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Print version

CEE 680: Water Chemistry

Lecture #15

Kinetics and Thermodynamics: Fundamentals and Temperature effects

(Stumm & Morgan, Chapt.2-3)

(Benjamin, Chapt 3,4)

Non-ideal conditions

- Ionic strength (I or μ)
  - Not zero (or infinite dilution)

Already talked about this (ionic strength corrections)

- Temperature (T)
  - Not 25°C

Focus of this section

- Concentration (C)
  - Not 1 M

Mostly of concern for G

Ionic Strength Effects

- Ideal or infinite dilution constants (K) are in terms of activity quotients
- These can be factored into molar concentrations and activity coefficients:

$$K \equiv \frac{\{H^+\}\{B\}}{\{HB\}}$$

$$= \frac{f_{H^+}[H^+]f_B[B]}{f_{HB}[HB]}$$

$$= \left(\frac{f_{H^+}f_B}{f_{HB}}\right)\boxed{\frac{[H^+][B]}{[HB]}}$$

${}^{c}K$

$$K = \frac{\{H^+\}f_B[B]}{f_{HB}[HB]}$$

$$= \left(\frac{f_B}{f_{HB}}\right)\boxed{\frac{\{H^+\}[B]}{[HB]}}$$

K'

Operational Acidity Constants

- The common practice of using molar concentrations results in a conditional constant:

$$^{c}K \equiv \frac{[H^+][B]}{[HB]} = K\left(\frac{f_{HB}}{f_{H^+} f_B}\right)$$

- And pH measurements generally give us H^+ activity, so it's often convenient to leave H^+ in these terms, which results in the mixed acidity constant:

$$K' \equiv \frac{\{H^+\}[B]}{[HB]} = {}^{C}Kf_{H^+} = K\frac{f_{HB}}{f_B}$$

Temperature Effects on rates

- Chemist's Approach: Arrhenius Equation

Activation energy

$$\frac{d(\ln k)}{dT_a} = \frac{E_a}{RT_a^2}$$

Pre-exponential Factor or frequency factor

$$k_{T_a} = Ae^{-E_a/RT_a}$$

$$k_{T_a} = k_{293^o K} e^{E_a(T_a - 293)/RT_a 293}$$

R = universal gas constant
= 1.987 cal/^{o}K/mole
T_a = absolute temp (^{o}K)

- Engineer's Approach:

$$k_T = k_{20^o C}\theta^{T-20^o C}$$

Or more generally where T_o is any "baseline" temperature

$$k_T = k_{T_o}\theta^{T-T_o}$$

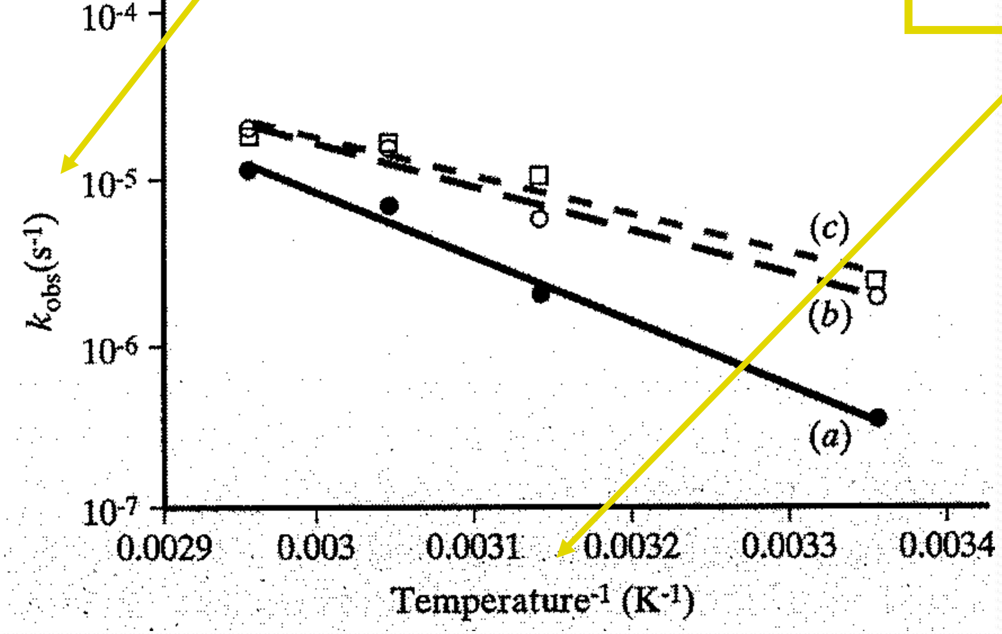
Typical values:
θ=1.02 to 1.15

Determination of E_a and A

$$k_{T_a} = Ae^{-E_a/RT_a}$$

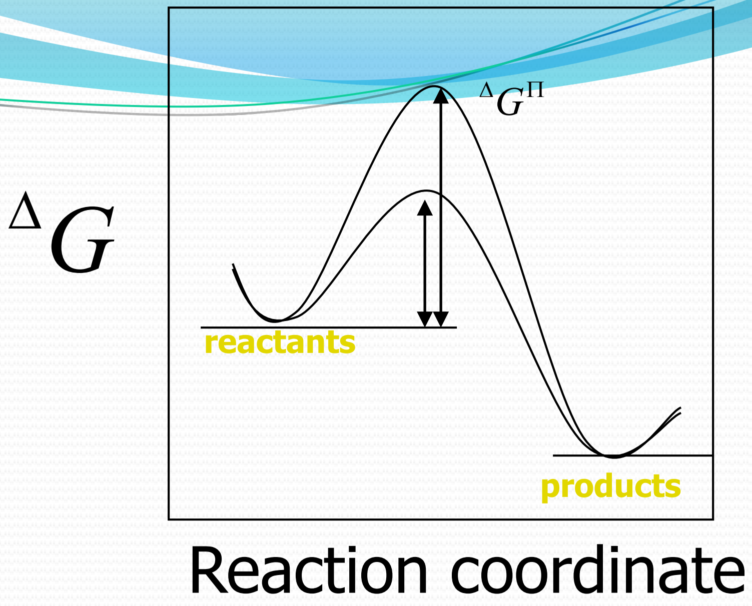
- Use Arrhenius equation
  - Take natural log of both sides
  - Evaluate slope and intercept

$$\ln k_{T_a} = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T_a}\right)$$



See: equation 3.4 (pg83) in Benjamin, 2015

Catalysis



- A Catalyst enhances rates by providing alternative pathways with lower activation energies
  - It is not "consumed" in the reaction
  - Homogeneous
    - Acid/base catalysis
    - Trace metal catalysis
  - Heterogeneous
    - Reactions on particle surfaces
    - Reactions mediated by microorganisms (enzymes)
    - Engineered surface catalysis
      - Catalytic converters, activated carbon

Chapt 2: Basics

- Thermodynamics
  - Will tell you
    - which reactions are favorable or “Possible”
    - composition of systems at equilibrium
  - Won’t tell you
    - how quickly the reactions proceed
  - good for systems with constant P & T
      - Air: 1.0 atm at sea level
      - Water: 1.0 atm for each additional 10.7 m of water
      - Earth: wt of overlying rock and soil
  - Governing property @ const. T&P is the **Gibbs Free Energy**
    - for constant T&V, it is the Helmholtz Free Energy

Sets limits

Gibbs Free Energy

- Combines enthalpy and entropy
  - 1st and 2nd laws of thermodynamics
- Determines whether a reaction is favorable or spontaneous
- Practical form is based on an arbitrary datum
  - the pure and most stable form of each element at standard state

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

Standard State

- Standard State
  - Conditions:
    - Unit activity (a=1)
  - Rarely encountered in practice; but easier to base calculations on
  - State variables: ΔG^o, μ^o
- Non-standard State
  - Conditions:
    - Non-unit activity, often quite low
  - This is the "real world"
  - State Variables: ΔG, μ

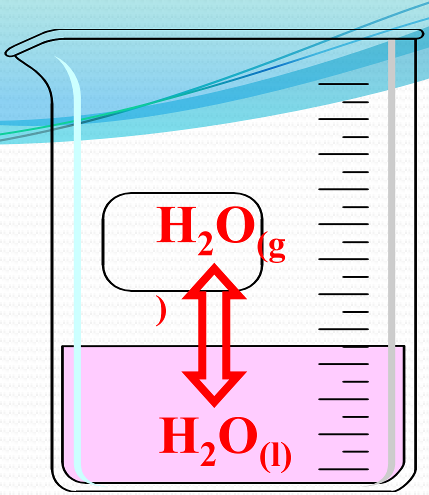
About:
1 mole/L for dissolved substances
1 atmosphere for gases

Enthalpy

- A fundamental thermodynamic variable
- enthalpy change is equal to heat of reaction (for systems at constant pressure)
  - $\Delta H<0$, heat is given off
    - exothermic
  - $\Delta H>0$, heat is absorbed
    - endothermic
  - ΔH can be calculated from standard enthalpies of formation (ΔH^o_f)
    - available in many texts
      - e.g., Snoeyink & Jenkins, Table 3-1

$$\Delta H^o = \sum \nu_i \Delta H^o_f$$

Example



- Evaporation of water
  - $H_2O_{(l)} = H_2O_{(g)}$

$H_2O_{(g)}$ $H_2O_{(l)}$

$$\Delta H^o = \sum \nu_i \Delta H_f^o$$
$$= (1 mole)\left(-57.80 \frac{kcal}{mole}\right) + (-1 mole)\left(-68.32 \frac{kcal}{mole}\right)$$
$$= +10.52\, kcal$$

  - $\Delta H > 0$, heat is absorbed
    - endothermic
    - However, this does not tell us if the reaction is favorable, or proceeds spontaneously
      - to answer this we need to know the entropy change

Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part I

Species	$\Delta \overline{H}^o_f$ kcal/mole	$\Delta \overline{G}^o_f$ kcal/mole
Ca^{+2}(aq)	-129.77	-132.18
$CaC0_3$(s), calcite	-288.45	-269.78
CaO (s)	-151.9	-144.4
C(s), graphite	0	0
CO_2(g)	-94.05	-94.26
CO_2(aq)	-98.69	-92.31
CH_4 (g)	-17.889	-12.140
H_2CO_3 (aq)	-167.0	-149.00
HCO_3^- (aq)	-165.18	-140.31
CO_3^{-2} (aq)	-161.63	-126.22
CH_3COO^-, acetate	-116.84	-89.0
H^+ (aq)	0	0
H_2 (g)	0	0
Fe^{+2} (aq)	-21.0	-20.30
Fe^{+3} (aq)	-11.4	-2.52
$Fe(OH)_3$ (s)	-197.0	-166.0
Mn^{+2} (aq)	-53.3	-54.4
MnO_2 (s)	-124.2	-111.1

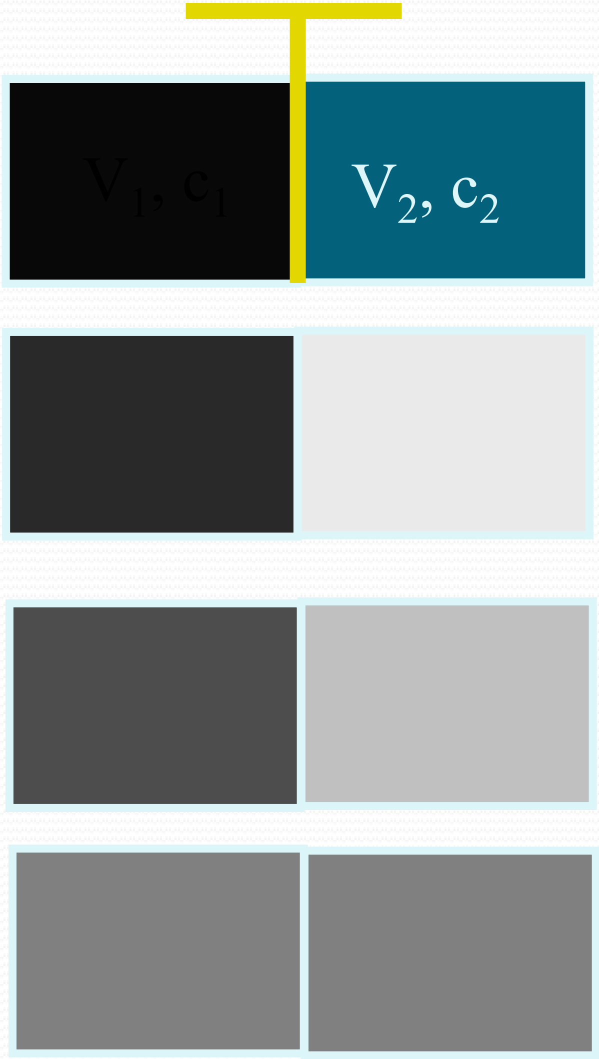
Conversion: 1kcal = 4.184 kJ

Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part II

Species	$\Delta\overline{H}_f^o$ kcal/mole	$\Delta\overline{G}_f^o$ kcal/mole	Species	$\Delta\overline{H}_f^o$ kcal/mole	$\Delta\overline{G}_f^o$ kcal/mole
Mg^{+2} (aq)	-110.41	-108.99	O_2 (g)	0	0
$Mg(OH)_2$ (s)	-221.00	-199.27	OH^- (aq)	-54.957	-37.595
NO_3^- (aq)	-49.372	-26.43	H_2O (g)	-57.7979	-54.6357
NH_3 (g)	-11.04	-3.976	H_2O (l)	-68.3174	-56.690
NH_3 (aq)	-19.32	-6.37	SO_4^{-2}	-216.90	-177.34
NH_4^+ (aq)	-31.74	-19.00	HS (aq)	-4.22	3.01
HNO_3 (aq)	-49.372	-26.41	H_2S(g)	-4.815	-7.892
O_2 (aq)	-3.9	3.93	H_2S(aq)	-9.4	-6.54

Conversion: 1kcal = 4.184 kJ

Entropy



T=0

T=1

T=2

T=large

- A measure of a system’s randomness
- remove the partition and randomness increases
  - 2nd law of Thermo.

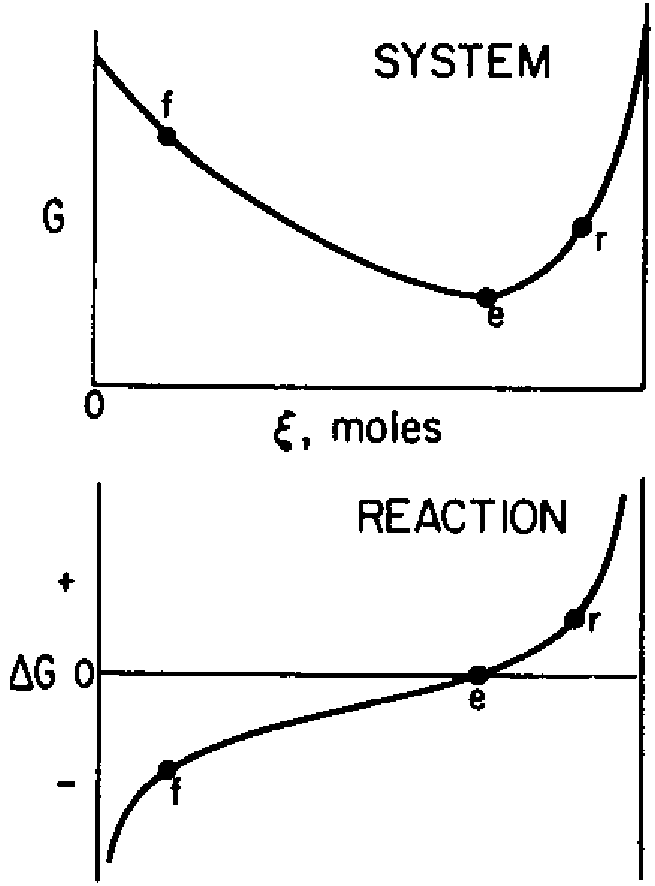
$$ {}^{\Delta}S^o = \sum v_i \, {}^{\Delta}S^o_f $$

  - Spontaneous in isolated system
    - Like water running downhill
    - Or hot objects heating colder ones

Gibbs Energy of a System

- G Changes as reaction progresses due to changing concentrations
- G reaches a minimum at the point of equilibrium

Fig. 2.5
Pg. 45



$$^{\Delta}G \equiv \frac{dG}{d\xi}$$

Extent of reaction

The G_f^o Convention

- Since the G_f^o values are essentially $^{\Delta}G$'s for the formation of chemical substances from the "most stable" (reference) forms of their constituent elements
    - The G_f^o values for those most stable elemental forms are zero, by definition
- Examples
    - Zero-valent, Metallic Ag, Al, Fe, Mn, Pb, Zn
    - graphite-C, white-P, rhombic-S
    - diatomic H_2, I_2, N_2, O_2

Simple examples

Reaction	$^{\Delta}G^{o}$
$H_{2\,(g)} + S_{(s)} = H_2S_{(aq)}$	-27.87
$H_{2\,(g)} + S_{(s)} = H_2S_{(g)}$	-33.56
$O_{2\,(g)} + S_{(s)} = SO_{2\,(g)}$	-300.2
$Hg_{(l)} + S_{(s)} = HgS_{(s)}$	-43.3
$H_{2\,(g)} + ½O_{2\,(g)} = H_2O_{(l)}$	-237.18
$O_{2(g)} = O_{2\,(aq)}$	16.32

- In all of these cases reactants have a G_f^o equal to zero, i.e., they are the reference forms of the elements
- so the $^{\Delta}G^o$ is simply equal to the G_f^o of the product compound

Solving problems with G

Recall, at any T & P: $^{\Delta}G^{o} = \sum \nu_i \mu_i^{o}$

- $^{\Delta}$G can be calculated at 25°C from standard gibbs free energies of formation (G^{o}_{f})
  - These are essentially $^{\Delta}$G's for the formation of chemical substances from the most stable forms of their constituent elements
  - available in many texts
    - e.g., Stumm & Morgan, Appendix 3
    - e.g., Benjamin, Table 2.1
    - e.g., Snoeyink & Jenkins, Table 3-1

But for STP, we use:

$$^{\Delta}G^{o} = \sum \nu_i G_f^{o}$$

In: kJ/mole

In: kcal/mole

Conversion: 1kcal = 4.184 kJ

Ammonia Problem (1/7)

- Determine ΔG^o for dissolution of ammonia in water at 25°C

$$NH_3(g) \leftrightarrow NH_3(aq)$$

  - Based on example 2.5 in text
  - Two approaches
    - A. Determine ΔG^o directly from individual G^o_f's
      - The easiest way
    - B. Determine ΔG^o from ΔH^o and ΔS^o

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

Ammonia Problem (2/7)

- A. Determine $^{\Delta}G^o$ directly from individual G^o_f's
  - Get thermodynamic data
    - from Appendix A (Benjamin) or Appendix 3 (S&M)
  - Expand equation and substitute data

$$^{\Delta}G^o = \sum \nu_i G_f^o$$

$$\begin{aligned} ^{\Delta}G^o &= \nu_{NH_3(g)} G^o_{f-NH_3(g)} + \nu_{NH_3(aq)} G^o_{f-NH_3(aq)} \\ &= (-1)(-16.48) + (1)(-26.57) \\ &= -10.09 \end{aligned}$$

Units are kJ/mole

	Formation from the Elements		**Entropy**	
Species	**G_f^o (kJ mol^{-1})**	**H_f^o (kJ mol^{-1})**	**S^o (J mol^{-1}K^{-1})**	**Reference**
$NH_3(g)$	**-16.48**	**-46.1**	**192**	**NBS**
$NH_3(aq)$	**-26.57**	**-80.29**	**111**	**NBS**
$NH_4^+(aq)$	**-79.37**	**-132.5**	**113.4**	**NBS**

Ammonia Problem (3/7)

- B. Determine $^{\Delta}G^o$ from $^{\Delta}H^o$ and $^{\Delta}S^o$
  - Get thermodynamic data from Appendix A (or 3)
  - Expand equations and substitute data

$$^{\Delta}H^o = \sum \nu_i \, ^{\Delta}H_f^o$$

$$\begin{aligned} ^{\Delta}H^o &= \nu_{NH_3(g)} \, ^{\Delta}H^o_{f-NH_3(g)} + \nu_{NH_3(aq)} \, ^{\Delta}H^o_{f-NH_3(aq)} \\ &= (-1)(-46.1) + (1)(-80.29) \\ &= -34.19 \end{aligned}$$

Units are kJ/mole

$$^{\Delta}S^o = \sum \nu_i S^o$$

$$\begin{aligned} ^{\Delta}S^o &= \nu_{NH_3(g)} S^o_{NH_3(g)} + \nu_{NH_3(aq)} S^o_{NH_3(aq)} \\ &= (-1)(192) + (1)(111) \\ &= -81 \end{aligned}$$

Units are J/mole/°K

Ammonia Problem (4/7)

- Now combine and solve for $^{\Delta}G^{o}$

$$
\begin{aligned}
{}^{\Delta}G^{o} &= {}^{\Delta}H^{o} - T\,{}^{\Delta}S^{o} \\
&= (-34.19) - (273.16 + 25)(-81)\left(\frac{1kJ}{1000J}\right) \\
&= -10.04
\end{aligned}
$$

Units are kJ/mole

- Conclusion: reaction is spontaneous since $^{\Delta}G^{o} < 0$
- Lingering question: what actually happens when we're not at standard state conditions (i.e., when activity isn't equal to one)?

Chemical Potential

- Like a Gibbs Free Energy normalized per mole
- a function of activity and temperature

kJ/mole

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

kJ

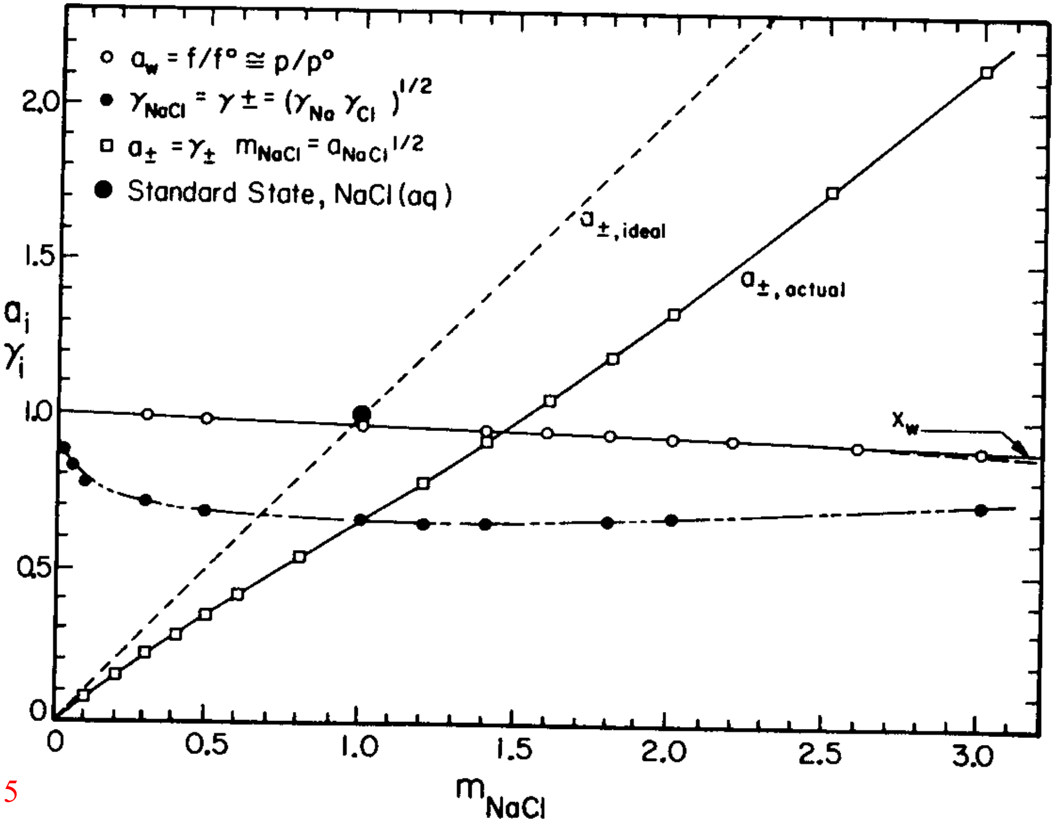
$$\mu_i = \mu_i^o + \underbrace{RT\ln a_i}_{\text{This term corrects for the fact that we're not at unit activity}}$$

Standard state (unit activity)

This term corrects for the fact that we’re not at unit activity

Example

- Activities in concentrated NaCl solution
  - S&M: Example 2.3 (pg 40)



General Condition

- And relating to the change in G for complete conversion to products

$$
\begin{aligned}
{}^{\Delta}G &= \sum \nu_i \mu_i \\
&= \sum \nu_i \left(\mu_i^o + RT \ln a_i \right) \\
&= \sum \nu_i \mu_i^o + RT \sum \nu_i \ln a_i
\end{aligned}
$$

and

$$ {}^{\Delta}G^o = \sum \nu_i \mu_i^o $$

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

where

$$ Q \equiv \frac{a_C^c a_D^d}{a_A^a a_B^b} $$

For the reaction: $aA + bB \leftrightarrow cC + dD$

Ammonia problem (5/7)

- Now lets see what the $^{\Delta}$G is for the following non-standard conditions
  - $[NH_3(aq)] = 10^{-3}$ M
  - $p_{NH_3} = 10^{-4}$ atm
- Now we need to determine Q
  - Recall the reaction:

$$NH_3(g) \leftrightarrow NH_3(aq)$$

  - So:

$$Q = \frac{a^1_{NH_3(aq)}}{a^1_{NH_3(g)}} \cong \frac{10^{-3}}{10^{-4}} = 10$$

Ammonia problem (6/7)

R=1.987 x10^{-3} kcal/mole °K
=8.314 x10^{-3} kJ/mole °K

- Now substitute back into the equation for $^{\Delta}G$

$$
\begin{aligned}
{}^{\Delta}G &= {}^{\Delta}G^{o} + RT\ln Q \\
&= -10.04 + (0.008314)(273.16+25)\ln(10) \\
&= -4.33 \qquad \text{Units are kJ/mole}
\end{aligned}
$$

- Conclusion: the reaction is still spontaneous at these non-standard concentrations
  - i.e., the reaction will proceed toward the right
- Another lingering question: how far to the right will it proceed before it reaches equilibrium and stops?
  - To answer this we need to determine "K"

Equilibrium Quotients

- at Equilibrium $^{\Delta}G=0$, so:
  - and:

$$^{\Delta}G^{o} = -RT\ln K$$
$$= -2.303RT\log K$$

  - or:

$$\log K = -\frac{^{\Delta}G^{o}}{2.303RT}$$

$$0 = {}^{\Delta}G^{o} + RT\ln K$$

Where K is defined as the quotient (Q) at equilibrium and is generally referred to as the "equilibrium constant"

$$K \equiv \frac{a_C^c a_D^d}{a_A^a a_B^b}\text{, at equilibrium}$$

Ammonia problem (7/7)

R=1.987 x10^{-3} kcal/mole °K
=8.314 x10^{-3} kJ/mole °K

- To determine the equilibrium position of ammonia dissolution, we need the equilibrium constant, K

$$\begin{aligned}\log K &= -\frac{\Delta G^o}{2.303RT} \\ &= -\frac{-10.04}{2.303(0.008314)(273.16+25)} \\ &= 1.76\end{aligned}$$

$$\begin{aligned}K &= 10^{1.76} \\ &= 57.4\end{aligned}$$

  - So as we approach equilibrium, Q will approach the value of K, which is 57.4

$$Q = \frac{a^1_{NH_3(aq)}}{a^1_{NH_3(g)}} \cong \frac{10^{-3}}{10^{-4}} = 10$$

Quotients (cont.)

- more generally, for non-equilibrium conditions, we can combine:

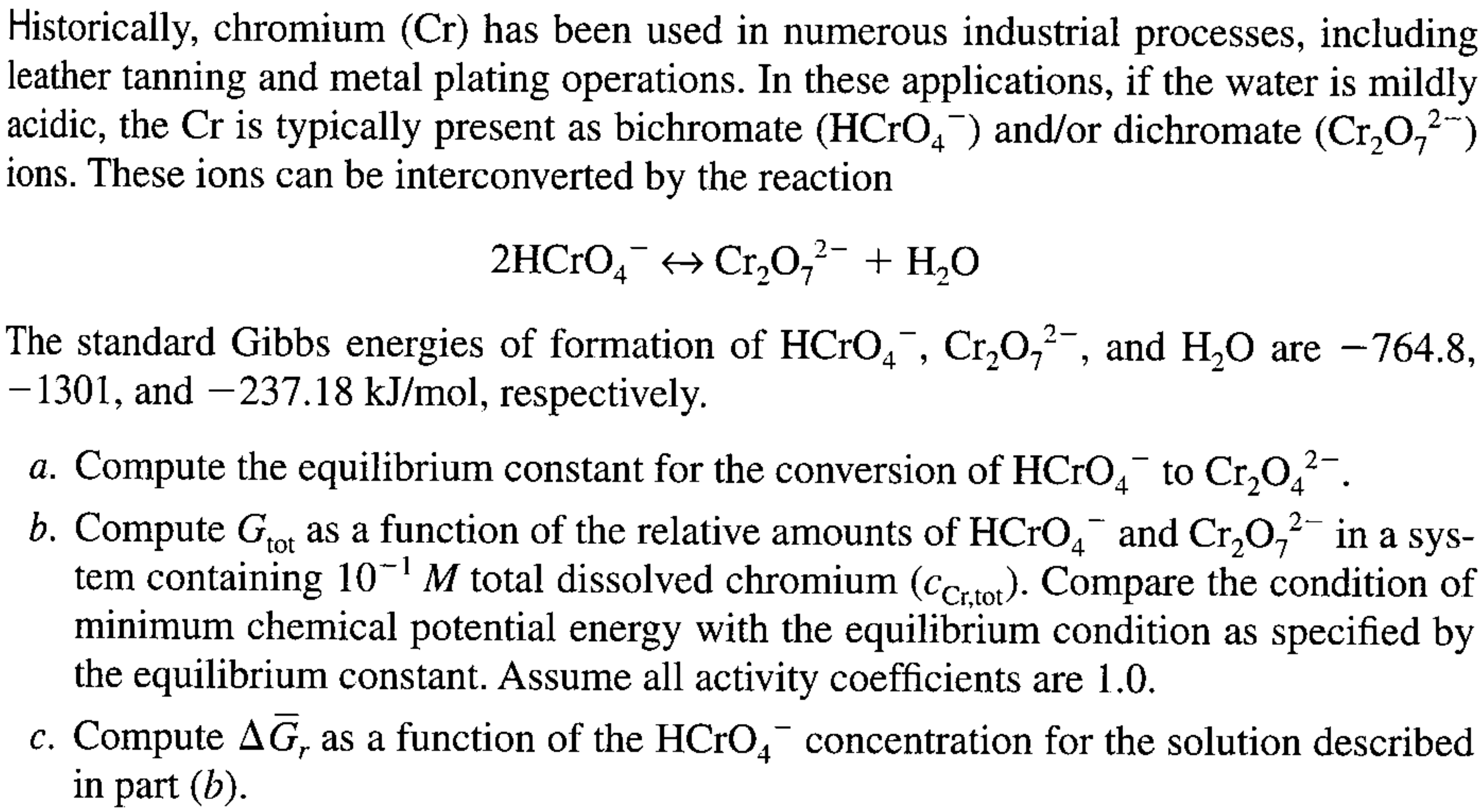
$$\begin{aligned} {}^{\Delta}G &= {}^{\Delta}G^{o} + RT\ln Q \\ &= -RT\ln K + RT\ln Q \\ &= RT\ln\left({Q}/{K} \right) \end{aligned}$$

$${}^{\Delta}G = 2.303RT\log\left({Q}/{K} \right)$$

- and if,
  - ${}^{\Delta}G<0$, $(Q/K)<1$, and equilibrium lies to the right
  - ${}^{\Delta}G>0$, $(Q/K)>1$, and equilibrium lies to the left
  - ${}^{\Delta}G=0$, $(Q/K)=1$, and system is at equilibrium

Chromium Example (1/6)

Hexavalent Cr is now a big regulatory issue



Historically, chromium (Cr) has been used in numerous industrial processes, including leather tanning and metal plating operations. In these applications, if the water is mildly acidic, the Cr is typically present as bichromate ($HCrO_4^-$) and/or dichromate ($Cr_2O_7^{2-}$) ions. These ions can be interconverted by the reaction

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$$

The standard Gibbs energies of formation of $HCrO_4^-$, $Cr_2O_7^{2-}$, and H_2O are −764.8, −1301, and −237.18 kJ/mol, respectively.

a. Compute the equilibrium constant for the conversion of $HCrO_4^-$ to $Cr_2O_4^{2-}$.

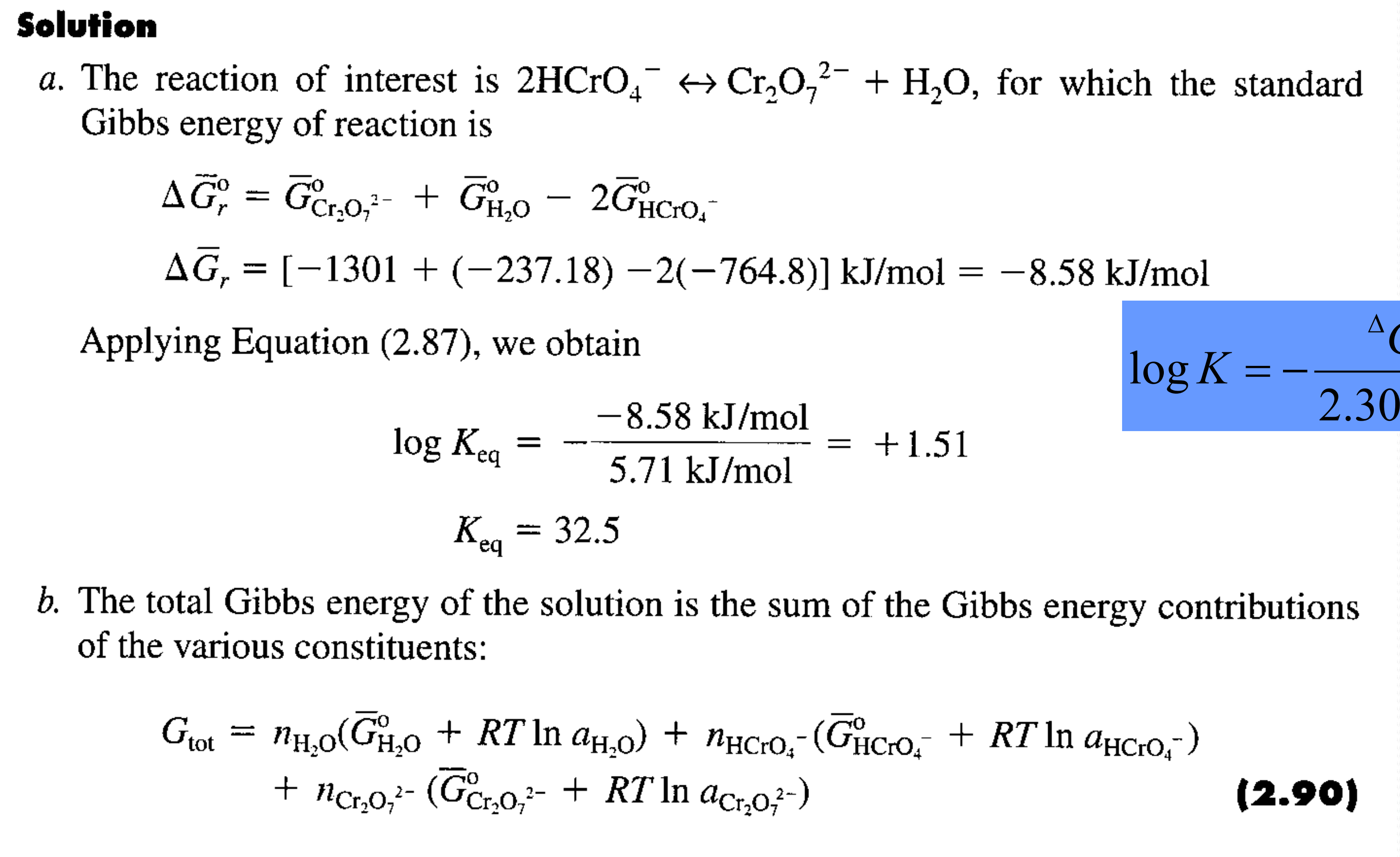
b. Compute G_{tot} as a function of the relative amounts of $HCrO_4^-$ and $Cr_2O_7^{2-}$ in a system containing 10^{-1} *M* total dissolved chromium ($c_{Cr,tot}$). Compare the condition of minimum chemical potential energy with the equilibrium condition as specified by the equilibrium constant. Assume all activity coefficients are 1.0.

c. Compute $\Delta\overline{G}_r$ as a function of the $HCrO_4^-$ concentration for the solution described in part (*b*).

Example 4.10 (pg 188) from Benjamin 2015

Example 2.10 (pg 111) in Benjamin, 2002

Chromium Example (2/6)



Solution

a. The reaction of interest is $2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$, for which the standard Gibbs energy of reaction is

$$\Delta\overline{G}_r^o = \overline{G}^o_{Cr_2O_7^{2-}} + \overline{G}^o_{H_2O} - 2\overline{G}^o_{HCrO_4^-}$$

$$\Delta\overline{G}_r = [-1301 + (-237.18) - 2(-764.8)]\ \text{kJ/mol} = -8.58\ \text{kJ/mol}$$

Applying Equation (2.87), we obtain

$$\log K_{eq} = -\frac{-8.58\ \text{kJ/mol}}{5.71\ \text{kJ/mol}} = +1.51$$

$$K_{eq} = 32.5$$

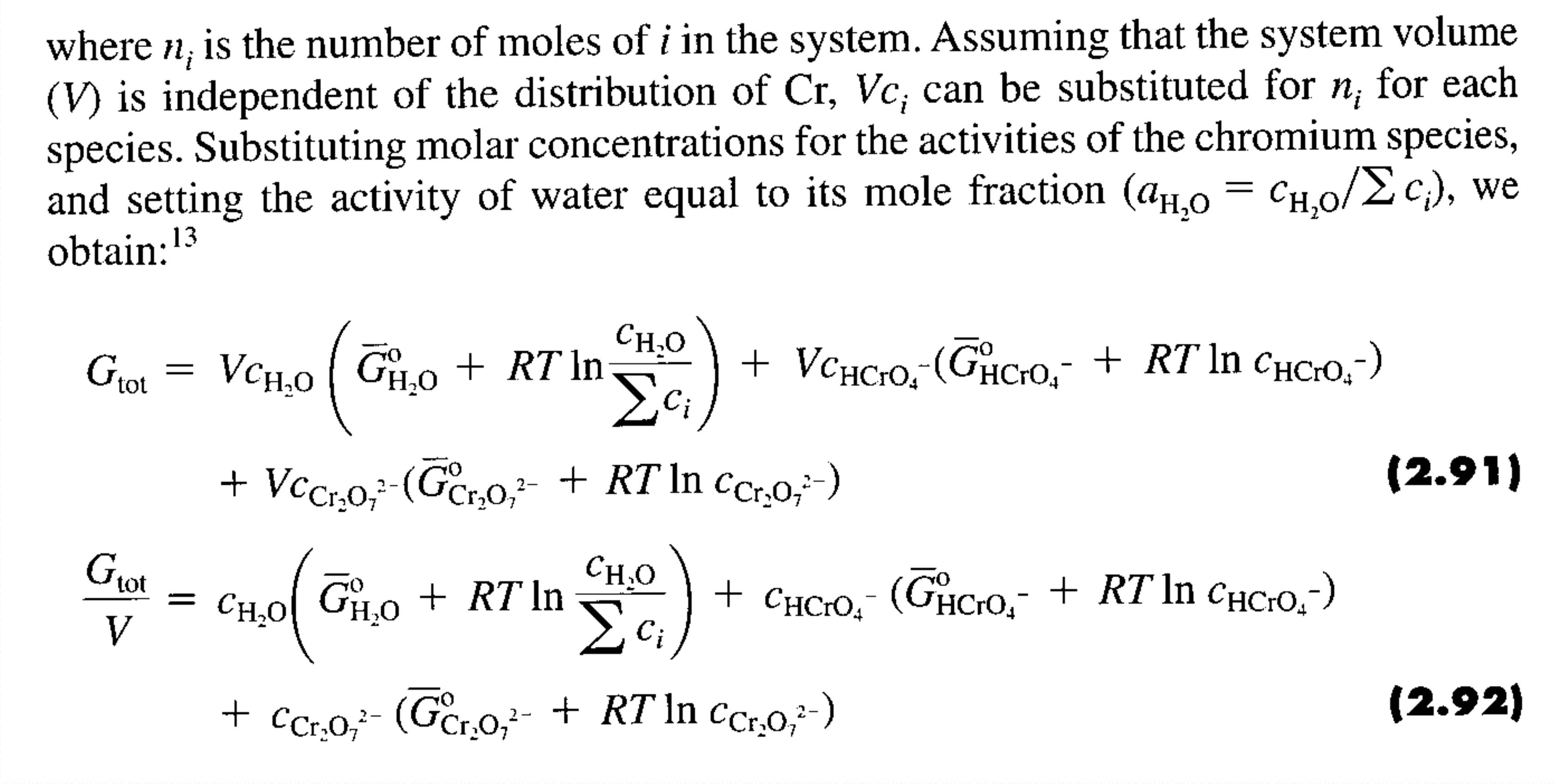
b. The total Gibbs energy of the solution is the sum of the Gibbs energy contributions of the various constituents:

$$G_{tot} = n_{H_2O}(\overline{G}^o_{H_2O} + RT\ln a_{H_2O}) + n_{HCrO_4^-}(\overline{G}^o_{HCrO_4^-} + RT\ln a_{HCrO_4^-}) + n_{Cr_2O_7^{2-}}(\overline{G}^o_{Cr_2O_7^{2-}} + RT\ln a_{Cr_2O_7^{2-}}) \qquad \textbf{(2.90)}$$

$$\log K = -\frac{\Delta G^o}{2.303RT}$$

Example 2.10 from (pg 111): Benjamin, 2002

Chromium Example (3/6)



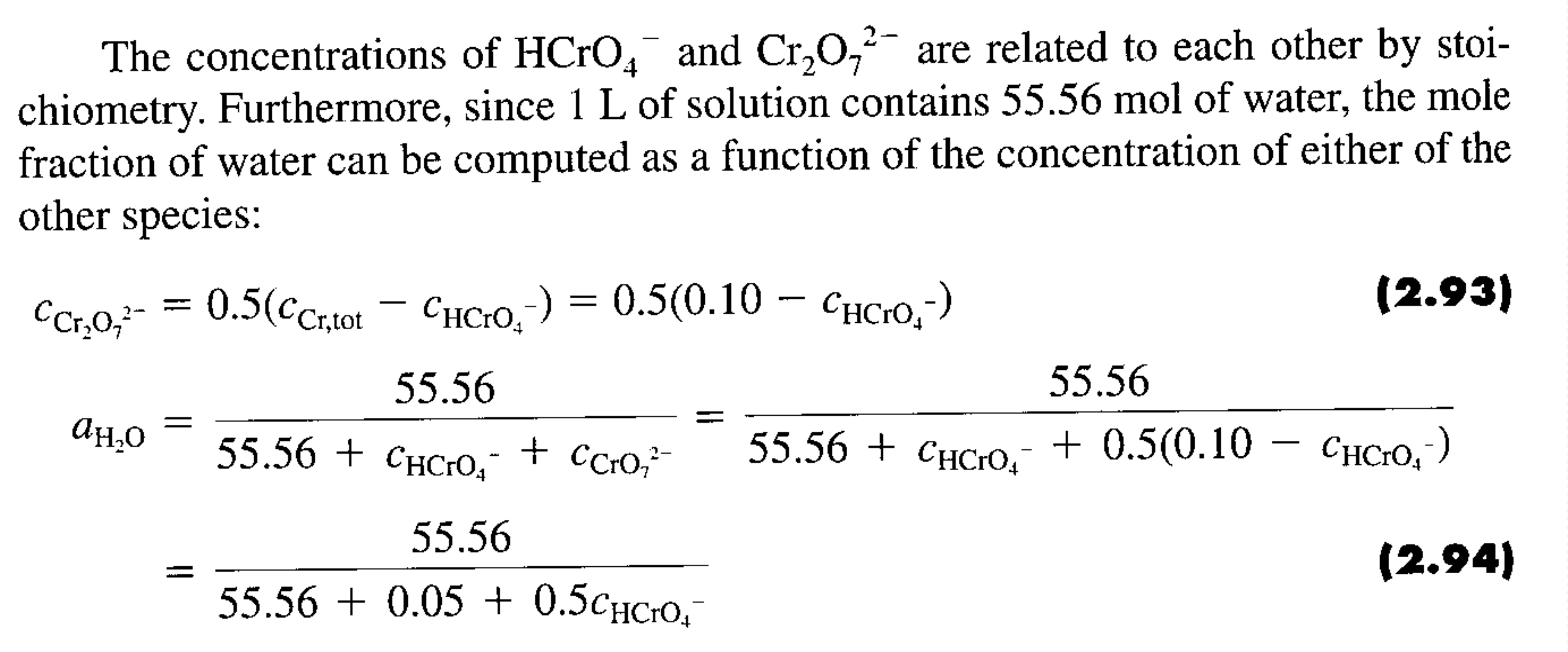
where n_i is the number of moles of i in the system. Assuming that the system volume (V) is independent of the distribution of Cr, Vc_i can be substituted for n_i for each species. Substituting molar concentrations for the activities of the chromium species, and setting the activity of water equal to its mole fraction ($a_{H_2O} = c_{H_2O}/\sum c_i$), we obtain:[13]

$$G_{tot} = Vc_{H_2O}\left(\bar{G}^{o}_{H_2O} + RT\ln\frac{c_{H_2O}}{\sum c_i}\right) + Vc_{HCrO_4^-}(\bar{G}^{o}_{HCrO_4^-} + RT\ln c_{HCrO_4^-}) + Vc_{Cr_2O_7^{2-}}(\bar{G}^{o}_{Cr_2O_7^{2-}} + RT\ln c_{Cr_2O_7^{2-}}) \quad \textbf{(2.91)}$$

$$\frac{G_{tot}}{V} = c_{H_2O}\left(\bar{G}^{o}_{H_2O} + RT\ln\frac{c_{H_2O}}{\sum c_i}\right) + c_{HCrO_4^-}\,(\bar{G}^{o}_{HCrO_4^-} + RT\ln c_{HCrO_4^-}) + c_{Cr_2O_7^{2-}}\,(\bar{G}^{o}_{Cr_2O_7^{2-}} + RT\ln c_{Cr_2O_7^{2-}}) \quad \textbf{(2.92)}$$

Example 4.10 (pg 188) from Benjamin 2015

Chromium Example (4/6)



The concentrations of $HCrO_4^-$ and $Cr_2O_7^{2-}$ are related to each other by stoichiometry. Furthermore, since 1 L of solution contains 55.56 mol of water, the mole fraction of water can be computed as a function of the concentration of either of the other species:

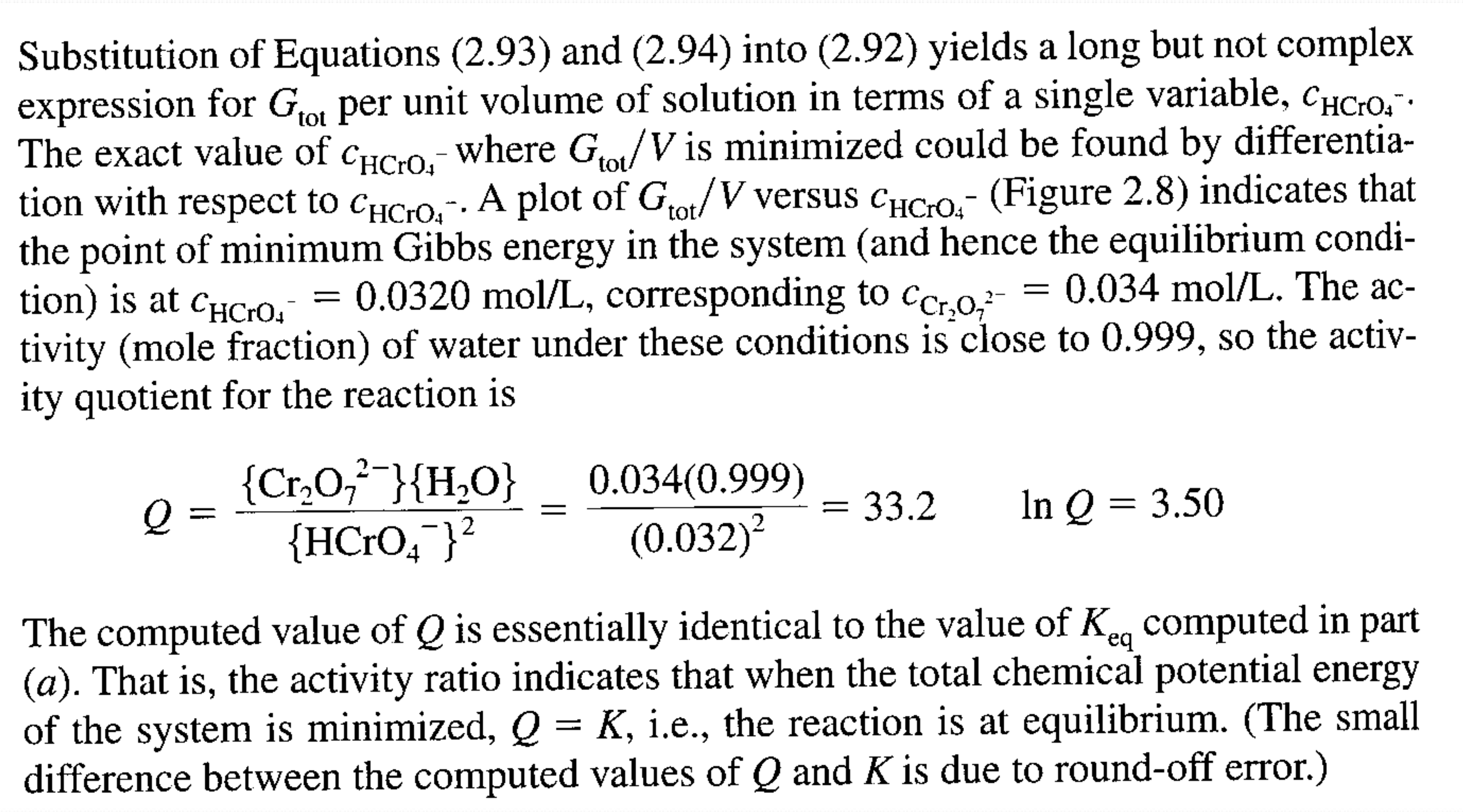
$$c_{Cr_2O_7^{2-}} = 0.5(c_{Cr,tot} - c_{HCrO_4^-}) = 0.5(0.10 - c_{HCrO_4^-}) \tag{2.93}$$

$$a_{H_2O} = \frac{55.56}{55.56 + c_{HCrO_4^-} + c_{CrO_7^{2-}}} = \frac{55.56}{55.56 + c_{HCrO_4^-} + 0.5(0.10 - c_{HCrO_4^-})}$$

$$= \frac{55.56}{55.56 + 0.05 + 0.5c_{HCrO_4^-}} \tag{2.94}$$

Example 2.10 from (pg 111): Benjamin, 2002

Chromium Example (5/6)



Substitution of Equations (2.93) and (2.94) into (2.92) yields a long but not complex expression for G_{tot} per unit volume of solution in terms of a single variable, $c_{\mathrm{HCrO_4^-}}$. The exact value of $c_{\mathrm{HCrO_4^-}}$ where G_{tot}/V is minimized could be found by differentiation with respect to $c_{\mathrm{HCrO_4^-}}$. A plot of G_{tot}/V versus $c_{\mathrm{HCrO_4^-}}$ (Figure 2.8) indicates that the point of minimum Gibbs energy in the system (and hence the equilibrium condition) is at $c_{\mathrm{HCrO_4^-}} = 0.0320$ mol/L, corresponding to $c_{\mathrm{Cr_2O_7^{2-}}} = 0.034$ mol/L. The activity (mole fraction) of water under these conditions is close to 0.999, so the activity quotient for the reaction is

$$Q = \frac{\{\mathrm{Cr_2O_7}^{2-}\}\{\mathrm{H_2O}\}}{\{\mathrm{HCrO_4}^-\}^2} = \frac{0.034(0.999)}{(0.032)^2} = 33.2 \qquad \ln Q = 3.50$$

The computed value of Q is essentially identical to the value of K_{eq} computed in part (*a*). That is, the activity ratio indicates that when the total chemical potential energy of the system is minimized, $Q = K$, i.e., the reaction is at equilibrium. (The small difference between the computed values of Q and K is due to round-off error.)

Example 4.10 (pg 188) from Benjamin 2015

Chromium Example (6/6)

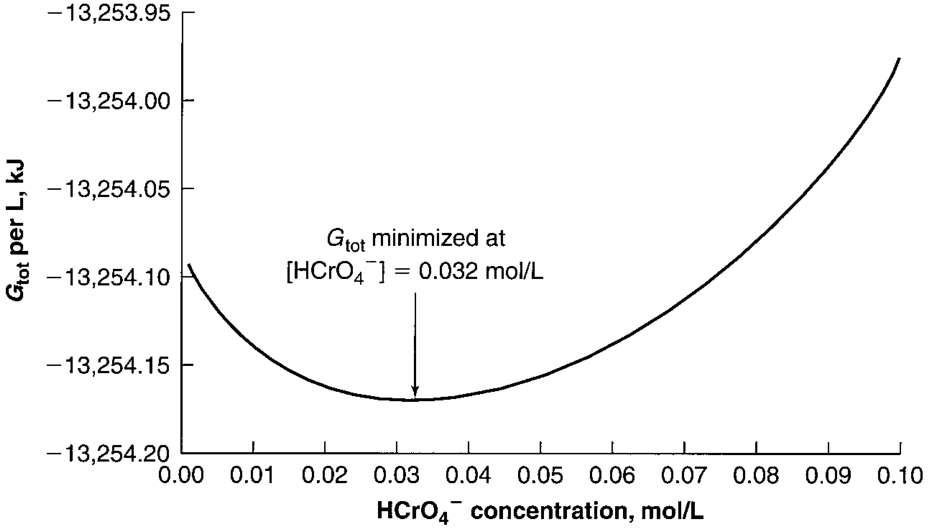


Figure 2.8 Total Gibbs energy per liter of a solution containing $HCrO_4^-$ and $Cr_2O_7^{2-}$ at a total Cr concentration of 10^{-1} mol/L, as a function of the $HCrO_4^-$ concentration.

- Minimum Gibbs free energy is where $\Delta G_r = 0$

Example 4.10 (pg 188) from Benjamin 2015

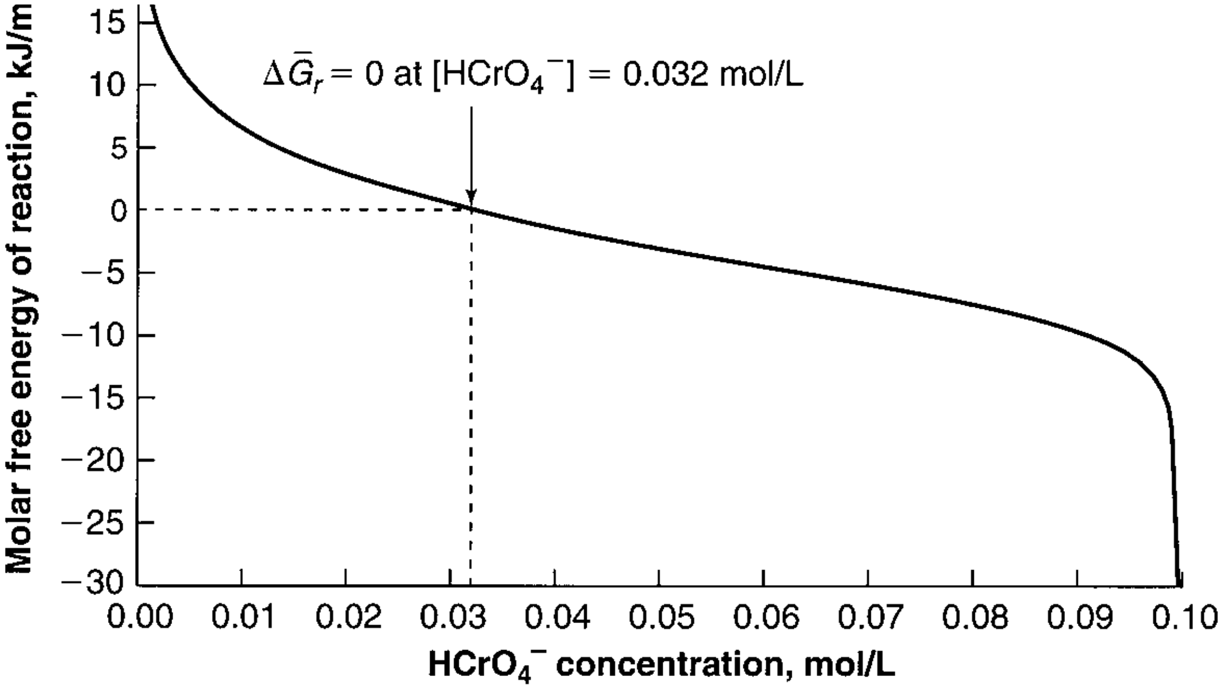


Figure 2.9 The molar Gibbs energy of reaction for conversion of $HCrO_4^-$ to $Cr_2O_7^{2-}$ in a system containing 0.1 *M* total Cr.

Alternative Direct Calculation

$$K = \frac{[Cr_2O_7^{-2}]}{[HCrO_4^-]^2}$$

- Assume standard activity for water
- Combine equilibrium and mass balance equations

$$Cr_{total} = 0.1 = [HCrO_4^-]+2[Cr_2O_7^{-2}]$$

  - Set bichromate = x

$$2[Cr_2O_7^{-2}]=0.1\text{-x}$$

$$K = 32.5 = \frac{[Cr_2O_7^{-2}]}{[HCrO_4^-]^2} = \frac{0.05 - 0.5x}{x^2}$$

$$32.5x^2 + 0.5x - 0.05 = 0$$

  - And using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.5 \pm \sqrt{0.25 - 6.5}}{65} = 0.032278$$

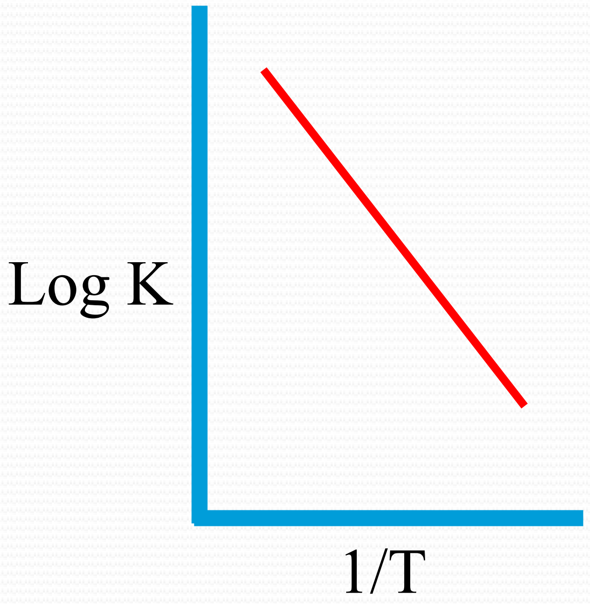
Ionic Species & Redox

- Conventions
  - $G_f^o = 0$, for H_2
  - $G_f^o = 0$, for H^+
  - this makes the hydrogen oxidation half reaction a reference point for Redox
    - for: $\frac{1}{2}H_{2\,(g)} = H^+ + e^-$, $\Delta G = 0$
- oxidations and reductions
  - must be coupled
  - we only concern ourselves with the differences in ΔG for the two half reactions

Temperature Effects on K

- Need ΔH (enthalpy change)
  - $\Delta H < 0$, exothermic (heat evolved)
  - $\Delta H > 0$, endothermic (heat absorbed)
- The Van't Hoff Equation:

$$\log \frac{K_2}{K_1} = \frac{\Delta H^o (T_2 - T_1)}{2.303 R T_2 T_1}$$



  - recall that:

$$\Delta H^o = \sum \nu_i \, \Delta H_f^o$$

Van’t Hoff Equation

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

- Where does it come from?
  - Note that we’re treating ΔH as a constant
    - Nevertheless it does change a bit with temperature, so this introduces some error

$$-RT\ln K = \Delta H^o - T\Delta S^o$$

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S}{R}$$

$$\frac{d\ln K}{dT} = \frac{\Delta H^o}{RT^2}$$

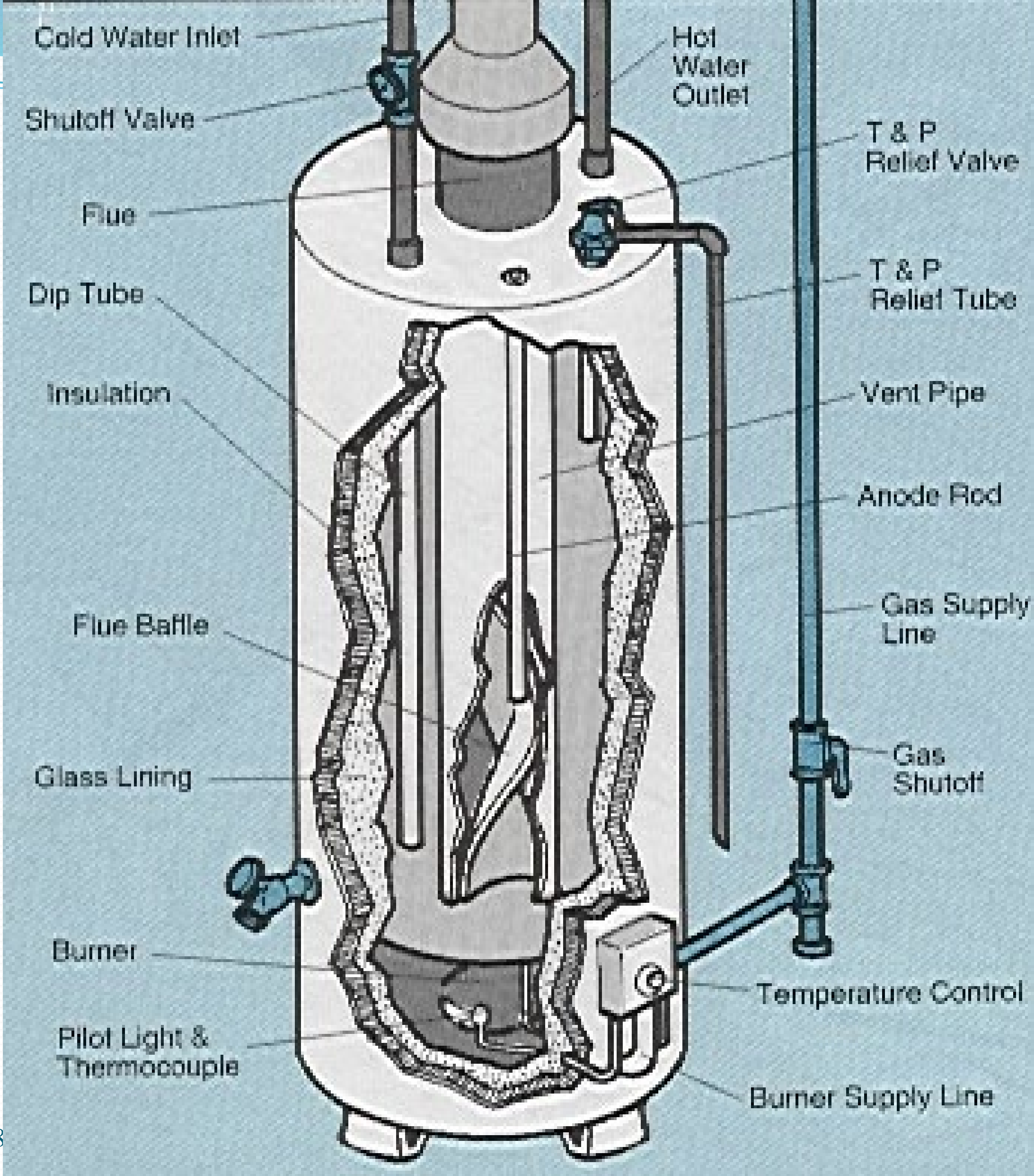
$$\int_{K_1}^{K_2} d\ln K = \frac{\Delta H^o}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

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

$$\log\frac{K_2}{K_1} = \frac{\Delta H^o (T_2 - T_1)}{2.303\,RT_2T_1}$$

Home Water Heater

- Gas fired



From: Quick Guide Plumbing, Creative Homeowner Press

Scale

A cross section of 1 & 1/2" copper pipe with a scale build-up of over 1/2" in thickness

Thickness of Scale in Inches	Loss of of Heat Transfer Efficiency
1/16	15%
1/8	20%
1/4	39%
1/2	70%
3/4	90%

Data: US National Bureau of Standards

Calcium scale formation on the inside of pipes and water heaters, on sinks, tubs, shower doors and other water contact surfaces is a *multi-million dollar problem* for individuals and businesses. A thin, one eighth inch layer of scale is such an effective insulator that it reduces the efficiency of your water heater by 20%. This translates directly to increased energy cost to attain the desired water temperature. Scale also increases the cost of equipment maintenance and shortens equipment life. When these costs are added together, the price of calcium scale is staggering

Example Problem

- Water is at equilibrium with calcium carbonate at 25°C. It enters a house at 15°C, then is heated to 60°C in a water heater.
  - Is the water supersaturated as it
    - A. enters the house?
    - B. leaves the water heater?
- Solution to A.
    - 1. Calculate $^{\Delta}G^{o}$
    - 2. Determine K_1 at 25°C
    - 3. Determine $^{\Delta}H^{o}$
    - 4. Determine K_2 at 15°C

Solution

- At neutral pH: $CaCO_{3\,(s)} + H^+ = HCO_3^- + Ca^{+2}$
  - 1. Calculate $^{\Delta}G^o$
    - =-140.31-132.18-(-269.78) = -2.71 kcal
  - 2. Determine K_1 at 25°C
    - $^{\Delta}G^o = -RT\,lnK = -2.303RT*\log K$
    - $-2.71 = -2.303(0.001987)298*\log K = -1.364\log K$
    - $\log K = 1.99$; $K = 10^{1.99}$
  - 3. Determine $^{\Delta}H^o$
    - =-165.18-129.77-(-288.345) = -6.5 kcal
  - 4. Determine K_2 at 15°C
    - $\log(K_2/10^{1.99}) = -6.5(288-298)/2.303(0.001987)288(298) = 0.1655$
    - $\log K_2 = 2.156$
    - $K_2 = 10^{2.16}$

Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part I

Species	$\Delta\overline{H}^{o}_{f}$ kcal/mole	$\Delta\overline{G}^{o}_{f}$ kcal/mole	Species	$\Delta\overline{H}^{o}_{f}$ kcal/mole	$\Delta\overline{G}^{o}_{f}$ kcal/mole
Ca^{+2}(aq)	-129.77	-132.18	CO_3^{-2} (aq)	-161.63	-126.22
$CaC0_3$(s), calcite	-288.45	-269.78	CH_3COO^-, acetate	-116.84	-89.0
CaO (s)	-151.9	-144.4	H^+ (aq)	0	0
C(s), graphite	0	0	H_2 (g)	0	0
CO_2(g)	-94.05	-94.26	Fe^{+2} (aq)	-21.0	-20.30
CO_2(aq)	-98.69	-92.31	Fe^{+3} (aq)	-11.4	-2.52
CH_4 (g)	-17.889	-12.140	$Fe(OH)_3$ (s)	-197.0	-166.0
H_2CO_3 (aq)	-167.0	-149.00	Mn^{+2} (aq)	-53.3	-54.4
HCO_3^- (aq)	-165.18	-140.31	MnO_2 (s)	-124.2	-111.1

Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part II

Species	$\Delta\overline{H}^{o}_{f}$ kcal/mole	$\Delta\overline{G}^{o}_{f}$ kcal/mole	Species	$\Delta\overline{H}^{o}_{f}$ kcal/mole	$\Delta\overline{G}^{o}_{f}$ kcal/mole
Mg^{+2} (aq)	-110.41	-108.99	O_2 (g)	0	0
$Mg(OH)_2$ (s)	-221.00	-199.27	OH^- (aq)	-54.957	-37.595
NO_3^- (aq)	-49.372	-26.43	H_2O (g)	-57.7979	-54.6357
NH_3 (g)	-11.04	-3.976	H_2O (l)	-68.3174	-56.690
NH_3 (aq)	-19.32	-6.37	SO_4^{-2}	-216.90	-177.34
NH_4^+ (aq)	-31.74	-19.00	HS (aq)	-4.22	3.01
HNO_3 (aq)	-49.372	-26.41	H_2S(g)	-4.815	-7.892
O_2 (aq)	-3.9	3.93	H_2S(aq)	-9.4	-6.54

Solution (cont.)

- Repeat step #4 for 60°C.
  - 4. Determine K_2 at 60°C
    - $\log (K_3/10^{1.99}) = -6.5(333\text{-}298)/2.303(0.001987)333(298) = -0.5$
    - $\log K_3 = 1.49$
    - $K_3 = 10^{1.49}$
- Compare K_1 and K_2 and K_3
  - what does this tell you about possible precipitation?
    - As temp increases, solubility decreases
    - This is an exothermic reaction, so rising temp drives reaction to the left

Le Chatelier’s Principle

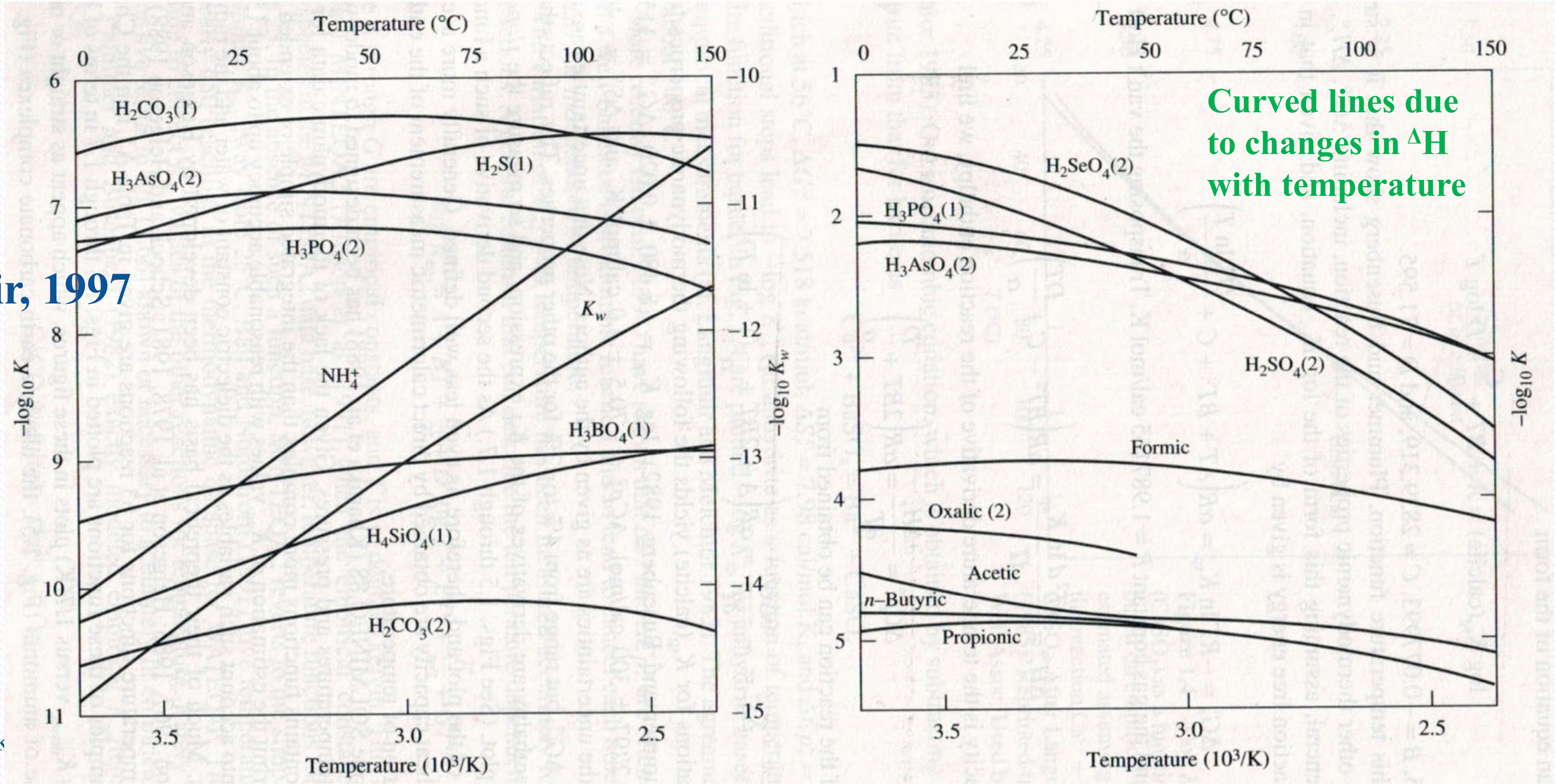
- A system at equilibrium, when subject to a perturbation, responds in a way that tends to minimize its effect
  - If $\Delta H>0$ (endothermic), $d\ln K/dT>0$, and K⇑ as T ⇑
    - if you heat endothermic reaction they will go further to the right
  - If $\Delta H<0$ (exothermic), $d\ln K/dT<0$, and K⇓ as T ⇑
    - if you heat exdothermic reaction they will go back to the left

$$\frac{d\ln K}{dT}=\frac{\Delta H^o}{RT^2}$$

Log K vs 1/T: based on empirical data

- Stepwise acid dissociation (1st or 2nd constant)
  - Note reciprocal T scale is descending, so lines should be sloping upward

Langmuir, 1997



Curved lines due to changes in ΔH with temperature

More log K vs 1/T data

Langmuir, 1997

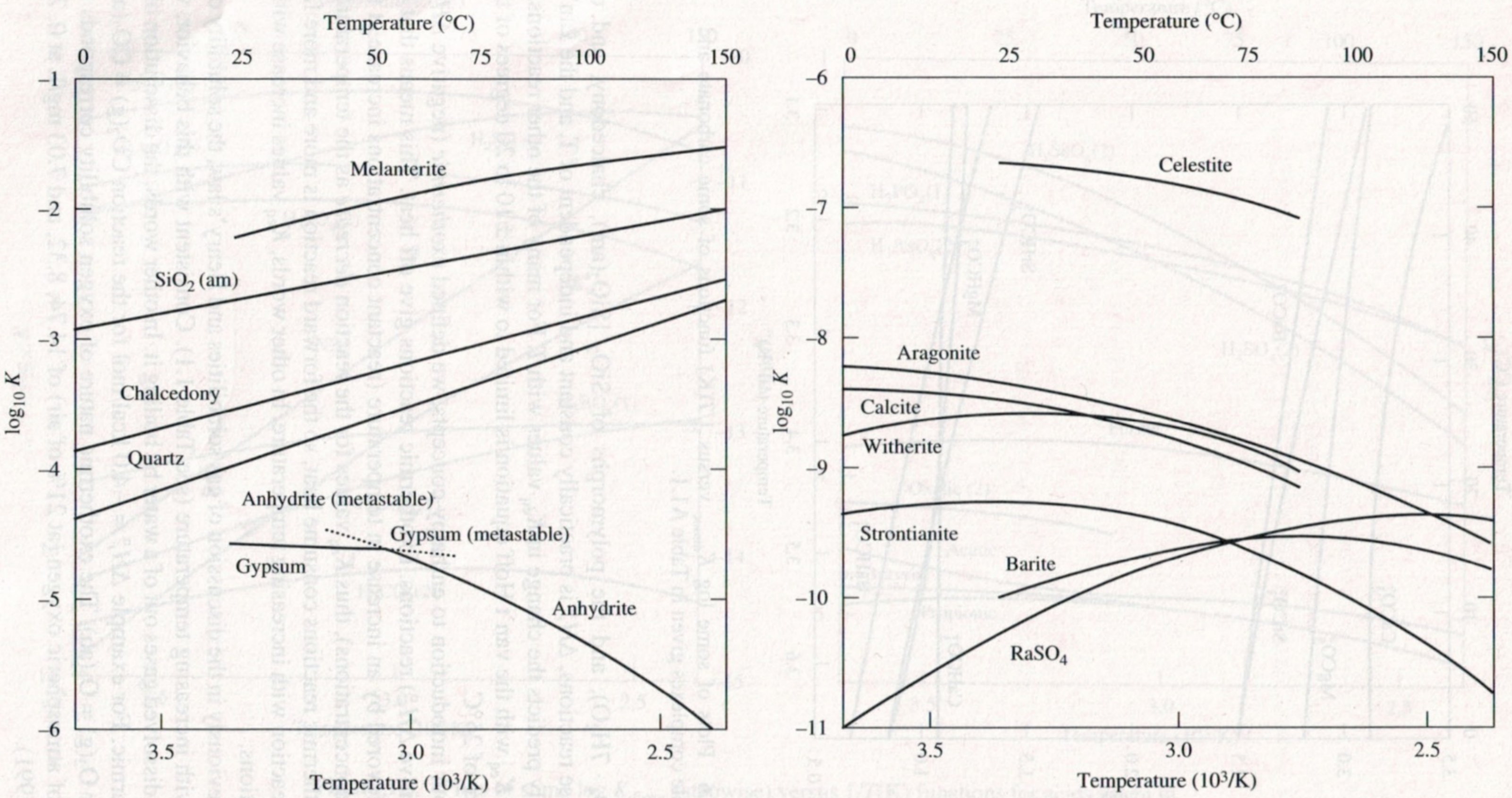


Figure 1.7 Plots of some log K_{sp} versus 1/*T*(K) functions for some silica polymorphs, sulfates, and carbonates given in Table 1.2.

- To next lecture

DAR