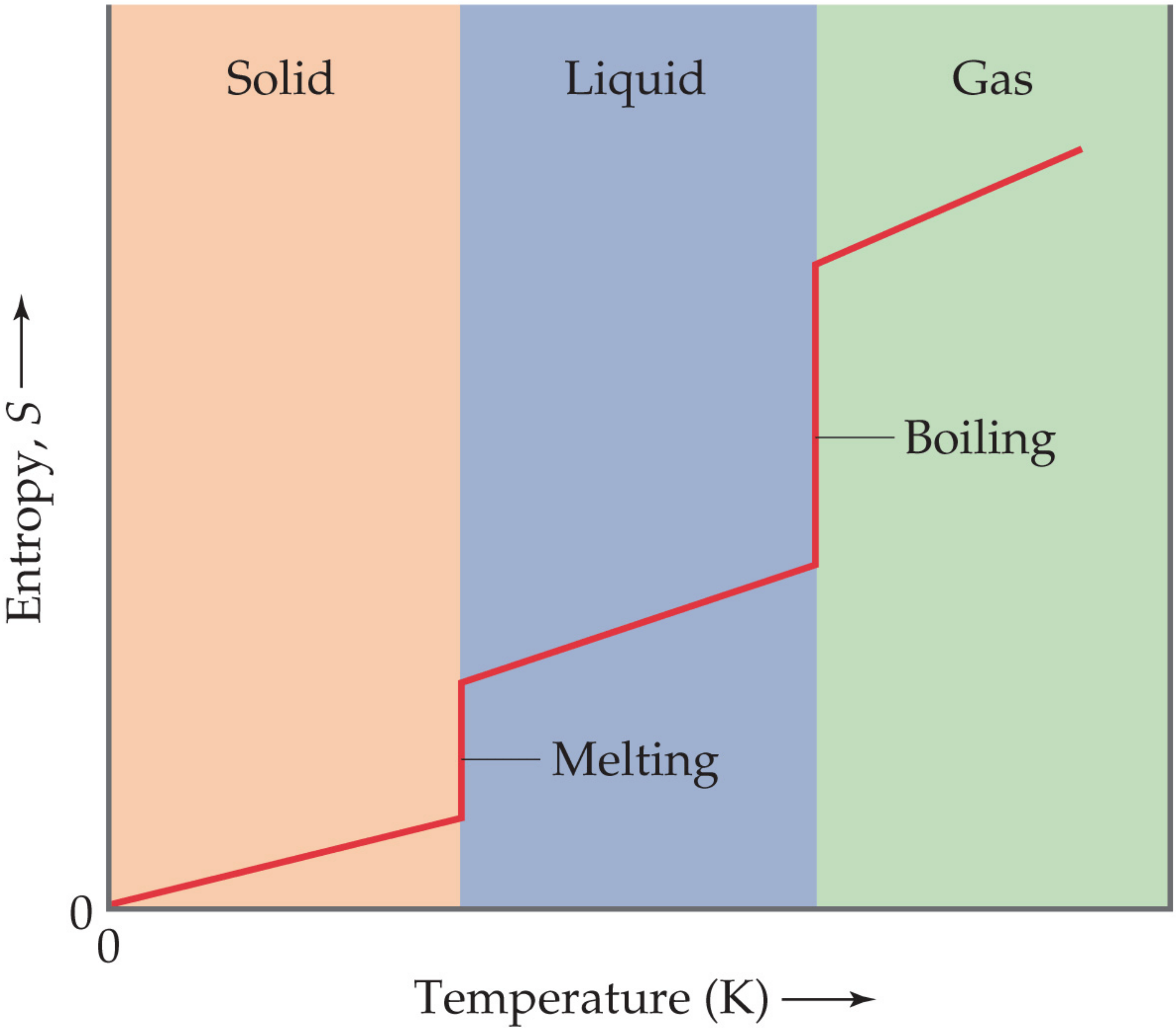
$S^o_{(H2O,\ liq)} = 69.91$ J/mol•K

$$2\ H_2\ (g)\ +\ O_2\ (g)\ \rightleftarrows\ 2\ H_2O\ (\ell)$$

$$\Delta S^\circ_{rxn} = 2\ S^o_{(H2O,\ liq)} - [2\ S^o_{(H2)} + S^o_{(O2)}]$$

$$= (2\text{ mol})\ (69.91\text{ J/mol•K}) - [(2\text{ mol})\ (130.58\text{ J/mol•K}) + (1\text{ mol})(205.0\text{ J/mol•K})]$$

$$= -\ 326.3\text{ J/K}$$


Solid
Liquid
Gas
Boiling
Melting
Entropy, S ⟶
0
0
Temperature (K) ⟶

V) Gibbs Free Energy & Spontaneity

$$G = H - TS$$

State Fnc: $\Delta G = G_{\mathbf{final}} - G_{\mathbf{initial}}$

At constant T & P

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

Under standard state conditions,

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

How does this relate to spontaneity?

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

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

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

Rearrange:

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

$$\Delta G = -\ T\,\Delta S_{univ}$$

Now have an eqn. which relates spont. to the system.

At constant T & P

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$\Delta G < 0$ spont.

$\Delta G > 0$ NONspont.

$\Delta G = 0$ equilibrium

A) Standard Free-Energy Change

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

$$\text{reactants in standard state} \xrightarrow[\Delta G]{} \text{products in standard state}$$

B) Standard Free Energies of Formation

ΔG° when 1 mole of substance is formed from its elements in their stablest states at 1 atm (or 1 M) at a specified temp. (usually 25°C).

$$\Delta G^\circ_{rx} = \sum_{prod.} n \Delta G^\circ_f - \sum_{react} m \Delta G^\circ_f$$

$$\Delta G^\circ_f \text{ (elments)} = 0$$

Ebbing, GENERAL CHEMISTRY, Third Edition
Table 18.2 Standard free energies of formation (Part 1)

Formula	ΔG°_f, kJ/mol	Formula	ΔG°_f, kJ/mol	Formula	ΔG°_f, kJ/mol
Hydrogen		***Carbon***		***Carbon (continued)***	
$H^+(aq)$	0	C(graphite)	0	$HCN(l)$	121
$H_2(g)$	0	C(diamond)	2.9	$CCl_4(g)$	−53.7
Sodium		$CO(g)$	−137.2	$CCl_4(l)$	−68.6
$Na^+(aq)$	−261.9	$CO_2(g)$	−394.4	$CH_3CHO(g)$	−133.7
$Na(s)$	0	$HCO_3^-(aq)$	−587.1	$C_2H_5OH(l)$	−174.8
$NaCl(s)$	−348.0	$CH_4(g)$	−50.8	***Silicon***	
$NaHCO_3(s)$	−851.9	$C_2H_4(g)$	68.4	$Si(s)$	0
$Na_2CO_3(s)$	−1048.1	$C_2H_6(g)$	−32.9	$SiO_2(s)$	−856.5
Calcium		$C_6H_6(l)$	124.5	$SiF_4(g)$	−1506
$Ca^{2+}(aq)$	−553.0	$HCHO(g)$	−110	***Lead***	
$Ca(s)$	0	$CH_3OH(l)$	−166.2	$Pb(s)$	0
$CaO(s)$	−603.5	$CS_2(g)$	66.9	$PbO(s)$	−189
$CaCO_3(s)$	−1128.8	$CS_2(l)$	63.6	$PbS(s)$	−96.7
		$HCN(g)$	125		

1) **Ex**: Calc. ΔG° at 25°C

	$CH_3CH_2OH(l)$	$+\ O_2(g)$	$\rightarrow CH_3COOH(l)$	$+\ H_2O(l)$
ΔG°_f (kJ/mol)	-174.8	0	-392.5	-237.2

$$\Delta G^\circ = (-392.5 + -237.2) - (-174.8 + 0)$$

$$\Delta G^\circ = -454.9 \text{ kJ}$$

2) **Ex**: Calc. ΔG° at 25°C for the conversion of diamond to graphite. Which is more stable under standard conditions?

$$C(\text{diamond}) \rightarrow C(\text{graphite})$$

ΔG_f° (kJ/mol)	2.9	0

c) ΔG° and Spontaneity

ΔG indicates spontaneity

However, if everything is in their standard states can use ΔG°

1) ΔG° is large (-) number (< -10 kJ)
spont. + mostly products at equil. (goes to completion)

2) ΔG° is large (+) number (> 10 kJ)
nonspont. + mostly reactants (very little rx.)

3) $-10 \text{ kJ} < \Delta G^\circ < 10 \text{ kJ}$
equil. mixture w. significant amts. of reactants + products

4) **Ex** : Predict sign of ΔS° for the following rx. & whether the rx. is spont. & where equil. lies.

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \longrightarrow$$

$$Ba(NO_3)_2(s) + 2NH_3(aq) + 10H_2O(\ell)$$

V) Interpretation of Free Energy

A) Maximum Work

ΔG is the max. energy available (free) to do useful work

$w_{max} = \Delta G$ (no entropy produced)

$-\Delta G$: max. useful work obtainable in spont. rx.

$+\Delta G$: min. work required to cause a process to occur.

B) Coupling Rx's

Use a spont. rx. to "drive" a nonspont. rx.

Ex: extract Cu from an ore

$Cu_2S(s) \longrightarrow 2Cu(s) + S(s)$ $\Delta G^\circ = +86.2$ kJ

nonspont.

Couple to a spont. rx.

$S(s) + O_2(g) \longrightarrow SO_2(g)$ $\Delta G^\circ = -300.1$ kJ

$Cu_2S(s) + O_2(g) \rightarrow 2Cu(s) + SO_2(g)$

$\Delta G^\circ = -213.9$ kJ

overall rx. is spont.

XV) Temperature Dependence of ΔG

A) Variation w. Temp.

$$\Delta G_T = \Delta H_{25°C} - T\Delta S_{25°C}$$

Assumes ΔH & ΔS do not vary much w. temp.

Applies to $\Delta G°$ as well

B) Predicting Spontaneity

ΔH	ΔS	ΔG	Result
−	+	(−) at all T	spont.
+	−	(+) at all T	Non spont
−	−	(−) if T low	Spont. at low T
+	+	(−) if T high	Spont. at high T

c) **Ex** : For a certain process $\Delta H = 178\ kJ$ & $\Delta S = 160\ J/K$. Estimate the min. temp. at which the process will be spontaneous.

VIII) Relationships Between ΔG, ΔG°, & K

ΔG for nonstandard states is related to ΔG° by,

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

Q (K, if at equil.) is the thermodynamic rx. quotient

Conc. of gases ⇒ partial pressures (atm)

Conc. of solutes in liq. soln. ⇒ molarities (M)

$$2\,NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

$$Q \text{ or } K = \frac{[NH_2CONH_2]}{P_{NH_3}^2 \cdot P_{CO_2}}$$

$$A(g) \rightleftharpoons B(g)$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_B}{P_A}$$

If P_A & P_B are both 1 atm,

$$\Delta G = \Delta G^\circ$$

A) Ex: What is ΔG at 25°C if

$\Delta G^\circ = 10.0\ \text{kJ}$

$P_A = 1.00\ \text{atm}$, $P_B = 1.00 \times 10^{-5}\ \text{atm}$

$\Delta G =$

B) Relating ΔG° to K

At equilibrium,

$$\Delta G = 0 \quad \& \quad Q = K$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\boxed{\Delta G^\circ = -RT \ln K}$$

C) 2 types of calc.

given conc. (calc. K) $\Rightarrow$ ΔG°

given ΔG_F° (calc. ΔG°) $\Rightarrow$ K

1) **Ex**: Determine ΔG° for a rx. by measuring conc. at equil.

$$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$$

$P_{HI} = 0.420$ atm , $P_{H_2} = 0.504$ atm ; 25 °C

$$K = K_p = \frac{P_{HI}^2}{P_{H_2}} = \frac{(0.420)^2}{0.504} = 0.350$$

$$\Delta G^\circ = -RT \ln K$$

$$= -(8.314 \times 10^{-3} \tfrac{kJ}{mol \cdot K})(298)(-1.05)$$

$$= +\ 2.60\ kJ$$

Nonspont., but value is small — Corresponds to K reflecting signif. amts. of react. & prod. at equil.

2) **Ex**: Use ΔG_f° values to determine ΔG° + then K + from K the equil. conc.

Calc. K_p at 25°C for.

$$2HCl(g) + F_2(g) \rightleftharpoons 2HF(g) + Cl_2(g)$$

ΔG_f° -95.3 0 -275 0

$$\Delta G^\circ = 2(-275) - 2(-95.3) = -359\ kJ$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-359\times 10^3\ J)}{(8.314\ J/mol\cdot K)(298)} = 144.9$$

$$K = K_p = 8.5 \times 10^{62}$$

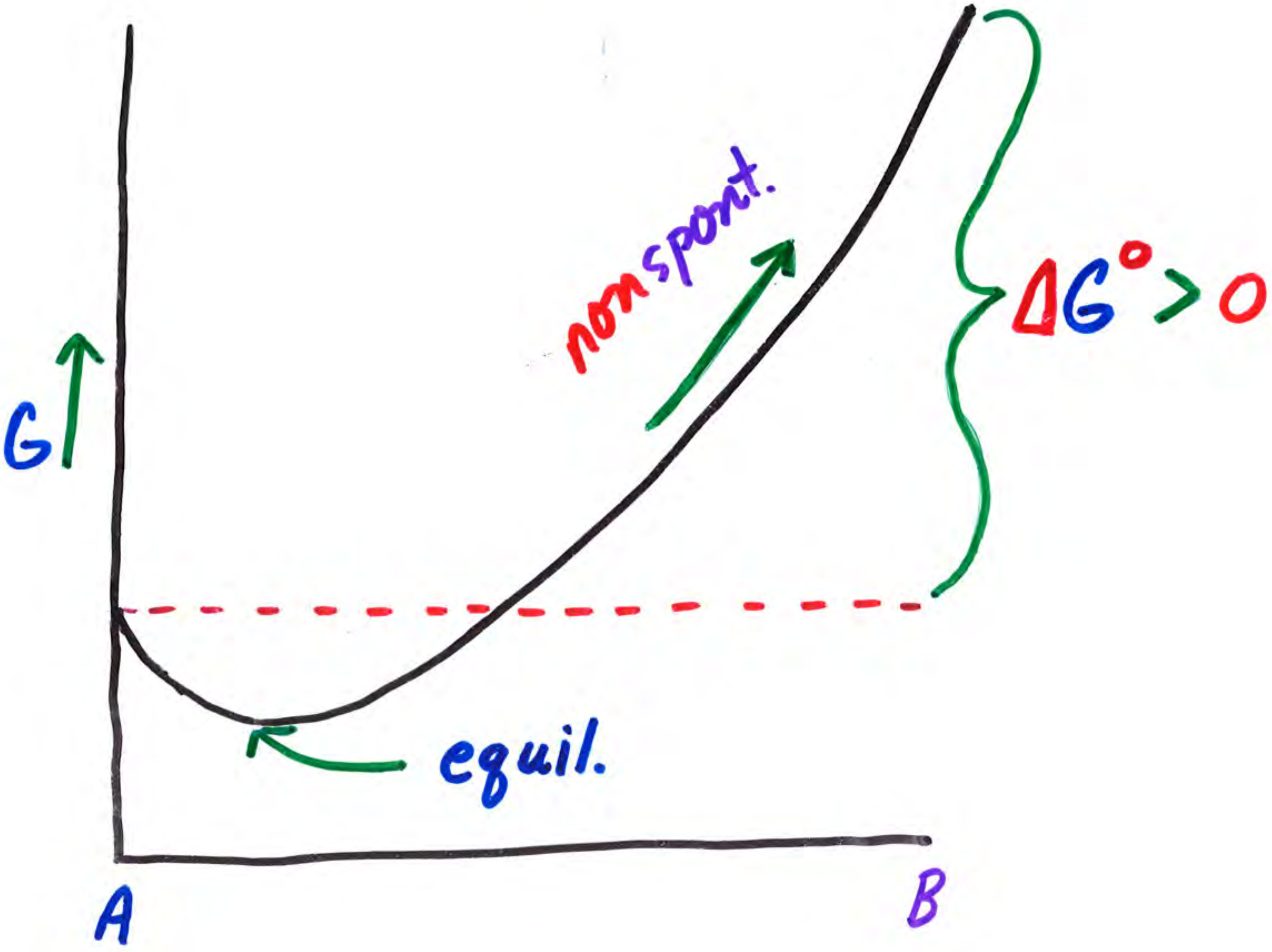
Large (-) ΔG° ⇒ large K

- essentially goes to completion

D) Free-Energy Change During Rx.

How does free energy change along free-energy curve from reactants to products?

$$A \rightleftharpoons B$$



Slope of free-energy curve, ΔG, determines spont. at given composition

ΔG° controls position of the min.

- depends on relative values of $G_{react.}$ & $G_{prod.}$ + always lies closer to lower energy

If reactants have lower energy, equil. is closer to reactants

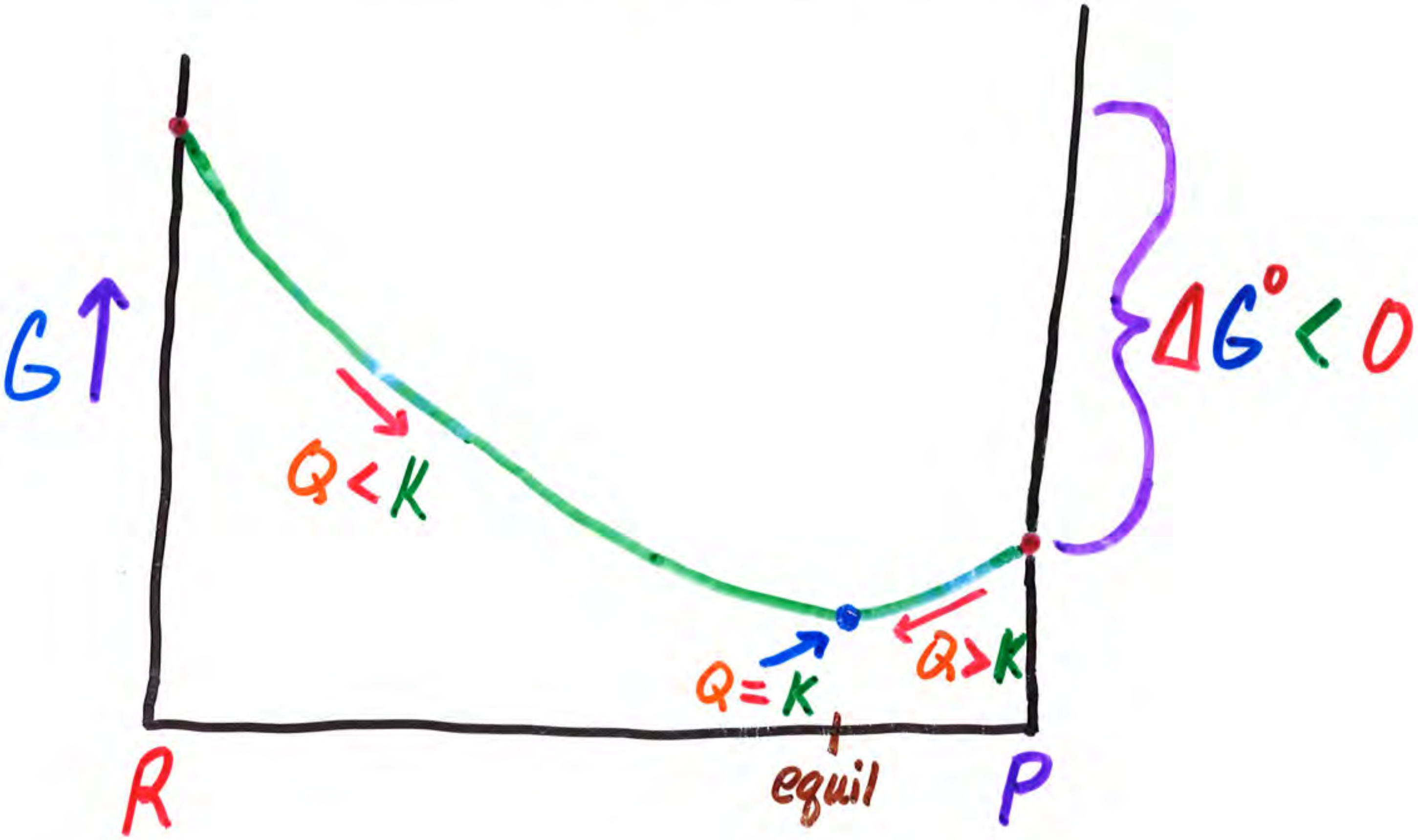
$\Delta G^\circ > 0$, nonspont.

If products have lower energy, equil. is closer to products

$\Delta G^\circ < 0$, spont.

E) Extent of Reaction

1) $\Delta G°$ is large & negative

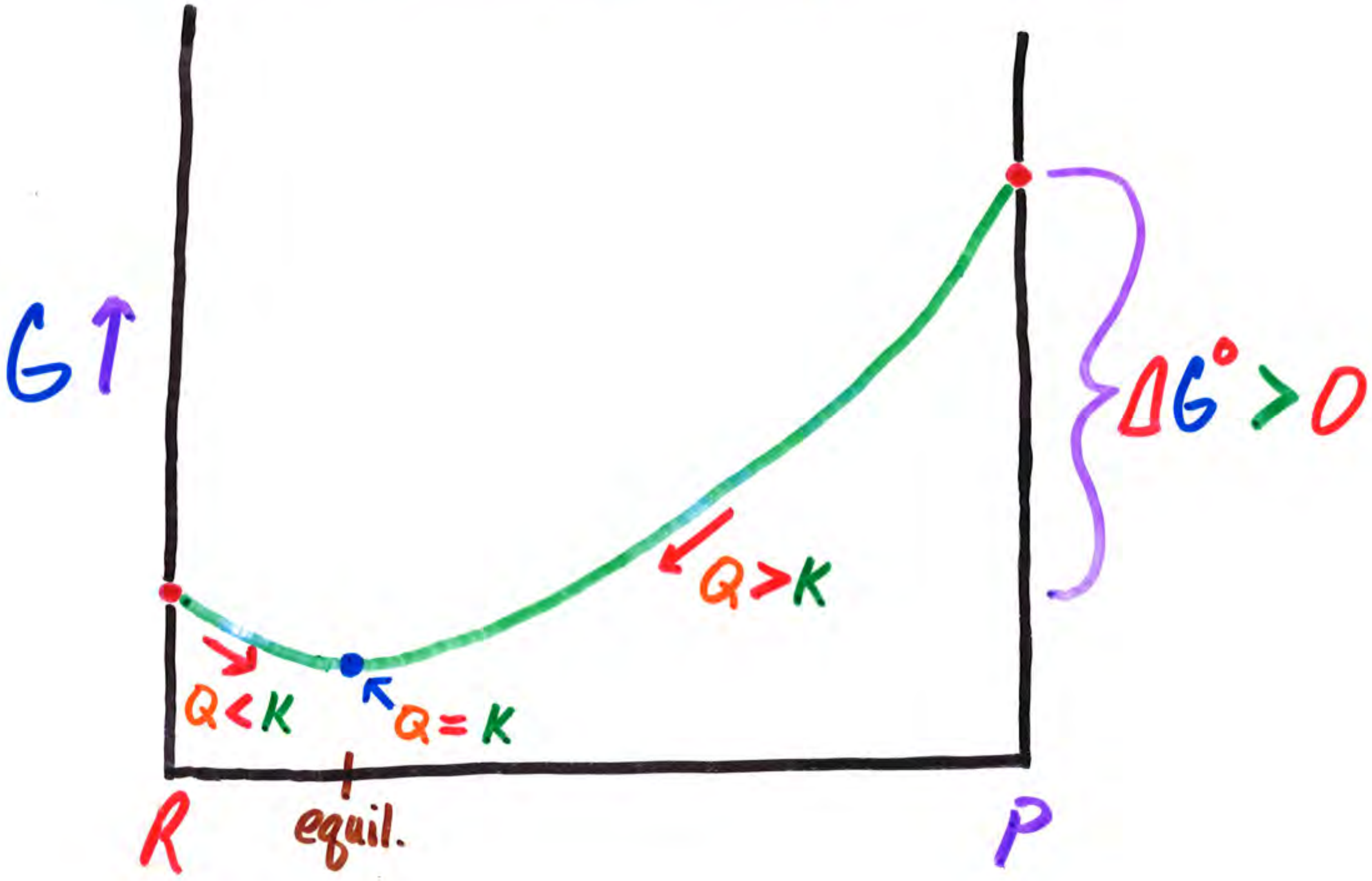


Forward rx is spontaneous

Extremely large K

- formation of products virtually complete

2) ΔG° is large & positive



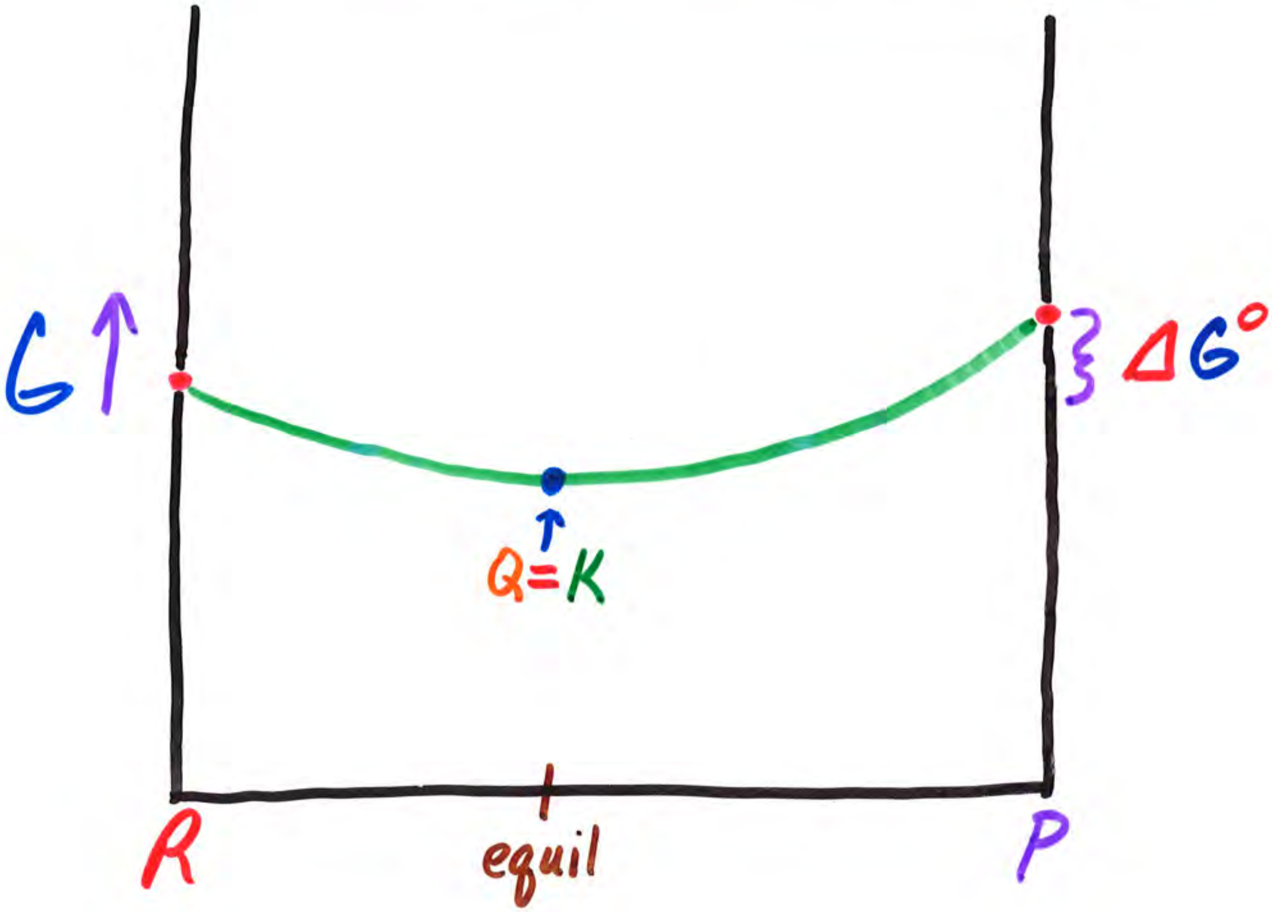
Forward rx. is nonspont.

- NOT complete rx.

Extremely small K

- mostly reactants at equil.

3) $-10\ kJ < \Delta G^\circ < 10\ kJ$



K in range of 57 to 0.018 (25°C)

Appreciable amounts of reactants AND products at equil.

VIII) Variation of K w. T

A) Method 1

$$\ln K = \frac{-\Delta G^\circ_T}{RT}$$

B) Method 2 : van't Hoff Eqn.

$$\ln K = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + C$$

or

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$