

Thermodynamics...

...or how to predict
chemical reactions without
doing experiments

- We want to answer these questions:
 - Will this reaction happen?
 - If so, how far can it proceed?
- We'll only review a small subset of thermodynamics...
 - Laws of Thermodynamics and how they apply to chemistry
 - Entropy, Enthalpy
 - Equilibrium
 - Using Gibbs free energy to determine if a reaction will proceed as written

Thermodynamics...

1. Conservation of energy – total energy remains constant (but can be converted from one form to another)
2. Entropy (disorder) tends to increase
3. Entropy is constant when the temperature equals absolute zero

Thermodynamics...

- Changes in enthalpy and entropy allows prediction of the feasibility of reactions

Definitions:

- Enthalpy – total energy of an element or compound
- Entropy – degree of disorder
 - (highly structured = low entropy, randomized = high entropy)
- Gibbs free energy – the part of the total energy available to perform “useful” work

Energy of a system cannot be created or destroyed

A change in energy U is equal to the change in heat and work

$$dU = dq - dw$$

dU = change in internal energy of the system

dq = heat absorbed by the system

dw = work done by the system

Energy is conserved

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$$dU = dq - dw$$

dU = change in internal energy of the system

dq = heat absorbed by the system

dw = work done by the system

- Internal energy of system is increased by gaining heat (q)
- Internal energy of system is decreased when work (w) is done **by** the system

Energy is conserved

Chemical thermodynamics: $dU = dq - dw$

- Heat (q) is measured in terms of:

$$q = \text{amt (m; mol)} \times \text{molar heat capacity (C; J K}^{-1} \text{ mol}^{-1}) \times \Delta \text{ temp. } (\Delta T; \text{K})$$

$$q = mC\Delta T$$

- **q is the heat of reaction**

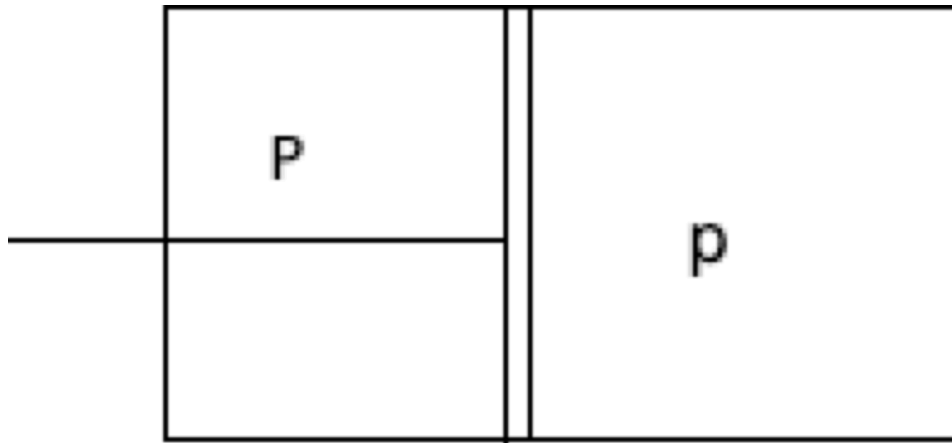
- Molar heat capacity = Heat energy per mole required to raise temperature of 6.022×10^{23} molecules 1°C

Chemical thermodynamics: $dU = dq - dw$

Work of expansion:

$$w = P \Delta V$$

- where P = pressure and ΔV is change in volume
- at constant volume $\Delta V = 0$, therefore $w = 0$ (no work is done)



- If fully reversible, change in pressure and volume compensate, no work is done (reversible process)

Chemical thermodynamics: $dU = dq - dw$

Work of expansion:

$$w = P \Delta V$$

- where P = pressure and ΔV is change in volume
- at constant volume $\Delta V = 0$, therefore $w = 0$ (no work is done)

- For a system at constant volume (all non-gas reactions are at constant volume)

$$P\Delta V = w = 0, \quad \Delta U = q_v \quad q_v = \text{heat at constant volume}$$

- For a system at constant pressure (all reactions open to atmosphere)

$$\Delta U = q_p - P\Delta V$$

Chemical thermodynamics: $dU = dq - dw$

$$\Delta U = q_p - P\Delta V$$

Using the Ideal gas law $P\Delta V = \Delta nRT$, (n = amount of substance),

R is the gas constant = $8.314 \text{ Joules mol}^{-1} \text{ K}^{-1}$

therefore $\Delta U = q_p - \Delta nRT$

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therefore $\Delta U = q_p - \Delta nRT$

rearranging:

$$q_p = \Delta U + \Delta nRT ; \quad q_p \text{ is called the enthalpy (H)}$$

For an infinitesimal change at constant pressure:

$$dH = dU + PdV$$

(U = Energy)

Heat of formation: ΔH_f

- $\Delta H_f^\circ_{298}$: heat of formation of 1 mole of a compound from its elements at 298°K
- ΔH is neg = exothermic reaction
- ΔH is pos = endothermic reaction
(seen from system perspective)
- ΔH is proportional to amount of material



This reaction releases 241.8 kJ of heat, \therefore heat of formation is: -241.8 kJ

Heat of formation: ΔH_f

- ΔH is equal in magnitude but opposite in sign for the reverse reaction, because it is a thermodynamic quantity

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

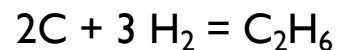
- ΔH for reaction is same regardless of number of steps between reactants and products

$$\Delta H = \Delta U + \Delta nRT$$

- Can use component reactions to calculate enthalpy change for unknown reaction

Reaction	Enthalpy	
$\text{H}_2 + 0.5 \text{O}_2 = \text{H}_2\text{O}$	$\Delta\text{H} = -285.8 \text{ kJ mol}^{-1}$	(a)
$\text{C} + \text{O}_2 = \text{CO}_2$	$\Delta\text{H} = -393.3 \text{ kJ mol}^{-1}$	(b)
$\text{C}_2\text{H}_6 + 3.5 \text{O}_2 = 2 \text{CO}_2 + 3\text{H}_2\text{O}$	$\Delta\text{H} = -1559.8 \text{ kJ mol}^{-1}$	(c)

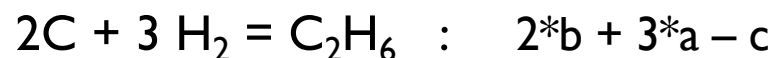
can use above to calculate ΔH for ethane formation:



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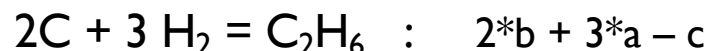
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$\text{C}_2\text{H}_6 + 3.5 \text{O}_2 = 2 \text{CO}_2 + 3\text{H}_2\text{O}$	$\Delta\text{H} = -1559.8 \text{ kJ mol}^{-1}$	(c)

can use above to calculate ΔH for ethane formation



canceling yields

$$\begin{aligned}
 2\text{C} + 3 \text{H}_2 = \text{C}_2\text{H}_6 \quad \Delta\text{H} &= 2* -393.3 + 3* -285.8 - (-1559.8) \\
 &= -84.2 \text{ kJ mol}^{-1}
 \end{aligned}$$

Enthalpy change alone is not enough

- Entropy change (dS) is also needed (2nd law of thermodynamics)

$$dS = \frac{dq_{\text{rev}}}{T}$$

- Change in entropy = amount of reversible heat absorbed by system divided by temperature

Entropy of an isolated system which is not in equilibrium will tend to increase over time

Enthalpy change alone is not enough

- Entropy change (dS) is also needed (2nd law of thermodynamics)

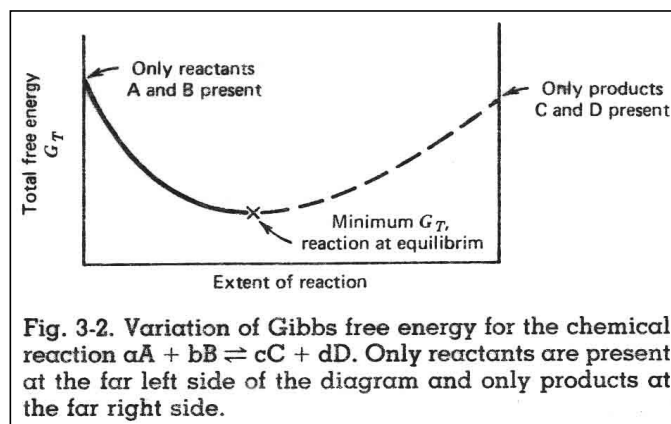
$$dS = \frac{dq_{\text{rev}}}{T}$$

- Change in entropy = amount of reversible heat absorbed by system divided by temperature
- Together, when we consider both enthalpy (H) and entropy (S) we get the Gibbs free energy (G):

$$G = H - TS$$

Free Energy – I

- A criterion for equilibrium is that the *total free energy (Gibbs free energy, G_T)* of the reaction is at a minimum:



- If we add more reactant or more product, the reaction will proceed *spontaneously* (without external help) as long as the value for G_r decreases.
- Thus, a reaction in the direction of decreasing G_r is *spontaneous*. A reaction in the direction of increasing G_r is not spontaneous, and will not occur in a closed system.

Free Energy - 2

As any reaction proceeds an incremental amount, the change in G_r can be calculated as:

$$\Delta G_r = \left(\sum_i v_i G_{fi} \right)_{products} - \left(\sum_i v_i G_{fi} \right)_{reactants}$$

where v_i is the stoichiometric coefficient (a,b,c,d) and G_{fi} is the free energy of formation per mole.

1. If $\Delta G < 0$, (*i.e.*, ΔG is negative and thus G_r decreases as the reaction proceeds), then the reaction proceeds spontaneously as written.
2. If $\Delta G > 0$, (*i.e.*, ΔG is positive and thus G_r increases as the reaction proceeds), then the reaction proceeds spontaneously in the opposite direction as written.
3. If $\Delta G = 0$, (*i.e.*, ΔG is at a minimum), then the reaction is at equilibrium and will not proceed spontaneously in either direction.

Free Energy - 3

Values for ΔG for a reaction give us a powerful tool to predict if a reaction is possible. We calculate *in-situ* ΔG_r using this equation:

$$\Delta G_r = \Delta G_r^\circ + RT \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

In-situ Std. state

where

$$\Delta G_r^\circ = \left(\sum_i v_i G_{fi}^\circ \right)_{\text{products}} - \left(\sum_i v_i G_{fi}^\circ \right)_{\text{reactants}}$$

(The superscript zero ($^\circ$) indicates standard state: 25°C (298°K), 1 atm pressure, and activity = 1.)

G_{fi}° is the *standard-state free energy of formation per mole of species i*.

$\{ \}$ = activity (active concentration)

R = the ideal gas constant = $1.987 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1} = 8.31 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1}$

T = $^\circ\text{K}$

Free Energy - 4

Standard free energy of formation ($\Delta G^\circ_{\text{fi}}$):

- $G^\circ_{\text{fi}} = 0$ at standard state for all pure elements (solid reference).
- $G^\circ_{\text{fi}} = 0$ for H^+ at a concentration of 1 mole/liter at standard state (solution reference).
- Allows the measure of the energy change involved in forming compounds at standard state from their component elements at standard state.
- Measured values are listed in tables. Units are:
 - kJ/mol (SI units)
 - kcal/mol

TABLE 3-1 Thermodynamic Constants for Species of Importance in Water Chemistry.^a

Species	ΔH_f° kcal/mole	ΔG_f° kcal/mole
$\text{Ca}_{(\text{aq})}^{2+}$	-129.77	-132.18
$\text{CaCO}_{3(\text{s})}$, calcite	-288.45	-269.78
$\text{CaO}_{(\text{s})}$	-151.9	-144.4
$\text{C}_{(\text{s})}$, graphite	0	0
$\text{CO}_{2(\text{g})}$	-94.05	-94.26
$\text{CO}_{2(\text{aq})}$	-98.69	-92.31
$\text{CH}_{4(\text{g})}$	-17.889	-12.140
$\text{H}_2\text{CO}_{3(\text{aq})}^*$	-167.0	-149.00
HCO_3^-	-165.18	-140.31
CO_3^{2-}	-161.63	-126.22
CH_3COO^- , acetate	-116.84	-89.0
$\text{H}_{(\text{aq})}^+$	0	0
$\text{H}_{2(\text{g})}$	0	0
$\text{Fe}_{(\text{aq})}^{2+}$	-21.0	-20.30
$\text{Fe}_{(\text{aq})}^{3+}$	-11.4	-2.52
$\text{Fe}(\text{OH})_{3(\text{s})}$	-197.0	-166.0
$\text{Mn}_{(\text{aq})}^{2+}$	-53.3	-54.4
$\text{MnO}_{2(\text{s})}$	-124.2	-111.1
$\text{Mg}_{(\text{aq})}^{2+}$	-110.41	-108.99
$\text{Mg}(\text{OH})_{2(\text{s})}$	-221.00	-199.27
NO_3^-	-49.372	-26.43
$\text{NH}_{3(\text{g})}$	-11.04	-3.976
$\text{NH}_{3(\text{aq})}$	-19.32	-6.37
NH_4^+	-31.74	-19.00
$\text{HNO}_{3(\text{aq})}$	-49.372	-26.41
$\text{O}_{2(\text{aq})}$	-3.9	3.93
$\text{O}_{2(\text{g})}$	0	0
OH^-	-54.957	-37.595
$\text{H}_2\text{O}_{(\text{g})}$	-57.7979	-54.6357
$\text{H}_2\text{O}_{(\text{l})}$	-68.3174	-56.690
SO_4^{2-}	-216.90	-177.34
HS^-	-4.22	3.01
$\text{H}_2\text{S}_{(\text{g})}$	-4.815	-7.892
$\text{H}_2\text{S}_{(\text{aq})}$	-9.4	-6.54

Be careful of units!

Formula	Form	Mol. wt. g mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	$\Delta_f G^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	V° cm ³ mol ⁻¹
Aluminum							
Al	s	26.9815	0	0	28.33	24.35	
Al ³⁺	aq	26.9815	-531.	-485.	-321.7	—	-45.3
Al(OH) ²⁺	aq		-767.0	-693.7	—	—	
Al(OH) ₂ ⁺	aq		-1010.7	-901.4	—	—	
Al(OH) ₃ ⁺ (aq)	aq		-1250.4	-1100.7	—	—	
Al(OH) ₄ ⁻	aq	95.0111	-1490.0	-1307.0	102.9	—	45.60
Al ₂ O ₃	α , corundum	101.9612	-1675.7	-1582.3	50.92	79.04	25.575
Al ₂ O ₃ · H ₂ O	boehmite	119.9766	-1980.7	-1831.7	96.86	131.25	39.07
Al ₂ O ₃ · H ₂ O	diaspore	119.9766	-1998.91	-1841.78	70.67	106.19	35.52
Al ₂ O ₃ · 3H ₂ O	gibbsite	156.0074	-2586.67	-2310.21	136.90	183.47	63.912
Al ₂ O ₃ · 3H ₂ O	bayerite	156.0074	-2576.5	—	—	—	
Al(OH) ₃	amorphous	78.0037	-1276.	—	—	—	
Al ₂ SiO ₅	andalusite	162.0460	-2590.27	-2442.66	93.22	122.72	51.53
Al ₂ SiO ₅	kyanite	162.0460	-2594.29	-2443.88	83.81	121.71	44.09
Al ₂ SiO ₅	sillimanite	162.0460	-2587.76	-2440.99	96.11	124.52	49.90
Al ₂ Si ₂ O ₇ · 2H ₂ O	kaolinite	258.1616	-4119.6	-3799.7	205.0	246.14	99.52
Al ₂ Si ₂ O ₇ · 2H ₂ O	halloysite	258.1616	-4101.2	-3780.5	203.3	246.27	99.30
Al ₂ Si ₂ O ₇ · 2H ₂ O	dickite	258.1616	-4118.3	-3795.9	197.1	239.49	99.30
Al ₆ Si ₂ O ₁₃	mullite	426.0532	-6816.2	-6432.7	255.	326.10	—
Al ₂ Si ₄ O ₁₀ (OH) ₂	pyrophyllite	360.3158	-5642.04	-5268.14	239.41	294.34	126.6
Barium							
Ba	s	137.3400	0	0	62.8	28.07	
Ba ²⁺	aq	137.3400	-537.64	-560.77	9.6	—	-12.9
BaO	s	153.3394	-553.5	-525.1	70.42	47.78	
BaO ₂	s	169.3388	-634.3	—	—	66.9	
BaF ₂	s	175.3368	-1207.1	-1156.8	96.36	71.21	
BaS	s	169.4040	-460.	-456.	78.2	49.37	
BaSO ₄	barite	233.4016	-1473.2	-1362.2	132.2	101.75	52.10
BaCO ₃	witherrite	197.3494	-1216.3	-1137.6	112.1	85.35	45.81
BaSiO ₃	s	213.4242	-1623.60	-1540.21	109.6	90.00	
Calcium							
Ca	s	40.0800	0	0	41.42	25.31	
Ca ²⁺	aq	40.0800	-542.83	-553.58	-53.1	—	-18.4
CaO	s	56.0794	-635.09	-604.03	39.75	42.80	
Ca(OH) ₂	portlandite	74.0948	-986.09	-898.49	83.39	87.49	
CaF ₂	fluorite	78.0768	-1219.6	-1167.3	68.87	67.03	24.542
CaS	s	72.1440	-482.4	-477.4	56.5	47.40	
CaSO ₄	anhydrite	136.1416	-1434.11	-1321.79	106.7	99.66	45.94

Formula	Form	Mol. wt. g mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	$\Delta_f G^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	V° cm ³ mol ⁻¹
Carbon							
CaSO ₄ · 2H ₂ O	gypsum	172.1724	-2022.63	-1797.28	194.1	186.02	
Ca ₃ (PO ₄) ₂	β , whitlockite	310.1828	-4120.8	-3884.7	236.0	227.82	
Ca ₃ (PO ₄) ₂	α	310.1828	-4109.9	-3875.5	240.91	231.58	
CaCO ₃	calcite	100.0894	-1206.92	-1128.79	92.9	81.88	36.934
CaCO ₃	aragonite	100.0894	-1207.13	-1127.75	88.7	81.25	34.150
CaSiO ₃	wollastonite	116.1642	-1634.94	-1549.66	81.92	85.27	39.93
CaSiO ₃	pseudowollastonite	116.1642	-1628.4	-1544.7	87.36	86.48	
CaAl ₂ SiO ₆	Ca-Al pyroxene	218.1254	-3298.2	-3122.0	141.4	165.7	
CaAl ₂ Si ₂ O ₈	anorthite	278.2102	-4227.9	-4002.3	199.28	211.42	100.79
CaTiO ₃	perovskite	135.9782	-1660.6	-1575.2	93.64	97.65	
CaTiSiO ₅	sphene	196.0630	-2603.3	-2461.8	129.20	138.95	
CaMg(CO ₃) ₂	dolomite	184.4108	-2326.3	-2163.4	155.18	157.53	64.365
CaMgSi ₂ O ₆	diopside	216.5604	-3206.2	-3032.0	142.93	166.52	66.090
Carbon							
C	graphite	12.0112	0	0	5.740	8.527	5.298
C	diamond	12.0112	1.895	2.900	2.377	6.113	3.417
CO ₂ ²⁻	aq	60.0094	-677.149	-527.81	-56.9	—	-6.1
HCO ₃ ⁻	aq	61.0174	-691.99	-586.77	91.2	—	24.2
CO	g	28.0106	-110.525	-137.168	197.674	29.142	24465.6
CO ₂	g	44.0100	-393.509	-394.359	213.74	37.11	24465.6
CO ₂	aq	44.0100	-413.80	-385.98	117.6	—	32.8
H ₂ CO ₃	aq	62.0254	-679.339	-623.109	283.65	—	
CH ₄	g	16.0432	-74.81	-50.72	186.264	35.309	24465.6
C ₂ H ₆	g	30.0704	-84.68	-32.82	229.60	52.63	24465.6
CN	g	26.0179	437.6	407.5	202.6	29.16	
CN ⁻	aq	26.0179	150.6	172.4	94.1	—	
HCN	g	27.0259	135.1	124.7	201.78	35.86	
HCN	aq	27.0259	107.1	119.7	124.7	—	
Chlorine							
Cl ₂	g	70.9060	0	0	233.066	33.907	24465.6
Cl ⁻	aq	35.4530	-167.159	-131.228	56.5	-136.4	17.3
HCl	aq	36.4610	-167.159	-131.228	56.5	-136.4	17.3
HCl	g	36.4610	-92.307	-95.299	186.908	29.12	24465.6
Copper							
Cu	s	63.5400	0	0	33.15	24.435	
Cu ⁺	aq	63.5400	71.67	49.98	40.6	—	
Cu ²⁺	aq	63.5400	64.77	65.49	-99.6	—	
CuO	tenorite	79.5394	-157.3	-129.7	42.63	42.30	
Cu ₂ O	cuprite	143.0794	-168.6	-146.0	93.14	63.64	
CuS	covellite	96.6040	-53.1	-53.6	66.5	47.82	
Cu ₂ S	chalcocite	159.1440	-79.5	-86.2	120.9	76.32	

Sample Calculation #1

Consider the dissolution of CaCO_3 (calcite) in aqueous solution:



Does the reaction proceed spontaneously as written?

Calculate the free energy of reaction at standard state (products and reactants at activity = 1, $P = 1 \text{ atm}$, $T = 25^\circ\text{C}$):

$$\Delta G^\circ_r = \left(\sum_i v_i G^\circ_{fi} \right)_{\text{products}} - \left(\sum_i v_i G^\circ_{fi} \right)_{\text{reactants}}$$

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TABLE 3-1 Thermodynamic Constants for Species of Importance in Water Chemistry.^a

Species	$\Delta \bar{H}_f^\circ$ kcal/mole	$\Delta \bar{G}_f^\circ$ kcal/mole
<u>$\text{Ca}^{2+}_{(aq)}$</u>	-129.77	<u>-132.18</u>
<u>$\text{CaCO}_{3(s)}$, calcite</u>	-288.45	<u>-269.78</u>
$\text{CaO}_{(s)}$	-151.9	-144.4
$\text{HCO}^{-}_{3(aq)}$	-165.18	-140.31
<u>$\text{CO}^{2-}_{3(aq)}$</u>	-161.63	<u>-126.22</u>
$\text{CH}_3\text{COO}^{-}$, acetate	-116.84	-89.0

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Calculate the free energy of reaction at standard state (products and reactants at activity = 1, $P = 1$ atm, $T = 25^\circ\text{C}$):

$$\Delta G^\circ_r = \left(\sum_i \nu_i G^\circ_{fi} \right)_{\text{products}} - \left(\sum_i \nu_i G^\circ_{fi} \right)_{\text{reactants}}$$

$$\begin{aligned} \Delta G^\circ_r &= (1(-132.18) + 1(-126.22) - (1(-269.78))) \text{ kcal/mol} \\ &= (-258.4 + 269.78) \text{ kcal/mol} \\ &= +11.38 \text{ kcal/mol} \end{aligned}$$

Therefore, at standard state, the reaction spontaneously proceeds in the opposite direction to what is written.

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$\text{CO}_{2(\text{g})}$	-94.05	-94.26
$\text{CO}_{2(\text{aq})}$	-98.69	-92.31
$\text{CH}_{4(\text{g})}$	-17.889	-12.140
$\text{H}_2\text{CO}_{3(\text{aq})}^*$	-167.0	-149.00
$\text{HCO}_{3(\text{aq})}^-$	-165.18	-140.31
$\text{CO}_{3(\text{aq})}^{2-}$	-161.63	-126.22
CH_3COO^- , acetate	-116.84	-89.0
$\text{H}_{(\text{aq})}^+$	0	0
$\text{H}_{2(\text{g})}$	0	0
$\text{Fe}_{(\text{aq})}^{2+}$	-21.0	-20.30
$\text{Fe}_{(\text{aq})}^{3+}$	-11.4	-2.52
$\text{Fe}(\text{OH})_{3(\text{s})}$	-197.0	-166.0
$\text{Mn}_{(\text{aq})}^{2+}$	-53.3	-54.4
$\text{MnO}_{2(\text{s})}$	-124.2	-111.1
$\text{Mg}_{(\text{aq})}^{2+}$	-110.41	-108.99
$\text{Mg}(\text{OH})_{2(\text{s})}$	-221.00	-199.27
$\text{NO}_{3(\text{aq})}^-$	-49.372	-26.43
$\text{NH}_{3(\text{g})}$	-11.04	-3.976
$\text{NH}_{3(\text{aq})}$	-19.32	-6.37
$\text{NH}_{4(\text{aq})}^+$	-31.74	-19.00
$\text{HNO}_{3(\text{aq})}$	-49.372	-26.41
$\text{O}_{2(\text{aq})}$	-3.9	3.93
$\text{O}_{2(\text{g})}$	0	0
$\text{OH}_{(\text{aq})}^-$	-54.957	-37.595
$\text{H}_2\text{O}_{(\text{g})}$	-57.7979	-54.6357
$\text{H}_2\text{O}_{(\text{l})}$	-68.3174	-56.690
$\text{SO}_{4(\text{aq})}^{2-}$	-216.90	-177.34
$\text{HS}_{(\text{aq})}^-$	-4.22	3.01
$\text{H}_2\text{S}_{(\text{g})}$	-4.815	-7.892
$\text{H}_2\text{S}_{(\text{aq})}$	-9.4	-6.54

Equilibrium at In-Situ Conditions - I

We have already seen that:

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

In-situ Std. state

We can define a *reaction quotient*, Q , using in-situ conditions:

$$Q \equiv \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

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In the case of equilibrium, $Q = K$ and $\Delta G = 0$:

$$\text{Thus: } 0 = \Delta G^\circ + RT \ln K$$

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

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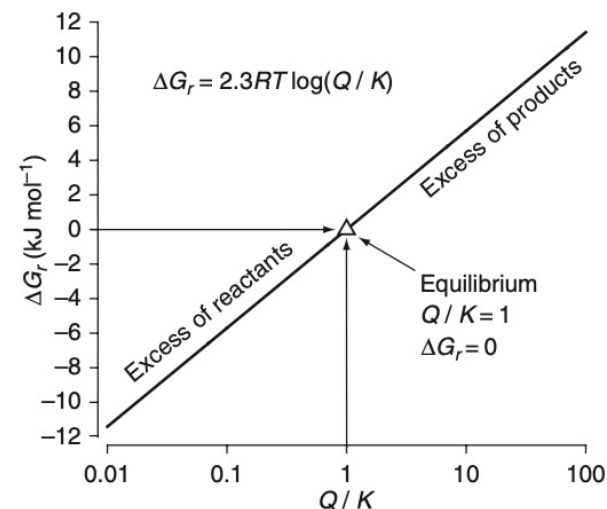
Substituting (for the general case): $\Delta G = -RT \ln K + RT \ln Q = RT \ln Q/K$

Equilibrium at In-Situ Conditions - 2

$$\Delta G = RT \ln Q/K$$

This allows us to develop a set of criteria to determine in which direction a reaction will proceed under *non-standard* conditions. This is because Q/K will determine the *sign* of ΔG :

1. If $Q/K < 1$, then ΔG is negative, and the reaction is spontaneous as written.
2. If $Q/K = 1$, then $\Delta G = 0$ and the system is at equilibrium.
3. If $Q/K > 1$, then ΔG is positive, and the reaction is spontaneous in the opposite direction as written.



Ion behavior in seawater does not equal concentration

- Seawater is a complex solvent
- Ions interact differently than we might assume from simple, single ion pairs

Ex. Consider the dissolution of NaCl in water:



If the reaction goes to completion, get 1 mole Na^+ and 1 mole Cl^- (i.e., 2 moles of ions total)

Expect freezing point depression of -3.72°C , but in fact get -3.01°C

- NaCl is acting as though there were less than 2 moles of ions
- Thus, solution is non-ideal

Activity

Ionic interactions cause non-ideality

- As ionic strength increases, interactions and non-ideality increase

To understand these effects, we need to know the effective concentration of ions \equiv *ACTIVITY*

Activity of an ion i is defined: $a_i \equiv \{i\} \equiv \gamma_i [i]$ $a_i = \gamma_i [i]$

where: $\gamma_i \equiv$ *activity coefficient* for the ion “ i ” (dimensionless)

$[i] \equiv$ ion concentration (measured, mol kg⁻¹)

$\{i\} \equiv$ ion activity, to be used instead of concentration

Note that dimension conventions can differ between texts/subfields

In dilute aqueous solutions:

- Ions behave independently of one another
- $\gamma = 1$
- Activity = measured molality

As concentrations of ions in solution increase:

- Electrostatic and covalent interactions increase between ions
- Activities of ions decrease from measured (analytical) concentrations

As Ionic strength (I) increases, activity decreases

- $I = \frac{1}{2} \sum m_i z_i^2$ (the sum of total charge from ions squared times the concentration of each ion)
- A 1.0 M solution of NaCl has an I of 1.0M
- A 1 M solution of $MgCl_2$ has an I of 3.0 M
- Ionic strength of SW is approx. 0.7

Approximations of activity coeff.

Debye-Huckel equation

$$\log \gamma_i = -A z_i^2 \sqrt{I}$$

A = a constant for the ion i

z_i = ion charge

I = solution ionic strength

Note:

Ionic strength of SW is ~ 0.7 !

(i.e. way off the top of scale shown here)

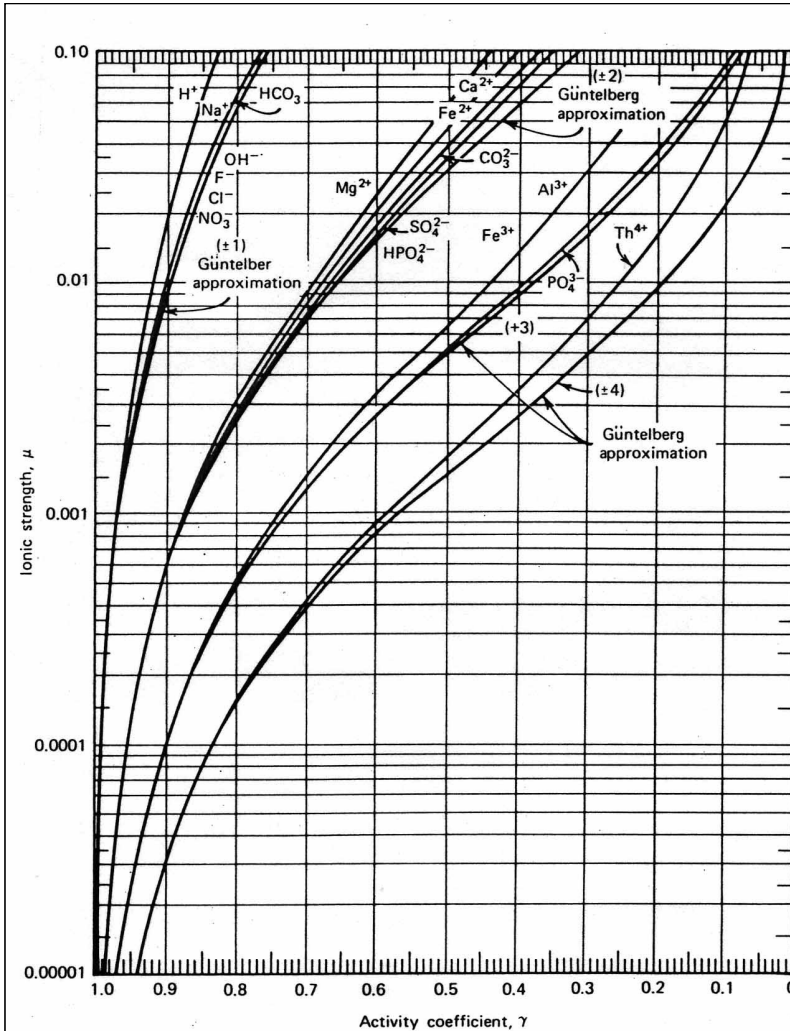


Fig. 3-4. Activity coefficients of aqueous ions based on the extended Debye-Hückel equation (Eq. 3-35) and the Güntelberg approximation (Eq. 3-36).

Activity in SW

- Different than solutions of individual salts
 - Ions from different salts can form pairs, such that the “true” activity (a_i) is even lower than that calculated from lab studies of electrical activity

$$a_i = \left(\% \frac{free_i}{100} \right) \times \gamma_i \times []_i = \gamma_{iT} []_i$$

Activities – How to Calculate

1. For ions and molecules in solution, $\{i\}$ is related to the molar concentration, $[i]$, by $\{i\} = \gamma_i[i]$ where γ_i = activity coefficient. As the solution becomes dilute (most cases of interest to us), γ_i approaches 1 and $\{i\}$ approaches $[i]$.
2. For the solvent in a solution, $\{i\} = \gamma_i X_i$ where X_i is the mole fraction. As the solution becomes more dilute, γ_i approaches 1. The activity generally is assumed to be 1 for the dilute solutions of concern to us. **Activity of water = 1**
3. For pure solids or liquids in equilibrium with a solution, $\{i\} = 1$.
4. For gases in equilibrium with a solution, $\{i\} = \gamma_i P_i$ where P_i is the partial pressure of the gas in atmospheres. As the total pressure decreases, γ_i approaches 1. When reactions take place at atmospheric pressure, the activity of a gas can be approximated closely by its partial pressure.
5. For mixtures of liquids, $\{i\} = X_i$ where X_i is the mole fraction.

Sample Calculation #2

Again consider the dissolution of CaCO_3 (calcite):



In the surface ocean, does the reaction proceed spontaneously as written?

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

From Sample Calculation #1, we know: $\Delta G^\circ = +11.38 \text{ kcal/mole}$

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From Sample Calculation #1, we know: $\Delta G^\circ = +11.38 \text{ kcal/mole}$

$$\text{Thus: } 11.38 \frac{\text{kcal}}{\text{mol}} = - \left(1.987 \frac{\text{cal}}{^\circ\text{K mol}} \right) \left(\frac{1 \text{ kcal}}{1000 \text{ cal}} \right) (298^\circ\text{K}) \ln(k)$$

(all units cancel out)

$$\ln K = -19.22$$

$$K = 4.5 \times 10^{-9} \text{ ("equilibrium constant")}$$

Sample Calculation #2 (cont.)

Surface seawater:

$$\{\text{CaCO}_3\} \equiv 1$$

$$[\text{Ca}^{2+}] = 0.01 \text{ mol/L}; \quad \gamma_{\text{T}} = 0.23; \quad \{\text{Ca}^{2+}\} = 0.0023 \text{ mol/L}$$

$$[\text{CO}_3^{2-}] = 23 \text{ mmol/L}; \quad \gamma_{\text{T}} = 0.029; \quad \{\text{CO}_3^{2-}\} = 6.7 \times 10^{-6} \text{ mol/L}$$

$$Q = \frac{\{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\}}{\{\text{CaCO}_3\}} = \frac{(2.3 \times 10^{-3}) \times (6.7 \times 10^{-6})}{1} = 1.53 \times 10^{-8}$$

$$\frac{Q}{K} = \frac{1.53 \times 10^{-8}}{4.5 \times 10^{-9}} = 3.4$$

Sample Calculation #2 (cont.)

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Therefore:

- The reaction goes in the opposite direction as written ($Q/K > 1$)
- CaCO_3 precipitates in the surface ocean
- Surface seawater is supersaturated with respect to calcite

Note: No information is given on the *kinetics* of the reaction!

Temperature and Pressure Effects - I

The amount of heat that is released or taken up by a reaction is called the *enthalpy change* (ΔH°).

Similarly to ΔG° , we can calculate ΔH° using tabulated data:

$$\Delta H_r^\circ = \left(\sum_i \nu_i H_{fi}^\circ \right)_{\text{products}} - \left(\sum_i \nu_i H_{fi}^\circ \right)_{\text{reactants}}$$

where ν_i is the stoichiometric coefficient (a,b,c,d), and H_{fi}° is the enthalpy of formation of species i (kcal/mol or kJ/mol) at standard state.

The van't Hoff equation gives the temperature dependence of K :

$$\left(\frac{\partial \ln K}{\partial T} \right)_P = \frac{\Delta H_r^\circ}{RT^2}$$

For a small change in T , ΔH° does not change much, so we can integrate directly:

$$\ln \left(\frac{K_{T^*}}{K_{298}} \right) = \frac{\Delta H_r^\circ}{R} \left(\frac{1}{298} - \frac{1}{T^*} \right)$$

where T^* is the temperature of interest.

Temperature and Pressure Effects - 2

The *change in the partial molar volume* (ΔV°) during a reaction at standard state is also calculated using tabulated data:

$$\Delta V_r^\circ = \left(\sum_i v_i V_{fi}^\circ \right)_{\text{products}} - \left(\sum_i v_i V_{fi}^\circ \right)_{\text{reactants}}$$

where v_i is the stoichiometric coefficient (a,b,c,d), and V_{fi}° is the partial molar volume of formation of species i (cm³/mol) at standard state.

The pressure dependence of K is also known:

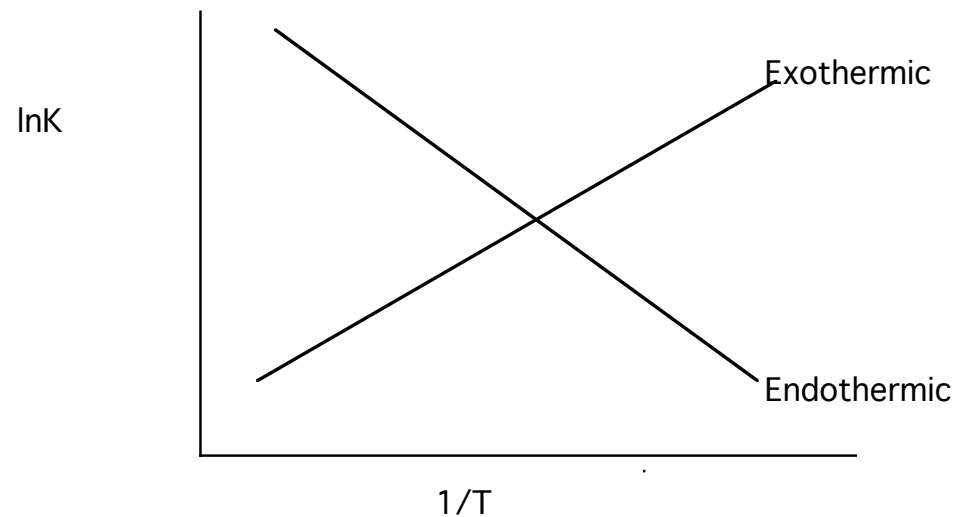
$$\left(\frac{\partial \ln K}{\partial P} \right)_T = \frac{\Delta V_r^\circ}{RT}$$

Again integrating directly:

$$\ln \left(\frac{K_{P^*}}{K_{1\text{atm}}} \right) = \frac{\Delta V_r^\circ}{RT} (P^* - 1\text{atm})$$

where P^* is the pressure of interest (in atm).

- For exothermic reactions $\ln K$ increases as $1/T$ increases, (T decreases), favouring product formation
- For endothermic reactions $\ln K$ increases as $1/T$ decreases (T increases) favouring product formation



Equilibrium vs. kinetics

- Equilibrium calculations give the energy available from a reaction & the direction it will proceed
 - Usually simpler & require less info than those for kinetics
- Often a good approximation for many systems
- In some cases, equilibrium calculations can predict kinetic rate constants
- HOWEVER, most natural water reactions are not at equilibrium and knowledge of kinetics is often required
 - States of dynamic equilibrium, reaction rates, are topics outside of the scope of this course