Chem 4110/6110 Thermodynamics! Kinetics

I Thermodynamics
Properties of bulk matter

Equilibrium
Heats of reaction
extent of reaction
phase equilibrium
electrochemistry

Nonequilibrium
transport (diffusion, conductivity...)
viscosity

Basic Definitions (Chapter 1)

System - those materials of special interest
reaction vessel + contents
Surroundings - everything else

Open System - matter can flow in and out
Closed System - " cannot " " " "

In a closed system, heat (energy) can
be exchanged with the surroundings

Example: water on a hotplate
Isolated System - matter and energy cannot be exchanged with surroundings.

Wall - separates system from surroundings. "Walls" can be rigid, flexible (like a rubber balloon), movable (like a piston), non-permeable, or permeable to heat (conductor) or matter (semi-permeable membrane).

Equilibrium - no macroscopic change in properties of system with time.

Temperature

The concepts of "hot" and "cold" are older than civilization. However, "temperature" as known today dates from early 18th century (Gabriel Daniel Fahrenheit - 1686-1736). Basically, "temperature" puts "hot" & "cold" on a quantitative scale.

<table>
<thead>
<tr>
<th>System of T</th>
<th>m.p. of ice (°)</th>
<th>b.p. of H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fahrenheit</td>
<td>32 °F</td>
<td>212 °F</td>
</tr>
<tr>
<td>Celsius (Centigrade)</td>
<td>0 °C</td>
<td>100 °C</td>
</tr>
</tbody>
</table>
Most materials expand/contract with temperature

\[ T \propto \left( \frac{l - l_0}{l_{100} - l_0} \right) (100°C) \]

\[ l_0 = \text{length at } 0°C \]

\[ l_{100} = \text{length at } 100°C \]

(assumes \( l \) varies linearly with \( T \))

For a liquid (Hg or ethanol, for example), the liquid density, \( \rho \), varies with \( T \). This is the basis of accurate thermometers

\[ T \propto \left( \frac{\rho - \rho_0}{\rho_{100} - \rho_0} \right) (100°C) \]

\[ \rho = \rho_0 + \left( \frac{\rho_{100} - \rho_0}{100} \right) T \]

For some materials, \( \rho \) does not always vary linearly with \( T \)
Behavior of gases

1) Low pressure, \( P \)

\[ \rho_m = \frac{m}{V} \]  (mass density: \( \frac{kg}{m^3}, \frac{g}{cm^3}, \text{etc.} \))

\[ \rho = \frac{n}{V} \]  (molar \( \nu \): moles/\( m^3 \), etc.)

For \( T \) and \( m \) constant \( PV = \text{constant} \)

(Boyle's Law)

2) Hold \( P \) and \( m \) (or \( n \)) constant and vary \( T \)

\[ V \text{ varies linearly with } T \]

\[ V \approx V_0 (1 + \alpha T) \]
\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right) \] is the coefficient of thermal expansion.

For gases at low \( P \) or high \( T \):

1. Same for all gases
2. \( \alpha = \frac{1}{273.15} \)

![Graph showing ideal and actual gas behavior]

An "ideal" gas is a hypothetical substance that has \( \alpha = 1/273.15 \) at all \( P \) and \( T \).

\[ \text{(ideal gas)} \quad V = V_0 \left( 1 + \frac{T}{273.15} \right) \]

Define Kelvin scale

\[ T(K) = T(\text{°C}) + 273.15 \]

\[ \text{(ideal gas)} \quad V = V_0 \cdot T(K) \quad \text{(constant \( PdV \))} \]

From Boyle's Law, \( PV = \text{constant if} \ T \text{ is const.} \)

\[ \text{(ideal gas)} \quad V = C \left( \frac{T}{P} \right) \quad \text{constant} \]
Avogadro's Hypothesis (circa 1820)

At the same \(T\) and \(P\), a given volume of gas contains the same number of particles.

One "mole" is that number of particles that occupy \(22.413\) litre at \(273.15\) K (\(T_0\)) and 1 atm pressure, \(P_0\).

For 1 mole of an ideal gas (\(T_0, P_0, V_0\))

\[
V_0 = R \left( \frac{T_0}{P_0} \right)
\]

\(\uparrow\) gas constant

\[
R = \frac{P_0 V_0}{T_0} = \frac{(1\text{ atm})(22.413\text{ liter})}{(273.15\text{ K})} = 0.0821 \frac{\text{L atm}}{\text{mole K}}
\]

In general, for \(n\)-moles of gas under any conditions

\[
V = nR \left( \frac{T}{P} \right) \Rightarrow \boxed{PV = nRT}
\]

Since all gases obey this law, we can generalize it to a mixture of different species number density

\[
PV = \sum_i n_iRT \quad \text{or} \quad P = \frac{\sum n_i}{V}RT = \sum_i \frac{n_i}{V_i}RT
\]
Define "partial pressure"

\[ P_i = p_i \frac{RT}{V} = \frac{n_i}{n_T} \frac{RT}{V} \]

Note that

\[ \frac{P_i}{P_{\text{Tot}}} = \left( \frac{n_i}{n_T} \right) \frac{RT}{V} / \left( \frac{n_{\text{Tot}}}{V} \right) = \frac{n_i}{n_T} = X_i \]

Pressure

\[ \text{Kg m}^2/\text{sec}^2 \]

\[ \text{pressure} = \frac{\text{force}}{\text{area}} = \frac{\text{Newton}}{\text{m}^2} = \frac{\text{Kg}}{\text{m sec}^2} = \text{Pascal (MKS)} \]

Suppose we have a 100 Kg box sitting on a 1m\(^2\) table.

\[ F = mg = (100 \text{ Kg}) (9.8 \frac{\text{m}}{\text{sec}^2}) = 980 \text{ Newton} \]

The pressure on the table (assuming (uniform) distribution of weight) is

\[ P = \frac{F}{A} = \frac{980 \text{ N}}{1 \text{ m}^2} = 980 \text{ Pa} \]

Now the earth's atmosphere has weight (due to gravity) in much the same way as the mass sitting on a table even though it is a gas (not a solid).
Easiest to detect this with a vacuum mass density

\[ m = \rho \cdot h \]

mass of fluid in column

\[ P_{\text{atm}} = mg = \rho \cdot gh \]

For water, \( h \approx 32 \text{ feet} \). For Hg, \( h \approx 760 \text{ mm} \) at sea level. (These numbers vary, however)

1 atm = pressure that supports a 760 mm (76 cm) column of Hg at 0°C,

(\( \rho_{\text{Hg}} = 13.5951 \, \text{g/cm}^3 \), \( g = 9.8065 \, \text{m/s}^2 \))

1 atm = 760 mm Hg = 760 torr = \( \rho_{\text{Hg}} \cdot g \cdot h \)

\[
= (13.5951 \, \text{g/cm}^3) (10^{-3} \, \text{kg/g}) (10^6 \, \text{cm}^3/\text{m}^3) (9.8065 \, \text{m/s}^2) (760 \, \text{mm}) (10^{-3} \, \text{m/m})
\]

\[ = 1.013 \times 10^5 \, \text{kg/m}^2 \cdot \text{s} \cdot \text{sec} = 1.013 \times 10^5 \text{ Pa} \]

Problem: What pressure does a scuba diver feel at a depth of 100 ft?

\[
P = P_{\text{atm}} + \rho gh = 1 \text{ atm} + (1 \, \text{g/cm}^3) (10^{-3} \, \text{kg/g}) (10^6 \, \text{cm}^3/\text{m}^3) (9.8065 \, \text{m/s}^2) \times (100 \, \text{ft}) (3048 \, \text{ft}) \\
\text{h} = 298,902 \, \text{Pa}
\]

\[
\text{in atm}
\]
Composition of air

\[ P_{\text{air}} = P_{N_2} + P_{O_2} + P_{H_2O} + P_{\text{Argon}} + P_{\text{CO}_2} + \ldots \]

Since the amounts of Argon, CO2, ... are small, we can ignore most of the components to a good approx.

\[ P_{\text{air}} \approx P_{N_2} + P_{O_2} + P_{H_2O} = (x_{N_2} + x_{O_2} + x_{H_2O}) P_{\text{air}} \]

Since "dry" air consists of 80% \(N_2\) and 20% \(O_2\) (by number of particles)

\[ P_{O_2} \approx \frac{1}{4} P_{N_2} \]

Problem:

Suppose \(P_{\text{atm}} = 761.3\) torr and \(P_{H_2O} = 21.1\) torr,

What are \(P_{N_2}\) and \(P_{O_2}\) ?

\[ 761.3 = P_{N_2} + P_{O_2} + P_{H_2O} = P_{N_2} + 0.25 P_{N_2} + 21.1 \]

\[ 740.2 \text{ torr} = 1.25 P_{N_2} \]

\[ P_{N_2} = \frac{740.2}{1.25} = 592.2 \text{ torr,} \quad P_{O_2} = 148.0 \text{ torr} \]
**Real Gases**

In real gases, \( V \to 0 \) as \( T \to 0 \) since: (a) the atoms/molecules of a real gas occupy volume, (b) atoms/molecules of a real gas interact with each other. Intermolecular attractions cause a gas to liquify (or form a solid) at sufficiently low \( T \).

To deal with (a), correct ideal gas law to account for volume occupied by gas atoms.

\[
P(V-nb) = nRT \quad \text{or} \quad P = \frac{nRT}{V-nb}
\]

\( b \) = molar volume of condensed gas.

(For \( H_2O \), \( b \approx 18 \text{ cm}^3 \ll 20 \text{ liters} \) which is typical volume of 1 mole of gas. Under many conditions, \( V \gg nb \) so ideal gas law works well.)

Also, attractive interactions reduce \( P \) further. This reduction in \( P \) is proportional to \( P^2 \) so we can write

\[
P = \frac{nRT}{V-nb} - a \left( \frac{n}{V} \right)^2 \quad \text{Van der Waals Equation.}
\]
Chapter 2

First Law of Thermodynamics

Energy is conserved

\[ \Delta U_{\text{Total}} = \Delta U_{\text{system}} + \Delta U_{\text{surr}} = 0 \]

\[ \Delta U_{\text{system}} = -\Delta U_{\text{surr}} \]

In most cases, we shall focus on what happens to the system of interest.

Usually (but not always!) \( U_{\text{system}} \) changes by

\( w = \text{mechanical work done on system} \)

\( q = \text{heat absorbed by system} \)

Omit "system" subscript for brevity)

Let's focus on \( q \) first

Example

\[
\begin{array}{c|c}
\text{high} & \text{low} \\
\hline
T & T
\end{array}
\Rightarrow
\begin{array}{c}
\text{insulation}
\end{array}
\]

Interpretation - "heat" flows from hot to cold regions until \( T \)'s are equal
Caloric Theory - Heat is like matter and flows from a region of high to low concentration.

Problem with this!

Take 2 pieces of ice at -10°C and rub them together. The ice melts!

Conclusion. Heat is produced by mechanical action. (Count Rumford)

We need to develop this more carefully.

State of a system

Conditions that unambiguously describe a system.

\[
\begin{array}{c|c|c}
\text{example} & P = 1 \text{ atm} & P = 1 \text{ atm} \\
\hline
\text{H}_2\text{O} & 20^\circ\text{C} & \text{H}_2\text{O} \\
\text{g} & 500 \text{m}^3 & 20^\circ\text{C} \\
& 500 \text{g} & \text{g} \\
\end{array}
\]

Equation of State

relates mass to volume

\[ m = \rho_m \nu \text{ (liquid)} \quad PV = nRT \text{ (ideal gas)} \]

State Function

Any quantity that depends only on the state of the system and not on how it was prepared.
Examples of state functions

(1) energy of a system \( U = \frac{3}{2}RT \)
(2) altitude of a city above sea level, \( h \)

Let \( F \) be an arbitrary state function and suppose our system undergoes some change

\[ F_{\text{init}} \rightarrow F_{\text{final}} \]

If we now return our system to its initial conditions

\[ F_{\text{init}} \leftrightarrow F_{\text{final}} \]

\( \Delta F_{\text{total}} = 0 \)

Suppose you drive from Atlanta to Chattanooga. The change in altitude is \( \Delta h \). The miles driven will, however, depend on path.

Now drive back to Atlanta. For the whole trip \( \Delta h = 0 \), but miles driven \( \neq 0 \).

\( h \) = state function
miles driven - not a state function
It shall now be demonstrated that $q$ and $\omega$ are not state functions.

Example:

<table>
<thead>
<tr>
<th>Path 1</th>
<th>Path 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>$H_2O(\ell)$</td>
<td>$H_2O(\ell)$</td>
</tr>
<tr>
<td>20°C</td>
<td>70°C</td>
</tr>
<tr>
<td>500 mL</td>
<td>500 mL</td>
</tr>
</tbody>
</table>

- **Path 1**
  - $q = \text{heat absorbed by system}$
  - $= C(T_f - T_i) = m \cdot c \cdot (T_f - T_i)$
  - For water, $c \approx 1 \text{ cal/gm K}$
  - $q = m \cdot c \cdot (T_f - T_i) = (500 \text{ gm})(1 \text{ cal/gm K})(50 \text{ K})$
  - $q = 25,000 \text{ cal} = 25 \text{ Kcal}$

Since we haven't done any work,

$\omega = 0$

So,

$\Delta U_1 = q + \omega = 25 \text{ Kcal}$
Path 2) 

Toule determined how much mechanical work required to raise the T of a given amount of water.

\[ d = x_i - x_f \]

mechanical work done on system = \[ W = Fd \]

Toule determined it took 4.189 Joule to raise the T of 1gm of water 1°C.

\[ \Delta U_c = W = 25 \text{ kcal} = 104.6 \text{ kJ} \]

Suppose \( m = 100 \text{ kg} \), what must \( d \) be to raise the temperature of 500gm of water by 50°C?

\[ 1.046 \times 10^5 \text{ Joule} = mgd \]

\[ d = \frac{1.046 \times 10^5 \text{ kg m}^2/\text{sec}^2}{(100 \text{ kg})(9.8 \text{ m/sec}^2)} = 106.7 \text{ meters} \approx 350 \text{ ft} \]

Now 1 lb = 0.453 kg so this corresponds to the energy expended in lifting 200 + lbs to 350 ft.
Expansions of an Ideal Gas

For ideal gases

\[ U = \frac{3}{2}RT \quad \text{(monatomic)} \]
\[ U = \frac{5}{2}RT \quad \text{(diatomic)} \]

For an expansion at constant \( T \), \( \Delta U = 0 \)

\[ w_1 = \text{work done on gas when we remove the first weight} = -F_0 \, d_1 = -P_1 \, A \, d_1 = -P_1 (V_1 - V_2) \]

Opposing force on gas as it expand

Note that for an expansion, \( w_1 < 0 \).
Negative work means work is done by system on the surroundings.

If the gas were being compressed,
\[ w = -P_0 \, \Delta V > 0 \quad \text{since} \quad \Delta V < 0 \]

What is \( q_1 \) for this first step?

Since \( \Delta U = 0 = q_1 + w_1 \)

\[ q = -w_1 \]

For expansion \( q > 0 \). Gas absorbs heat from surroundings as it does work.
As expansion proceeds, we can analyze each step and arrive at a similar conclusion. For overall expansion (n-steps)

\[ w = w_1 + w_2 + \ldots + w_n = -P_1(V_1 - V_2) - P_2(V_2 - V_3) \ldots - P_n(V_n - V_{n-1}) \]

\[ q = -w_1, -w_2, \ldots, -w_n = -w \]

\[ \Delta U = 0 \]

It is worthwhile to look at this graphically.

\(-w = \text{sum of areas under } PV\text{-curve.}\)

It is important to note that \(w\) will depend on how expansion is carried out.

\(1\text{-step}\)

\(\infty\text{-step}\)
Suppose we have one mole of an ideal gas at 25°C with $P_i = 2\text{ atm}$, $P_f = 1\text{ atm} = 1.013 \times 10^5 \text{ Pa}$.

What is $W$ for a 1 step expansion?

$$W = -P_o (V_f - V_i) = -P_f (V_f - V_i)$$

$$V_f = \frac{nRT}{P_f} = \frac{(1\text{ mole})(0.082 \text{ dm}^3/\text{atm/mole K})(298.15\text{ K})}{1\text{ atm}} = 24.45 \text{ dm}^3 = 24.45 \text{ liters}$$

Since $P_i$ is twice $P_f$, $V_i = \frac{1}{2} V_f = 12.225 \text{ liters}$

$$W = -(1.013 \times 10^5 \text{ Pa})(12.225 \text{ dm}^3)(10^{-3} \text{ m}^3/\text{dm}^3) = -1238 \text{ Joule} = -1.238 \text{ kJ}$$

What is $W$ for the $n=\infty$ (reversible) isothermal expansion?

$$W = -\int_{V_i}^{V_f} P_o dV = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = -nRT \ln \frac{V_f}{V_i}$$

$$= -nRT \ln \frac{V_f}{V_i} = -nRT (\ln V_f - \ln V_i)$$

$$= -nRT \ln \frac{V_f}{V_i} = -(1)(8.314 \frac{\text{ J}}{\text{ mole K}})(298.15\text{ K}) \ln \frac{2}{.693}$$

$$= 1718 \text{ Joule} = 1.718 \text{ kJ}$$

Note that we get more work as the expansion is carried out in more steps.
Summary on the isothermal expansion of 1 mole of ideal gas at 25°C, \( P_f = 1 \text{ atm} \) (reversible)

\[
\begin{array}{ccc}
\text{step} & \text{step} \\
\hline
q & +1.238 & +1.718 \\
w & +1.238 & -1.718 \\
\Delta U & 0 & 0 \\
\end{array}
\]

For a general process

\[ \Delta U = \Delta W + dq \]

\( \text{slashes indicate path dependence or inexact differentials} \)

Before leaving gas expansions, let's briefly discuss \underline{adiabatic} expansions.

Adiabatic - system is thermally insulated

\[ \Delta U = q + W = 0 \]

\( \Rightarrow q = 0 \)

\[ \begin{array}{c}
\text{Insulation} \\
\hline
P_i, V_i, T_i \\
\hline
\end{array} \quad \rightarrow \quad \begin{array}{c}
W < 0 \\
\text{(gas expands)} \\
g = 0 \\
\text{(adiabatic)} \\
\end{array} \\
\begin{array}{c}
\Delta U = q + W = W < 0 \\
\text{(monatomic)} \\
\text{(diatomic)} \\
\end{array} \\
\begin{array}{c}
\text{m} \\
\hline
P_f, V_f, T_f \\
\hline
\end{array}
\]

Since \( \Delta U < 0 \) and \( U = \frac{3}{2} nRT \) or \( \frac{5}{2} nRT \), \( T_f < T_i \)

As the gas does work, it loses energy and \( T \) decreases. We shall return to this later.
Processes at constant volume

\[ dU = dq_v + dw \]

- heat absorbed at constant volume.

Types of work

P-V: \[ dw = -P \, dV \]

electric: \[ dw = -\frac{d\phi}{\delta} \, dQ \]

torque difference

elastic stretching: \[ = \delta \, dL \]

We shall be primarily interested in systems where only P-V work is involved.

For a process with V constant,

\[ dw = -P \, dV = 0 \]

\[ \therefore \quad dU = dq_v = dq_v \text{ at constant volume.} \]

For a process at

Energy change = heat absorbed!

For simple heating of a material

\[ dq_v = C_v \, dT = m \, C_v, m \, dT = m \, C_v, sp \, dT \]

total heat capacity

\[ C_v, m = \text{molar heat capacity} \quad (\text{per mole}) \]

\[ C_v, sp = \text{specific h.c.} \quad (\text{per gram}) \]
**Bomb Calorimetry**

System = contents inside B.C.
Surroundings = metal B.C.

Since the calorimeter + contents are isolated

\[ \Delta U_{\text{total}} = \Delta U_{\text{B.C.}} + \Delta U_{\text{sys}} = 0 \]

\[ \Delta U_{\text{sys}} = -\Delta U_{\text{B.C.}} \]

Suppose 1 gm of benzene \((M_{\text{benzene}} = 78.12 \text{ gm})\) is ignited and the \(T\) of the B.C. rises by 8.4 °C. Also, \(C_{\text{B.C.}} = 1.193 \text{ kcal/°C} \)

What is \(\Delta U\) for the combustion of 1 mole of benzene? \((1 \text{ kcal} = 4.184 \text{ J})\)

For 1 gm, \(\Delta U_{\text{sys}} = -C_{\text{B.C.}} \Delta T = (-1.193 \text{ kcal})(8.4) = -41.92 \text{ kJ/gm per mole} \)

\[ \Delta U_{\text{combustion}} = (78.12 \frac{\text{g_mole}}{\text{g}})(-41.92 \frac{\text{kJ}}{\text{g_mole}}) \]

\[ = -3275 \text{ kJ/mole} \]
In chemistry, it is usually far more convenient to deal with processes at constant \( P \) instead of constant \( V \).

**Processes at constant \( P \)**

\[
dU = dq_p + dw = dq_p - PdV
\]

However \( d(PV) = PdV + VdP = PdV \)

\[
\therefore \ dq_p = dU + d(PV) = d(U + PV) = dH
\]

\( dH < 0 \) exothermic (heat released)
\( dH > 0 \) endothermic (heat absorbed)

**Simple heating of a material**

\( V \)-constant

\[
dU = dq_v = C_v dT
\]

\[
C_v = \left. \frac{dU}{dT} \right|_{V \ const} = \left. \frac{\partial U}{\partial T} \right|_V
\]

\( P \)-constant

\[
dH = dq_p = C_p dT
\]

\[
C_p = \left. \frac{dH}{dT} \right|_{P \ const} = \left. \frac{\partial H}{\partial T} \right|_P
\]

In general, \( C_v \neq C_p \)
Consider Ideal Gases

\[ U = \frac{3}{2} RT \quad \text{(one mole monatomic gas)} \]
\[ = \frac{5}{2} RT \quad \text{(" ") diatomic "")} \]

\[ H = U + PV = U + RT = \begin{cases} \frac{3}{2} RT & \text{(monatomic)} \\ \frac{5}{2} RT & \text{(diatomic)} \end{cases} \]

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} R \quad \text{or} \quad \frac{5}{2} R \]

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p = \frac{5}{2} R \quad \text{or} \quad \frac{7}{2} R \]

Note that \( C_p = C_v + R \)

Physically, it takes more energy to raise the temperature at constant \( P \) than at constant \( V \).

\[ \text{Const } V \quad \begin{array}{c} P_i, V_i, T_i \uparrow \end{array} \quad \rightarrow \quad \begin{array}{c} P_f, V_f, T_i + 1^\circ C \uparrow \end{array} \]

\[ Q_V = \frac{3}{2} R \]

(heat used to increase energy (speed) of atoms)

\[ \text{Const } P \quad \begin{array}{c} P_i, V_i, T_i \uparrow \end{array} \quad \rightarrow \quad \begin{array}{c} P_f, V_f, T_i + 1^\circ C \uparrow \end{array} \]

\[ Q_p = \frac{5}{2} R \]

(heat used to: 1) increase energy of atoms + 2) do "work" on surroundings)
Example 1) Irreversible A.E. against constant opposing P.

\[ \Delta U = q + w = -P_f (V_f - V_i) \]

0 (because exp. is adiabatic)

Also,

\[ \Delta U = nC_v \Delta T = nC_v (T_f - T_i) \]

\[ \Delta C_v (T_f - T_i) = -P_f \left( \frac{\Delta RT_f}{P_f} - \frac{\Delta RT_i}{P_i} \right) \]

\[ C_v (T_f - T_i) = -RT_f + RT_i \frac{P_f}{P_i} \]

\[ (C_v + R)T_f = T_i (C_v + R \frac{P_f}{P_i}) \]

\[ \Rightarrow \frac{C_v}{C_p} T_f = T_i \left( \frac{C_v}{C_p} + \frac{R}{C_p} \frac{P_f}{P_i} \right) \]

Suppose we have a monatomic gas \((C_v = \frac{1}{2} R, \ C_p = \frac{5}{2} R)\) with \(T_i = 298.15 \text{ K}, \ P_i = 2 \text{ atm}, \ P_f = 1 \text{ atm}.\)

\[ T_f = 298.15 \left( \frac{\frac{3}{2}}{\frac{5}{2}} + \frac{R}{\frac{3}{2} R} \left( \frac{1}{2} \right) \right) = (298.15) \left( \frac{4}{5} \right) = 239 \text{ K} \]

\((-34^\circ C\)
Example 2) Reversible Adiabatic Expansion

\[ nC_vdT = 0 \]

\[ \Rightarrow \]

\[ dU = dq + dw = -P_o dV \]

You have to be careful here because \( P_o = P \) and as the gas expands, it cools

\[ \int C_v dT = -PdU = -\frac{nRT}{V} dV \]

\[ \frac{C_v dT}{T} = -R \frac{dV}{V} \]

Integrate

\[ C_v \int \frac{T_F}{T} \frac{dT}{T_i} = -R \int \frac{V_F}{V_i} \frac{dV}{V} \]

\[ C_v \ln \frac{T_F}{T_i} = -R \ln \frac{V_F}{V_i} = -R \ln \left( \frac{nRT_F}{nRT_i} \right) \]

\[ = -R \ln \frac{T_F}{T_i} - R \ln \frac{P_F}{P_i} \]

\[ (C_v + R) \ln \frac{T_F}{T_i} = -R \ln \left( \frac{P_F}{P_i} \right) = R \ln \left( \frac{P_i}{P_F} \right) \]

\[ \frac{C_p}{C_v} \ln \frac{T_F}{T_i} = \frac{R}{C_p} \ln \left( \frac{P_i}{P_F} \right) = \ln \left( \frac{P_F}{P_i} \right) \]

\[ \frac{R}{C_p} \ln \frac{T_F}{T_i} = \ln \left( \frac{P_F}{P_i} \right) \]

\[ T_F = T_i \left( \frac{P_F}{P_i} \right)^{R/C_p} \]

For previous example

\[ T_F = 298.15 \left( \frac{1}{2} \right)^{\frac{3}{2}} \]

\[ = 298.15 \left( \frac{1}{2} \right) = 226 \text{ K} \]
Relationship of $P$, $V$, $T$ in Reversible Adiabatic Expansions/Compressions of Ideal gases

\[ T_f = T_i \left( \frac{P_f}{P_i} \right)^{R/c_p} \]

\[ C_p \ln \left( \frac{T_f}{T_i} \right) = R \ln \left( \frac{P_f}{P_i} \right) \]

\[ (C_v + R) \ln \left( \frac{P_f}{P_i} \cdot \frac{V_f}{V_i} \cdot \frac{1}{nR} \right) = R \ln \left( \frac{P_f}{P_i} \right) \]

\[ (C_v + R) \ln \left( \frac{P_f}{P_i} \right) + (C_v + R) \ln \left( \frac{V_f}{V_i} \right) = R \ln \left( \frac{P_f}{P_i} \right) \]

\[ C_v \ln \left( \frac{P_f}{P_i} \right) + C_p \ln \left( \frac{V_f}{V_i} \right) = 0 \]

\[ \ln \left( \frac{P_f}{P_i} \right) + \left( \frac{C_p}{C_v} \right) \ln \left( \frac{V_f}{V_i} \right) = 0 \]

\[ \ln \left( \frac{P_f V_f^{C_v}}{P_i V_i^{C_v}} \right) = 0 \]

$P V^Y = \text{constant}$

- Isothermal $(P V = \text{const})$
- Adiabatic $(P V^\gamma = \text{const})$
Speed of Sound (Newton's mistake)

\[ u_{\text{sound}}^2 = -\frac{V}{\rho} \left( \frac{dP}{dV} \right) \rightarrow \text{theory of Newton} \]

\[ \rho = \text{mass density of air} \approx 1.286 \frac{\text{kg}}{\text{m}^3} \]

Boyle was a contemporary of Newton's (circa 1700) I told him

\[ PV = \text{constant} = A \quad (T = \text{const}) \]

\[ \Rightarrow \left( \frac{dP}{dV} \right) = \frac{d}{dV} \left( \frac{A}{V} \right)^2 = -\frac{A}{V^2} = -\frac{P}{V} \]

At 1 atm = 1.013 x 10^5 Pa = 1.013 x 10^5 \frac{\text{kg} \cdot \text{m}^2}{\text{sec}^2}

\[ u_{\text{sound}}^2 = -\frac{V}{\rho} \left( -\frac{P}{V} \right) = \frac{P}{\rho} = 7.88 \times 10^4 \frac{\text{m}^2}{\text{sec}^2} \quad u_{\text{sound}} = 281 \frac{\text{m}}{\text{sec}} \]

Experiments: \( u_{\text{sound}} = 332 \frac{\text{m}}{\text{sec}} \)

Since air expands/contracts rapidly as sound moves through it, it behaves adiabatically.

\[ PV^n = \text{constant} \quad \frac{dP}{dV} = \frac{d}{dV} \left( P \left( \frac{A'}{V^{n-1}} \right)^n \right) = -A' V^{-n-1} = -\frac{n}{V} P \]

\[ u_{\text{sound}}^2 = -\frac{V}{\rho} \left( -\frac{n}{V} P \right) = \frac{n}{\rho} P = \left( \frac{n}{\kappa} \right) \left( 7.88 \times 10^4 \frac{\text{m}^2}{\text{sec}^2} \right) \]

\[ u_{\text{sound}} = 332 \frac{\text{m}}{\text{sec}} \]
Chapter 3

A) Digression on Partial Derivatives

Start with the example of the surface area, \( S \), of a rectangle with sides of length \( x \) and \( y \), and change by \( \delta x \) and \( \delta y \).

\[
S_0 = xy
\]

\[
\text{area} = x \delta y
\]

\[
\text{small area} = \delta x \delta y
\]

\[
S = (x + \delta x)(y + \delta y) = xy + x \delta y + y \delta x + \delta x \delta y
\]

\[
S - S_0 \approx x \delta y + y \delta x
\]

\[
\delta S = \left( \frac{\partial S}{\partial y} \right) \delta y + \left( \frac{\partial S}{\partial x} \right) \delta x
\]

All a partial derivative is is a derivative of a multivariable function treating all variables except 1 as constant.
Examples:

\[ f(x, y) = x^2 \sin(ay) \]

\[ \frac{2F}{\delta x} = \frac{2}{\delta x} (x^2 \sin(ay)) = \sin(ay) \frac{2x^2}{\delta x} = 2x \sin(ay) \]

\[ \frac{2F}{\delta y} = \frac{2}{\delta y} (x^2 \sin(ay)) = x^2 \frac{2}{\delta y} (\sin(ay)) = ax^2 \cos(ay) \]

For small changes in \( x \) and \( y \):

\[ \delta F \approx \frac{2F}{\delta x} \delta x + \frac{2F}{\delta y} \delta y = [2x \sin(ay)] \delta x + [ax^2 \cos(ay)] \delta y \]

Also consider mixed partial derivatives:

\[ \frac{2^2 F}{\delta x \delta y} = \left( \frac{\partial}{\partial x} \left( \frac{2F}{\delta y} \right) \right)_y = \left( \frac{\partial}{\partial x} (ax^2 \cos(ay)) \right) \]

The "x" subscript indicates we hold it constant in this step of the problem.

Note that \( \frac{\partial}{\partial y} (\frac{\partial f}{\partial x}) = \frac{\partial}{\partial x} (\frac{\partial f}{\partial y}) \)
Consider the volume of some material to be a function temperature, \( T \), and pressure, \( P \). If we change \( T \) and \( P \) by amounts \( \delta T \) and \( \delta P \)

\[
dV = \left( \frac{\partial V}{\partial T} \right)_p \delta T + \left( \frac{\partial V}{\partial P} \right)_T \delta P
\]

Define

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad \text{Thermal Expansion Coeff.}
\]

\[
\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \text{Isothermal Compressibility Coeff.}
\]

Using these coefficients

\[
dV = V\beta \delta T - \kappa V \delta P
\]

Dividing this by \( \kappa V \), we also have an expression for \( \delta P \) in terms of \( dV \) and \( \delta T \)

\[
dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa} \frac{dV}{V} dP
\]

Frequently, \( \beta \) and \( \kappa \) can be treated as constants.

Integrate the above expression

\[
\int_{P_i}^{P_f} dP = (P_f - P_i) = \frac{\beta}{\kappa} \int_{T_i}^{T_f} dT - \frac{1}{\kappa} \int \frac{dV}{V}
\]

\[
\Delta P = \frac{\beta}{\kappa} (T_f - T_i) - \frac{1}{\kappa} \ln \left( \frac{V_f}{V_i} \right)
\]

\[
\Delta P = \frac{\beta}{\kappa} (T_f - T_i) - \frac{1}{\kappa} \ln \left( \frac{V_f}{V_i} \right)
\]
Problem (3.5): A vessel is completely filled with water and sealed at 25°C & \( P_i = 1 \text{ atm} \). If this is heated to 60°C, what is \( P_f \)?

(Do not do this at home!) \(^7\)

You are given:
- \( \beta_{\text{water}} = 2.04 \times 10^{-4} \text{ K}^{-1} \)
- \( \beta_{\text{vessel}} = 1.02 \times 10^{-4} \text{ K}^{-1} \)
- \( K_{\text{water}} = 4.59 \times 10^{-5} \text{ L bar}^{-1} \)
- \( K_{\text{vessel}} = 0.0 \) (Solids are highly incompressible)

As the vessel is warmed, it expands

\[
dV_{\text{vessel}} = \beta_{\text{vessel}} \cdot V_i \cdot (T_f - T_i) = V_f - V_i = V_i \left[ 1 + \beta_{\text{vessel}} (T_f - T_i) \right]
\]

Use this in the expression for \( dP \) for the water in the vessel.

\[
P_f = P_i + \beta_{\text{water}} \frac{(T_f - T_i)}{K_{\text{water}}} - \frac{1}{K_{\text{water}}} \ln \left( \frac{V_f}{V_i} \right)
\]

\[
1.013 \text{ bar} + \frac{(2.04 \times 10^{-4} \text{ K}^{-1}) (35 \text{ K})}{(4.59 \times 10^{-5} \text{ bar})} - \frac{1}{(4.59 \times 10^{-5} \text{ bar})} \ln \left( 1 + \beta_{\text{vessel}} (135 \text{ K}) \right)
\]

\[
= 1.013 \text{ bar} + 155.5 \text{ bar} - 77.63 \text{ bar} = 78.8 \text{ bar}
\]

Starting \( P \) pressure change due to expansion at constant \( V \) change due to expansion of vessel.
Cyclic Rule: (apply first to $V, T, P$)
\[ dV = \left( \frac{\partial V}{\partial T} \right)_P \, dT + \left( \frac{\partial V}{\partial P} \right)_T \, dP \]

Consider a process carried out at constant $V$

\[ 0 = \left( \frac{\partial V}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_V + \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial V} \right)_V \]

divide by $(\partial T)_V$ and subtract $(\frac{\partial V}{\partial T})_P$

\[ -\left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial V} \right)_V \]

\[ -1 = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V / \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P \]

where 2nd equality holds since $(\frac{\partial V}{\partial T})_P = +(\frac{\partial T}{\partial V})_P$

In general, if $x, y, z$ are three interrelated variables

\[ -1 = \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y \]

Application (from #)

\[ -1 = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{A}{\chi} \]

If we know how $V$ varies with $T$ ($\beta$) and how $V$ varies with $P$ ($\chi$), we know how $P$ varies with $T$ ($V$ constant)
Energy as a state function

It is convenient to choose the natural variable of $U$ to be $TdV$. (For cylinder, the natural variables are $TdP$.) Formally, we can write

\[ dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV = C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV \]

From 1st law, we also have

\[ dU = dq - PdV \quad \text{(only PV work)} \]

Equating the above 2 expressions for $dU$

\[ dq = C_v dT + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] dV \]

If we hold $P$ constant, $dq \rightarrow dp = C_p dT$

\[ C_p(\delta T) = C_v(\delta T)_p + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] (\delta V)_p \]

\[ C_p - C_v = (P + (\frac{\partial U}{\partial V})_T) (\frac{\partial U}{\partial V})_p \]

valid for any material

For ideal gas, $C_p - C_v = R$, $P = \frac{RT}{V}$

\[ (\frac{\partial U}{\partial T})_p = (\frac{\partial}{\partial T}(\frac{RT}{P}))_p = \frac{R}{P} \]

\[ R = R + \frac{R}{P} (\frac{\partial U}{\partial V})_T \Rightarrow (\frac{\partial U}{\partial V})_T = 0 \]
General Dependence of $U$ on $T$ and $V$

Temperature dependence ($V$ const.)

$$dU = dU_V = C_V dT$$

Volume dependence ($T$ const.)

$$dU = dU_T = \left( \frac{\partial U}{\partial V} \right)_T dV$$

Using results we will discuss later in the course, it can be shown

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

but

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}$$

$$\left( \frac{\partial U}{\partial V} \right)_T = T \frac{\beta}{\kappa} - P$$

Apply this to liquid water at $P = 1$ bar, $T = 298.15$ K, $\beta = 2.09 \times 10^{-4}$ K$^{-1}$, $\kappa = 1259 \times 10^{-5}$ m$^{-3}$.

$$\left( \frac{\partial U}{\partial V} \right)_T = (298.15 \text{ K}) \left( \frac{2.09 \times 10^{-4}}{4.59 \times 10^{-5} \text{ m}^{-3}} \right) - 1 \text{ bar}$$

$$= 13.24 \text{ bar}$$

Suppose we heat one mole of water $1 \ ^\circ C$ (1K) at constant $P$ ($V = 18 \text{ cm}^3 = 1.8 \times 10^{-5} \text{ m}^3$)

$$dV \approx \beta V \delta T = \left( 2.09 \times 10^{-4} \right) \left( 1.8 \times 10^{-5} \text{ m}^3 \right) (1 \text{ K}) = 3.67 \times 10^{-7} \text{ m}^3$$
\[ dU_T = \left( \frac{\partial U}{\partial V} \right)_T \, dV = \left( 1324 \text{ bar} \right) \left( 10 \frac{\text{Pa}}{\text{bar}} \right) \left( \frac{\text{J}}{\text{m}^3 \text{Pa}} \right) \left( 3.67 \times 10^{-3} \right) \]

\[ = 486 \text{ Joules} \] (energy change due to expansion)

\[ dU_V = \left( \frac{\partial U}{\partial T} \right)_V \, dT = C_v \, dT = \left( 18 \text{ cal} \right) \left( 4.184 \frac{\text{J}}{\text{cal}} \right) (1 \text{ K}) \]

\[ = 75.31 \text{ Joules} \] (energy change due to heating)

Note that \( dU_V \gg dU_T \). This is true for most liquids and solids due to their small compressibilities.

**Chemical Reactions at constant \( T \)**

\[ \Delta H = \Delta U + \Delta (PV) \]

Typically, molar volumes of liquids and solids are small (\( \sim 0.05 \text{ litre} \)) relative to gases (\( \sim 20 \text{ litre} \)).

\[ \Delta H \approx \Delta U + \left( n_{\text{product}} - n_{\text{reactant}} \right) RT \]

**Example:** \( C_6H_6(\ell) + \frac{7}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell) \)

For combustion of 1 mole of benzene (298K)

\[ \Delta H = \Delta U + \left( 6 - \frac{9}{2} \right) RT = \Delta U - \frac{3}{2} RT \approx -3279 \text{ kJ} \]

\[ \approx \frac{-3279 \text{ kJ}}{3.72 \text{ kJ/mole}} \]
Consider the "throttling" experiment.

For this process (gas not ideal)

\[ \omega = P_1 V_1 - P_2 V_2, \quad \text{but} \quad q = 0 \quad \text{(adiabatic)} \]

\[ \Delta U = U_2 - U_1 = \omega = P_1 V_1 - P_2 V_2 \]

rearrange

\[ U_2 + P_2 V_2 = U_1 + P_1 V_1 \]

\[ H_2 = H_1 \]

In this experiment, \( H \) is constant and we can measure changes in \( T \) and \( P \) for any gas.

From above example,

Joule-Thompson coefficient (measurable)

\[ \mu_JT = \left( \frac{\partial T}{\partial P} \right)_H = \frac{T_2 - T_1}{P_2 - P_1} \]

What does this tell us?
\[ dH = \left( \frac{\partial H}{\partial P} \right)_T \, dP + \left( \frac{\partial H}{\partial T} \right)_P \, dT \]

At constant \( H \)

\[ 0 = \left( \frac{\partial H}{\partial P} \right)_T \, (\partial P)_H + \left( \frac{\partial H}{\partial T} \right)_P \, (\partial T)_H \]

\[ \div \Delta V \, (\partial P)_H \]

\[ 0 = \left( \frac{\partial H}{\partial P} \right)_T + \left( \frac{\partial H}{\partial T} \right)_P \, (\frac{\partial T}{\partial P})_H \]

\[ \left( \frac{\partial H}{\partial P} \right)_T = -c_p \, \left( \frac{\partial T}{\partial P} \right)_H \]

What is \( \mu_{JT} \) for an ideal monoatomic gas?

(note: \( H \) depends only on \( T \) for an ideal gas.)

\[ \left( \frac{\partial H}{\partial P} \right)_T = 0 \Rightarrow \mu_{JT} = 0 \]

Problem:

If \( \text{NH}_3 \) gas (\( \mu_{JT} = 28.2 \text{ K MPa} \))

initially compressed to 10 bar expands isentropically (\( H \)-constant) to a final pressure of 1 bar, what is \( \Delta T \)?

\[ T_f - T_i = \mu_{JT} \left( P_f - P_i \right) \]

\[ = (28.2 \text{ K MPa}) \left( 10^{-6} \text{ MPa} \right) \left( 10^5 \text{ Pa} \right) (1 \text{ bar} - 10 \text{ bar}) \]

\[ = -25.4 \text{ K} \]

(The reason \( \text{NH}_3 \) has been widely used in refrigeration is because \( \mu_{JT} \) is large and positive.)
Thermochemistry

Deals with $\Delta H$ and all of chemical reactions

Since $\Delta H$ all depend, to some extent, on $P$ and $T$, it is convenient to define "Standard State Conditions" or STP for short.

STP: $P = 1$ bar

$T = 25^\circ C$

Standard state of element

$= \underline{\text{stable form of element at STP}}$

Examples:

- Oxygen
- Carbon
- Phosphorus

Enthalpies of Formation (STP)

Enthalpies of forming one mole of a molecule (or element) from the stable form of its elements under STP conditions

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H^\circ (H_2O(l)) = -285.85 \frac{kJ}{mole}$$
Table 4.1 gives many $\Delta H^\circ$'s

$\Delta H^\circ_f (\text{PbSO}_4 (s)) = -920.0 \text{ kJ/mole}$

$\text{Pb}(s) + \text{S(rhomboic)} + 2\text{O}_2 (g) \rightarrow \text{PbSO}_4 (s)$

all species at $25^\circ\text{C}$ and 1 atm pressure

What is useful about Tables of $\Delta H^\circ$'s is that they can be combined to give $\Delta H^\circ$'s for an almost infinite number of reactions

Example 1)

$\Delta H^\circ_f (\text{H}_2\text{O}(l)) = -285.85 \text{ kJ/mole}$

$\Delta H^\circ_f (\text{H}_2\text{O}(g)) = -241.8 \text{ kJ/mole}$

These can be combined to determine $\Delta H^\circ_{\text{vap}}$

$\Delta H^\circ_{\text{vap}} (\text{H}_2\text{O}(l)) = +285.8 \text{ kJ/mole}$

$\Delta H^\circ_{\text{vap}} (\text{H}_2\text{O}(g)) = -241.8 \text{ kJ/mole}$

$\Delta H^\circ_{\text{vap}} = \Delta H_1 + \Delta H_2 = 285.8 - 241.8 = +44.0 \text{ kJ/mole}$

This is allowed since enthalpy is a state function!
This additivity principle can be generalized

\[ \Delta H = \sum n_r \Delta H_f^\circ (r) - \sum n_p \Delta H_f^\circ (p) \]

**Example 1:**

\[ C_6H_6 (l) + \frac{15}{2} O_2 (g) \rightarrow 6 CO_2 (g) + 3 H_2 O (l) \]

\[ \Delta H^\circ = 6 \Delta H_f^\circ (CO_2 (g)) + 3 \Delta H_f^\circ (H_2 O (l)) - \Delta H_f^\circ (C_6H_6 (l)) - \frac{15}{2} \Delta H_f^\circ (O_2 (g)) \]

\[ = 6 [-393.5] + 3 [-285.8] - 1 [49.1] - \frac{15}{2} [0] \]

\[ = -3268 \text{ kJ/mol} \]

**Example 2:**

\[ CH_4 (g) \rightarrow C (g) + 4 H (g) \]

\[ \Delta H_f^\circ = 4 \Delta H_f^\circ (H (g)) + \Delta H_f^\circ (C (g)) - \Delta H_f^\circ (CH_4 (g)) \]

\[ = 4 \times 218 + 716.7 - 74.6 \]

\[ = 1663 \text{ kJ/mol} \]

Bond enthalpy of \( \text{C-H bond} \) is \( \frac{1663}{4} = 415.8 \text{ kJ/mol} \)
Additivity is not restricted to "formation" reactions. Indeed, "heats" of formation are not usually determined directly, but indirectly.

Example: What is $\Delta H^\circ_f(\text{CaC}_2(\text{s}))$ given:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ_f$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$</td>
<td>$-127.9$</td>
</tr>
<tr>
<td>2. $\text{C}_2\text{H}_2(\text{g}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$</td>
<td>$-1300$</td>
</tr>
<tr>
<td>3. $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$</td>
<td>$-635.1$</td>
</tr>
<tr>
<td>4. $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s})$</td>
<td>$-65.2$</td>
</tr>
<tr>
<td>5. $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$</td>
<td>$-393.5$</td>
</tr>
</tbody>
</table>

Add up these reactions in such a way to yield the desired formation reaction: $\text{Ca}(\text{s}) + 2\text{C}(\text{graphite}) \rightarrow \text{CaC}_2(\text{s})$

3. $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$ $-635.1$
+ 4. $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s})$ $-65.2$
- 1. $\text{Ca(OH)}_2(\text{s}) + \text{C}_2\text{H}_2(\text{g}) \rightarrow \text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ $+127.9$
- 2. $2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + \frac{3}{2}\text{O}_2(\text{g})$ $+1300$
+ 2. $2\text{C}(\text{graphite}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$ $-787$

Net: $\text{Ca}(\text{s}) + 2\text{C}(\text{graphite}) \rightarrow \text{CaC}_2(\text{s})$ $\Delta H^\circ = -59.4$
Enthalpies of Reaction not at STP

Consider:

\[ H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{T} H_2O(l) \]
\[ \Delta H_1 \]
\[ H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{T=298.5K} H_2O(l) \]
\[ \Delta H_2 \]
\[ \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \]

\[ \Delta H_2 = \Delta H_f^0(H_2O(l)) \text{, but } \Delta H_1, \Delta H_3 \text{ are new} \]

Consider \( \Delta H \) for heating or cooling one mole of a substance at constant P.

\[ (T=T_i) \quad (T=T_f) \]
\[ A \xrightarrow{\Delta} A \]

For a small change in \( T \)

\[ \Delta H = C_p(A) \, \Delta T \]

Since \( C_p \) may depend on \( T \)

\[ \Delta H(A) = \int_{T_i}^{T_f} C_p(A) \, dT \]

We can now use this to determine \( \Delta H_1 \).
\[ \Delta H_1 = \int_{T_1}^{T} \left[ C_p(H_2) + \frac{1}{2} C_p(O_2) \right] dT \]

\[ \Delta H_3 = \int_{298.15}^{T} C_p(H_2O(l)) dT \]

Putting all this together

\[ \Delta H = \Delta H_f^0(H_2O(l)) + \int_{H_2O(l)}^{H_2(g)} \left[ C_p(H_2O(l)) - C_p(H_2(g)) - \frac{1}{2} C_p(O_2(g)) \right] dT \]

\[-285.8 \text{ kJ mole}^{-1} \]

From Table 2.3 \( C_p(H_2O(l)) \approx 75.3 \text{ mole}^{-1}K \)

From Table 2.4

\[ C_p(H_2(g)) \approx 22.66 + 0.4381 T - 1.0835 \times 10^{-2} T^2 \]

\[ C_p(O_2(g)) = 32.93 - 0.3633 T + (1.1532 \times 10^{-4}) T^2 + (-1.2194 \times 10^{-7}) T^3 \]

Suppose \( T = 373.15 \)

\[ \Delta H_{H_2O} - \Delta H_{H_2} - \Delta H_{O_2} / 2 \]

\[ \int_{298.15}^{T} dT \Delta C_p = \int_{298.15}^{T} \left[ \Delta A(1) + \Delta A(2)T + \Delta A(3)T^2 + \Delta A(4)T^3 \right] dT \]

\[ = \Delta A(1)(T - 298.15) + \frac{\Delta A(2)}{2}(T^2 - (298.15)^2) \]

\[ + \frac{\Delta A(3)}{3}(T^3 - 298.15^3) + \frac{\Delta A(4)}{4}(T^4 - (298.15)^4) \]

\[ = (36.23)(75) + \frac{1}{2}(-62565)(5.035 \times 10^{-4}) + \frac{1}{3}(6.665 \times 10^{-7})(254^2) \]

\[ + \frac{1}{4}(-5.613 \times 10^{-9})(1.49 \times 10^{10}) \]

\[ = 2717 - 645.7 + 429.8 - 161.2 = 2339 \text{ J} = 2.339 \text{ kJ} \]

\[ \Delta H_{373.15} = \Delta H_{298.15} + 2.34 \Delta T = -285.85 \]

\[ \Delta H_{373.15} = \Delta H_{298.15} + 2.34 \Delta T = -283.5 \text{ kJ} \]
In most cases, $\Delta H$ varies weakly with $T$.

**Dependence of $\Delta H$ on $P$ (T constant)**

$$\Delta H \approx \left( \frac{\partial H}{\partial P} \right)_T \Delta P = \left[ V - T \left( \frac{\partial V}{\partial P} \right)_T \right] \Delta P \approx V \Delta P$$

(from Chapter 3)

Consider changing 1 mole of $H_2O(l)$ at 298.15 K from 1 bar to 2 bar ($V \approx 0.018$ liter/mole)

$$\Delta H = (0.018 \text{ liter/mole}) \left( 10^{-3} \text{ m}^3/\text{l liter} \right) (1 \text{ bar}) \left( 10^5 \text{ Pa/bar} \right) \left( \frac{3}{2} \frac{\text{J}}{\text{mol}} \right) \left( 10^{-3} \text{ m}^3/\text{Pa} \right)$$

$$= 0.0018 \text{ kJ/mole}$$

This is a very small change, considering $\Delta H$ for typical reactions are $\approx 1 \text{ to } 1000 \text{ kJ/mole}$

**Bond Enthalpies**

$$\Delta H = 3 \Delta H_b(N-H)$$

$$\begin{align*}
\text{NH}_3(g) & \rightarrow N(g) + 3H(g) \\
\Delta H_1 & \uparrow \\
\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) & \rightarrow \frac{1}{2} \text{N}_2(g) + 3H(g) \\
\Delta H_2 & \\
\Delta H & = \Delta H_1 + \Delta H_2 + \Delta H_3
\end{align*}$$

$$3\Delta H_b(N-H) = -\Delta H_f^0(\text{NH}_3(g)) + 3\Delta H_f^0(\text{H}_2(g)) + \Delta H_f^0(\text{N}_2(g))$$

$$= -( -45.9 ) + 3( 218 ) + ( 472.7 )$$

$$= 1172.6 \text{ kJ}$$

$$\Delta H_b(N-H) = \frac{1172.6}{3} = +390.9 \frac{\text{kJ}}{\text{mole}}$$
What is $\Delta U_b (NH)$?

$$\frac{1}{3} \text{NH}_3 (g) \rightarrow \frac{1}{3} \text{N}_2 (g) + \frac{1}{3} \text{H}_2 (g)$$

$$\Delta U_b (NH) = \Delta H_b (NH) - \frac{\Delta n}{n} RT$$

$$= 390.9 \Delta T - (8.319)(298.15)/(1000)$$

$$= +388.4 \text{kJ/mole}$$
Criteria for spontaneous processes

This is a very important problem in chemistry since it is related to whether or not specific reactions are feasible.

Examples of spontaneous processes
1) rock rolls down a hill
2) heat flows from hot to cold body
3) many combustion reactions \( \Delta H < 0 \)
4) gas expands when Pop drops
5) ice melts above 0°C \( \Delta H > 0 \)
6) water freezes below 0°C \( \Delta H < 0 \)

Statement of 2nd Law of Thermodynamics:

Spontaneously transferring heat from a cold body to a hot body without doing work is impossible.
For any cycle that returns a system to its starting point

\[ \Delta U = 0, \text{ but } q \neq w \neq 0 \]

**Schematic of a general engine**

\[ T_h \quad \text{hot reservoir} \]

\[ q_h > 0 \]

\[ T_c \quad \text{cold reservoir} \]

\[ q_e \]

\[ w < 0 \]

\[ q_h = \text{heat absorbed by engine from hot reservoir} \ (> 0) \]

\[ w = \text{work done on engine} \ (< 0) \]

\[ q_e = \text{heat absorbed by engine from cold reservoir} \ (< 0) \]

\[ \Delta U = 0 = q_h + q_e + w \]

\[ \text{Efficiency} = e = -\frac{w}{q_h} = \frac{q_h}{q_h} \]
1) Expand isothermally: \((P_1, V_1, T_h) \rightarrow (P_2, V_2, T_h)\)
2) Expand adiabatically: \((P_2, V_2, T_h) \rightarrow (P_3, V_3, T_c)\)
3) Compress isothermally: \((P_3, V_3, T_c) \rightarrow (P_4, V_4, T_c)\)
4) Compress adiabatically: \((P_4, V_4, T_c) \rightarrow (P_1, V_1, T_h)\)

How efficient is this engine?
1) **Reversible Isothermal Expansion**
\[
\begin{align*}
\Delta U_1 &= 0; \quad \omega_1 = -nRT \ln \left( \frac{V_2}{V_1} \right); \quad \varphi_1 = -\omega_1 = +nRT \ln \frac{V_2}{V_1}
\end{align*}
\]

2) **Adiabatic Reversible Expansion**
\[
\begin{align*}
\Delta U_2 &= -nC_v(T_h - T_c); \quad \omega_2 = \Delta U_2 = -nC_v(T_h - T_c); \quad \varphi_2 = 0
\end{align*}
\]

3) **Reversible Isothermal Compression**
\[
\begin{align*}
\Delta U_3 &= 0; \quad \omega_3 = -nRT \ln \left( \frac{V_4}{V_3} \right); \quad \varphi_3 = \omega_3 = -nRT \ln \left( \frac{V_3}{V_4} \right)
\end{align*}
\]

4) **Adiabatic Reversible Compression**
\[
\begin{align*}
\Delta U_4 &= +nC_v(T_h - T_c); \quad \omega_4 = \Delta U_4 = nC_v(T_h - T_c); \quad \varphi_4 = 0
\end{align*}
\]
\[
\Delta U_{total} = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 = 0
\]
\[
W_{total} = W_1 + W_2 + W_3 + W_4
\]
\[
= -nRT_h \ln \left( \frac{V_2}{V_1} \right) + nRT_c \ln \left( \frac{V_3}{V_4} \right)
\]
For an adiabatic process

\[
PV^\gamma = \text{constant}
\]

\[
TV^{\gamma-1} = \text{constant}
\]

\[
T_c V_3^{\gamma-1} = T_h V_2^{\gamma-1} \quad \text{(step 2)}
\]

\[
T_h V_1^{\gamma-1} = T_c V_4^{\gamma-1} \quad \text{(step 4)}
\]

\[
\frac{T_h V_2^{\gamma-1}}{T_h V_1^{\gamma-1}} = \frac{T_c V_3^{\gamma-1}}{T_c V_4^{\gamma-1}}
\]

\[
\frac{V_2}{V_1} = \frac{V_3}{V_4}
\]

\[
W_{Tot} = -nR(T_h - T_c) \ln\left(\frac{V_2}{V_1}\right)
\]

\[
\frac{\gamma_h}{\gamma} = nRT_h \ln\left(\frac{V_2}{V_1}\right)
\]

\[
e = \frac{W}{\gamma_h} = \frac{nR(T_h - T_c) \ln\left(\frac{V_2}{V_1}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)}
\]

\[
e = 1 - \frac{T_c}{T_h}
\]

Examples: \(T_h = 100^\circ C, \ T_c = 0^\circ C\)

Remember we need to use \(T\) in Kelvin (because the analysis of the Carnot engine was in Kelvin).

\[
e = 1 - \frac{273.15}{373.15} = .268 \approx 26.8\%
\]
Problem: Can we find a "superengine" that is more efficient than a reversible Carnot engine? Use our "superengine", with $e' > e$, to drive a reversible Carnot engine in reverse.

By assumption $e' > e$

$$-\frac{w'}{q_h} > -\frac{w}{q_h}$$

$$\frac{w}{q_h} > \frac{w'}{q_h} \leq 0 \text{ (all are } > 0)$$

$$\frac{1}{q_h} > \frac{1}{q_h'}$$

or $|q_h| > q_h'$ (also, $q_c > |q_c'|$)

Conclusion:

More heat is returned to hot reservoir than is drawn out. We are moving heat from cold to hot reservoir without doing net work. This violates 2nd Law!
In general, \( e' \leq e \)

For reversible cycles

\[
e_{\text{rev}} = 1 + \frac{e_c}{e_h} = 1 - \frac{T_c}{T_h}
\]

\[
\frac{e_c}{e_h} = -\frac{T_c}{T_h}
\]

or

\[
\frac{e_c}{T_c} + \frac{e_h}{T_h} = 0
\]

For an arbitrary cycle, it is always possible to find a reversible Carnot path

\[
0 = \sum \frac{e_i}{T_i} = \oint \frac{d\varphi}{\varphi}
\]

The quantity \( \frac{d\varphi}{\varphi} \) is a state function and is called "entropy."

\[
ds = \frac{d\varphi}{\varphi}
\]

Since \( S \) is a state function, it is path independent.

**Example 1) Reversible Isothermal Expansion (Ideal Gas)**

\[
\Delta S_{\text{sys}} = \int_{V_i}^{V_f} \frac{d\varphi}{T} = \frac{e_{\text{rev}}}{T} = -\omega_{\text{rev}} = +nRT\ln\frac{V_f}{V_i}
\]
For the surroundings, \( \mathcal{F}_{\text{surr}} = -\mathcal{F}_{\text{rev}} \)

\[
\Delta S_{\text{surr}} = -\frac{\mathcal{Q}_{\text{rev}}}{T} = -nR \ln \left( \frac{V_F}{V_i} \right) = -\Delta S_{\text{sys}}
\]

Thus, the total entropy change

\[
\Delta S_{\text{Tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0
\]

Suppose we have 1 mole and \( \frac{V_F}{V_i} = 2 \)

at \( T = 298 \text{ K} \)

\( \mathcal{F}_{\text{rev}} = 1718 \text{ Joule} \)

\[
\Delta S_{\text{sys}} = \frac{\mathcal{Q}_{\text{rev}}}{T} = +5.76 \text{ J/K}
\]

\[
\Delta S_{\text{surr}} = -5.76 \text{ J/K}
\]

**Example 2)** Suppose we have an irreversible isothermal expansion

\[
\mathcal{F}_{\text{irr}} < \mathcal{F}_{\text{rev}} \text{ (suppose } \mathcal{F}_{\text{irr}} = 1000 \text{ J)}
\]

For surroundings, we have withdrawn 1000 J of heat, so

\[
\Delta S_{\text{surr}} = -\frac{1000}{298} = -3.36 \text{ J/K}
\]

For the system we must have \( \Delta S_{\text{sys}} = +5.76 \) (Why?)

\[
\Delta S_{\text{Tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 5.76 - 3.36 = +2.4 \text{ J/K}
\]
Alternate Statement of 2nd Law

$$\Delta S_{\text{Tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

Entropy changes can be determined for systems by finding a reversible path and computing $\int p \, dv$. Entropy change of Ideal Gas

$$(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)$$

I) Expand/Compress isothermally

$$\Delta S_i = nR \ln \left(\frac{V_2}{V_1}\right)$$

II) Heat at constant $V$

$$\Delta S_{\text{II}} = \int_{T_1}^{T_2} \frac{q_{\text{rev}}}{T} \, dT = \int_{T_1}^{T_2} \frac{nC_V}{T} \, dT = nC_V \ln \left(\frac{T_2}{T_1}\right)$$

$$\Delta S_{\text{Tot}} = nR \ln \left(\frac{V_2}{V_1}\right) + nC_V \ln \left(\frac{T_2}{T_1}\right)$$

Heating/Cooling Material at constant $P$ (no phases transition)

$$\text{1 bar} \begin{array}{c|c} 20^\circ \text{C} \rightarrow 60^\circ \text{C} \\ \hline \text{H}_2\text{O} \end{array}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{q_{\text{rev}}}{T} \, dT = \int_{T_1}^{T_2} \frac{nC_p}{T} \, dT \approx nC_p \ln \left(\frac{T_2}{T_1}\right)$$

valid if $C_p$ is constant
\[ \Delta S_{\text{Total}} = \Delta S_{\text{left}} + \Delta S_{\text{right}} = C_p \ln \left( \frac{313.15}{293.15} \right) + C_p \ln \left( \frac{313.15}{333.15} \right) \\
= 75.31 \left( 0.066 - 0.0619 \right) \\
= +.308 \frac{J}{K} \]

**Phase Transitions (P = constant)**

\[ \Delta S = \frac{\Delta H}{T} = \frac{\Delta H_{A \rightarrow B}}{T_{\text{phase trans.}}} \]

For many liquids \( \Delta S_v = 88 \frac{J}{\text{mole K}} \)  

*(Trouton's Rule)*

We can estimate \( \Delta H_{vap} \) if \( T_b \) is known.

**Entropy of Mixing (Ideal Gases)**

\[
\begin{align*}
\text{n}_1, V_1, P, T & \quad \rightarrow \quad \text{n}_2, V_2, P, T \\
& \quad \rightarrow \quad \frac{V = V_1 + V_2}{P_i} = \frac{n_1 + n_2}{n_1} \\
& \quad \rightarrow \quad \frac{P_i}{n_1 P_1} = \frac{n_2}{n_2 \text{ mole K}} \]
\]

(Note: This is an ideal gas equation)

allow each species to expand reversibly and isothermally

\[ \Delta S_i = n_i R \ln \left( \frac{V_i + V_2}{V_i} \right) = n_i R \ln \left( \frac{n_i + n_2}{n_i} \right) \\
= n_i R \ln \left( \frac{1}{x_i} \right) = - n_i R \ln x_i, \quad \text{where} \ x_i = \text{fraction of} \ n_i. \]
\[ \Delta S_L = -n_L R \ln x_2 \]
\[ \Delta S_{\text{Total}} = -n_1 R \ln x_1 - n_2 R \ln x_2 \]
\[ = -n R \left( x_1 \ln x_1 + x_2 \ln x_2 \right) \]

Suppose \( x_1 = x_2 = \frac{1}{2} \) \( \Rightarrow n = 1 \text{ mole} \)

\[ \Delta S_{\text{Total}} = -R \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = R \ln 2 \geq 0 \]

---

**General Processes**

Following procedures of Chapter 3 (Sections 5.12 & 5.13)

\[ dS = \frac{C_v}{T} dT + \frac{\beta}{x} dV \]

\( \beta = \frac{1}{V} \left( \frac{\partial U}{\partial T} \right)_p \)

\( x = -\frac{1}{V} \left( \frac{\partial U}{\partial P} \right)_T \)

If \( \beta \) and \( x \) don't change with \( T \)

\[ \Delta S = \int_{T_i}^{T_f} \frac{C_v}{T} dT + \frac{\beta}{x} (V_f - V_i) \]

Alternatively, (if pressure changes)

\[ dS = \frac{C_p}{T} dT - \beta dP \]

\[ \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \beta \int_{P_i}^{P_f} V dP \]
Problem:

1 mole of ice, initially at 0°C and 1 atm pressure is 1) first melted 2) heated to 25°C at 1 atm, 3) compressed at 25°C from 1 to 1000 atm. What are $\Delta S_1$, $\Delta S_2$, $\Delta S_3$ given

$\Delta H_{\text{fus}} = 6.01 \text{ kJ/mole}$

$C_p = 75.25 \text{ J/mole K}$

$\beta = 2.04 \times 10^{-4} \text{ 1/K}$

$V = 0.018 \text{ litre/mole}$

$\Delta S_1 = \frac{\Delta H_{\text{fus}}}{T_{\text{melt}}} = \frac{6010 \text{ J/mole}}{273.15} = 22.0 \frac{\text{ J}}{\text{ mole K}}$

$\Delta S_2 = \int \frac{C_p dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right) = 6.59 \frac{\text{ J}}{\text{ mole K}}$

$\Delta S_3 = -\beta V (p_f - p_i) = -(2.04 \times 10^{-4} \text{ 1/K})(18 \times 10^{-6} \frac{\text{ m}^3}{\text{ mole}})$

$\Sigma_n (999 \text{ atm}) \times (1.013 \times 10^5 \frac{\text{ Pa}}{\text{ atm}}) (\frac{\text{ J}}{\text{ Pa}}) = -0.37 \frac{\text{ J}}{\text{ mole K}}$

Note that $|\Delta S_3| \ll |\Delta S_1|$ or $|\Delta S_2|$. For an (incompressible) liquid or solid, $S$ depends weakly on $P$. 
Absolute Entropies (only consider $P = 1$ bar)

3rd Law of Thermodynamics
- The entropy of a pure (perfectly crystalline) material at $0 \, K$ is 0 (molar entropy)

$$S_m (T) = \int_0^{T_1} \frac{C_p}{T} \, dT + \frac{\Delta H_1}{T_1} + \int_{T_1}^{T_2} \frac{C_p}{T} \, dT$$

$$+ \frac{\Delta H_2}{T_2} + \ldots$$

where $\Delta H_1, \Delta H_2$ are enthalpy changes at phase transitions (see Figs. 5-9, 11-10)

Standard molar entropies

$$S_m^0 = \int_0^{T_1} \frac{C_p}{T} \, dT + \frac{\Delta H_1}{T_1} + \ldots \text{ up to } 298.15 \, K$$

Tabulated in Table 4.1 for many substances

Low Temperatures

$$C_p \approx a T^3 \quad a T^3$$

$$S_m (T) = \int_0^{T} \frac{C_p}{T} \, dT = a \int_0^{T} T^2 \, dT = \frac{1}{3} a T^3$$
Free Energy (Gibbs, Helmholtz)

We have a criteria for spontaneous processes

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

Disadvantage: You need to consider changes in both system and surroundings. This is inconvenient.

Experiments with $T_{final} = T_{initial}$

Reactions may heat up, but above conditions may prevail eventually.

$$\frac{dQ_{rev}}{T} - \frac{dQ_{irrev}}{T} > 0$$

$$\frac{dQ_{rev}}{dS_{sys}} \geq \frac{dQ_{irrev}}{dS_{surr}}$$

Go back to 1st law & consider small change

$$dU = dQ + dW$$

$$dQ = dU - dW$$

but

$$dQ \leq TdS$$
Consequently, \( TdS \geq dU - dW \) for \( T \) is constant.

\[ dW \geq dU - TdS = dU - d(A) = dA \]

where \( A = U - TS \) (Helmholtz Free Energy).

Change in \( A \) is always less than the work done on the system. If no work is done \((U = \text{constant})\)

\[ dA \leq 0 \quad (V\&T\ \text{constant}) \]

For a process at constant \( V\&T \), \( dA < 0 \) for any spontaneous process irrespective of the surroundings.

Suppose \( AA = -10 \text{kJ} \)

Conclusions:
1) process is spontaneous
2) from condition \( dW \geq dA = -10 \text{kJ} \)

We can, at most, get 10 kJ of work out of the process. (We might only get 9.6, 6, or no useful work out of it.)
Examples of Work

1) P-V expansion
\[ dW = -P \, dV \]

2) electrochemical work
(move charge, dq, through a voltage drop, \( E \))
\[ dW = -E \, dq \]

3) stretching a rubber band (\( k \) = force constant, \( dl \) = change in length)
\[ dW = -k \, dl \]

In general
\[ dW = -P \, dV + dW_{\text{other}} \]

Processes at constant \( P \), \( V \), \( T \)

\[ dA \leq dW = -P \, dV + dW_{\text{other}} \]
\[ d(U-TS) \leq -d(PV) + dW_{\text{other}} \]
\[ d(U+PV-TS) = d(H-TS) \leq dW_{\text{other}} \]

\[ G = H-TS \quad \text{(Gibbs Free Energy)} \]

\[ dG \leq dW_{\text{other}} \]

For a spontaneous process at constant \( P \), \( V \), \( T \), we should be able to harness that process to

1) move charge \( ( \text{battery} ) \)
2) lift objects \( ( \text{water wheel} ) \)

etc.
Even if $\Delta w_{other} = 0$ (we don't "harness" the process) we must have

$$\Delta G \leq 0 \quad \text{(spontaneous process, } T \neq P \text{ const.)}$$

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

Summarize possible situations

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>conditions for $\Delta G &lt; 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>all $T$ (combustion)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>low $T$ (condensation, freezing, polymerization)</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>high $T$ (melting, boiling) never!</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>(graphite $\rightarrow$ diamond)</td>
</tr>
</tbody>
</table>

**Differential Forms**

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

but

$$dU = TdS - PdV$$

so

$$dA = -SdT - PdV$$

We can also view $A$ as a function of $(U,T)$,

$$dA = \left( \frac{\partial A}{\partial T} \right)_U dT + \left( \frac{\partial A}{\partial V} \right)_T dV$$

comparing \( \left( \frac{\partial A}{\partial V} \right)_T = -P \) and \( \left( \frac{\partial A}{\partial T} \right)_V = -S \)
Problem: One mole of an ideal gas expands from $V_1$ to $V_2$ at constant $T$. What is $\Delta A$? 

\[
(\frac{\partial A}{\partial V})_T = -P \implies \Delta A = -P dV = -\frac{RT}{V} dV
\]

\[
\Delta A = -RT \int_{V_1}^{V_2} \frac{dV}{V} = -RT \ln \left( \frac{V_2}{V_1} \right)
\]

For Gibbs Free energy

\[
dG = -SdT + VdP
\]

\[
(\frac{\partial G}{\partial P})_T = +V; \quad (\frac{\partial G}{\partial T})_P = -S
\]

"VAT - VUSH" - Diagram - a useful way to remember these relationships.

\[
(\frac{\partial U}{\partial S})_V = +T; \quad (\frac{\partial G}{\partial T})_P = -S; \quad \text{etc.}
\]
Problem: What is $\Delta G$ of one mole of $H_2O(l)$ on raising $P$ from 1 to 100 atm at constant $T$ (298 K). $V_{H_2O} = 18 \text{ mL}$ and assume $H_2O(l)$ is incompressible.

\[
\left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow \Delta G = VdP \quad (T \text{ const})
\]

\[
\Delta G = V(P_f - P_i) = (18 \times 10^{-3} \text{ m}^3)(99 \text{ atm})(1.013 \times 10^5 \frac{\text{ Pa}}{\text{ atm}})
\]

= 180.5 Joules

Problem: What is $\Delta G$ of one mole of $N_2(g)$ on raising $P$ from 1 to 100 atm. Assume ideal gas behavior at $T = 298 K$

\[
dG = VdP = \frac{RT}{P}dP
\]

\[
\Delta G = RT \ln \left(\frac{P_f}{P_i}\right) = (8.314 \frac{\text{ J}}{\text{ mole} \cdot \text{ K}}) \ln (100)
\]

= 11,420 Joules

$\Delta G$ varies much more strongly with pressure for gases than solids and liquids. For a mole

\[
dG \approx VdP \quad (T \text{ const})
\]

much larger for gases
Chemical Equilibrium

Start with ideal gases at constant $T$

\[ dG = \frac{nRT}{P} \, dP \]

\[ G - G_0 = nRT \ln \frac{P}{P_0} \]

Choose $P_0 = 1$ bar (standard state pressure)

Free energy at a partial pressure of 1 bar:

\[ G = G_0 + nRT \ln P \]

Now $G$ is an extensive variable, which means it is proportional to amount.

Define chemical potential

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, \text{other species}} \]

For now, consider a single species and hold $T$ constant

\[ G = \gamma n \quad \text{free energy/mole, } G_m \]

\[ \gamma = M_0 + RT \ln P \quad \text{partial pressures} \]

\[ G_m = G^0 + RT \ln P \]
Standard State Free Energies

$G_m^0 = H_m^0 - TS_m^0 = \Delta H_f^0 - TS_m^0$

$G_m^0 (el) = -TS_m^0 (el)$  (for element in its stable form at STP)

Consider free energies of formation, $\Delta G_f^0$

Elements in stable form $\rightarrow$ product

$$\Delta G_f^0 = G_m^0 (product) - \sum_{i} n_i G_{m_i}^0 (el)$$

$$= \Delta H_f^0 (p2k) - TS_m^0 (p2k) + T \sum_{i} n_i S_{m_i}^0 (el)$$

stoichiometry

Consider $NH_3(g)$

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightarrow NH_3(g)$$

$$\Delta G_f^0(NH_3(g)) = \Delta H_f^0(NH_3(g)) - TS_m^0(NH_3(g))$$

$$+ T \left[ \frac{1}{2} S_m^0(N_2(g)) + \frac{3}{2} S_m^0(H_2(g)) \right]$$

The $\Delta H_f$ and $S_m^0$ are tabulated in Table 4.1

$\left( T = 298.15 K \right)$

$$\Delta G_f^0(NH_3(g)) = -45.9 \frac{kJ}{mole} - 298.15 \left[ 192.8 - \frac{1}{2} (191.6) - \frac{3}{2} (130.2) \right]$$

$$\text{(in } J/mole \text{ K})$$

$$= -45.9 \frac{kJ}{mole} + 29.53 \frac{kj}{mole}$$

$$= -16.37 \frac{kJ}{mole}$$
Consider the reaction

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

At equilibrium, we will have a mixture of N\(_2\), H\(_2\), and NH\(_3\) present.

**Case 1**  Start with 1 mole of N\(_2\), 3 moles of H\(_2\), and no NH\(_3\). Reaction proceeds spontaneously as drawn.

\[ \Delta G < 0 \quad \text{(for reaction as drawn)} \]

**Case 2**  Start with 2 moles NH\(_3\) and no N\(_2\) or H\(_2\). Reaction proceeds **backward** to form N\(_2\) and H\(_2\).

\[ \Delta G > 0 \quad \text{(for reaction as drawn)} \]

\[
\begin{align*}
&\text{Case 1} \\
&\text{Case 2} \\
&\Delta G^0 = -33.26
\end{align*}
\]
\[ \Delta G^0 = \text{free energy change of taking one mole of} \]
\[ \text{N}_2 \text{ at } P_0 = 1 \text{ bar and 3 moles of H}_2 \text{ at} \]
\[ P_0 = 1 \text{ bar and convert it to 2 moles} \]
\[ \text{of H}_3(\text{g}) \text{ at } P_{\text{H}_3} = 1 \text{ bar. All at } 25^\circ \text{C.} \]

Suppose we have conditions different from these.

\[ G_{\text{NH}_3} = n_{\text{NH}_3} \mu_{\text{NH}_3} = n_{\text{NH}_3} (\mu_{\text{NH}_3}^0 + R T \ln \frac{P_{\text{NH}_3}}{P_{\text{H}_3}}) \]
\[ G_{\text{N}_2} = n_{\text{N}_2} \mu_{\text{N}_2} = n_{\text{N}_2} (\mu_{\text{N}_2}^0 + R T \ln \frac{P_{\text{N}_2}}{P_{\text{H}_3}}) \]
\[ G_{\text{H}_2} = n_{\text{H}_2} \mu_{\text{H}_2} = n_{\text{H}_2} (\mu_{\text{H}_2}^0 + R T \ln \frac{P_{\text{H}_2}}{P_{\text{H}_3}}) \]
\[ G_{\text{Total}} = G_{\text{NH}_3} + G_{\text{N}_2} + G_{\text{H}_2} \]

Now consider a small change.

Suppose (\( x \) is a small amount)

\[ \# \text{ moles NH}_3 \text{ changes by } +2x \]
\[ \text{ i } \quad \text{N}_2 \quad \text{ii } - x \]
\[ \text{ i } \quad \text{H}_2 \quad \text{ii } - 3x \]

\[ \Delta G = 2x \mu_{\text{NH}_3} - x \mu_{\text{N}_2} - 3x \mu_{\text{H}_2} \]
\[ = x \left[ 2 \mu_{\text{NH}_3}^0 - \mu_{\text{N}_2}^0 - 3 \mu_{\text{H}_2}^0 + 2 R T \ln \frac{P_{\text{NH}_3}}{P_{\text{H}_3}} - R T \ln \frac{P_{\text{N}_2}}{P_{\text{H}_3}} \right. \]
\[ \quad \left. - 3 R T \ln \frac{P_{\text{H}_2}}{P_{\text{H}_3}} \right] \]
\[ = x \left[ \Delta G^0 + R T \ln \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^2} + R T \ln \frac{P_{\text{NH}_3}}{P_{\text{H}_2}} \right. \]
\[ \quad \left. + R T \ln \left( \frac{P_{\text{N}_2}^2}{P_{\text{H}_2}^3} \right) \right] \]
\[ = x \left[ \Delta G^0 + R T \ln \left( \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^2 P_{\text{H}_2}} \right) \right] = x \left[ \Delta G^0 + R T \ln \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^2 P_{\text{H}_2}} \right] \]

Call this \( K \)
If our p's are at the equilibrium partial pressures, \( \Delta G \) should be at a minimum.

\[
\Delta G = 0
\]

Consequently, \( \Delta G^0 + RT \ln K_p = 0 \)

\[
\Delta G^0 = -RT \ln K_p \\
K_p = \left( \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}} \right)
\]

If \( \Delta G^0 = -33.26 \text{ kJ/mol} \), \( T = 298.15 \text{ K} \)

\[
K_p = e^{-\Delta G^0/RT} = 6.71 \times 10^5
\]

**Problem:** \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)

Initially, we have one mole of \( \text{N}_2 \) and one mole of \( \text{H}_2 \) at 298.15 K subject to a constant pressure \( P_{\text{tot}} \) of 1 atm. A catalyst is added and \( \text{NH}_3(g) \) is formed. What is the equilibrium partial pressures of \( \text{N}_2, \text{H}_2, \text{NH}_3 \). (x = moles of \( \text{N}_2 \) used up)

Limiting reagent (y = " " \( \text{H}_2 \) at eq.)

<table>
<thead>
<tr>
<th>initial moles</th>
<th>( \text{N}_2 )</th>
<th>( \text{H}_2 )</th>
<th>( \text{NH}_3 )</th>
<th>total moles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{final moles:} & \\
1-x & 1-3x & 2x & 2-2x \\
\text{mole fraction:} & \\
\frac{1}{2} & \frac{3}{4}y & \frac{1}{2} & \frac{4}{3}y \\
\text{partial P:} & \\
\frac{1}{2} & \frac{3}{4}y & \frac{1}{2} &
\end{align*}
\]

We expect almost all \( \text{H}_2 \) to be used up. Let \( 1-3x = y \)
\[ K_p = 6.71 \times 10^5 \times \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(1/2)^2}{(1/2)(3/4)^3} = \frac{1.19}{y^3} \]

\[ y^3 = \frac{1.19}{6.71 \times 10^5} = 1.77 \times 10^{-6} \]

\[ y = 1.21 \times 10^{-2} \]

From table on previous page

\[ P_{NH_3} \times 3y = 0.908 \text{ atm} \]

\[ P_{N_2} \times 0.5 \]

\[ P_{H_2} \times 0.5 \]

Other Standard States

Choosing a standard state as 1 bar pressure is arbitrary. Going back to the original (ideal gas) expression

\[ y = \mu_{ref} + RT \ln \frac{P}{P_{ref}} \Rightarrow \mu = \mu^0 + RT \ln P \]

where the last equality occurs when \( P_{ref} = 1 \text{ bar} \).

Suppose it is more convenient to work in concentration units of moles/liter

\[ P = \frac{n}{V}RT = cRT \quad (c \text{ in } \text{mole/liter}) \]

If we chose our standard state as \( \frac{1}{1} \text{ mole} \)

\[ \mu = \mu^0 + RT \ln \frac{cRT}{\mu_{ref}RT} = \mu^0 + RT \ln c \]
For the reaction

\[ aA + bB \rightarrow yY + zZ \]

\[ K_P = \frac{P_Y^y P_Z^z}{P_A^a P_B^b} \quad \Delta G^0 = -RT \ln K_P \]

\[ K_e = \frac{c_Y^y c_Z^z}{c_A^a c_B^b} \quad \Delta G^0_e = -RT \ln K_e \]

Since \( P = (\frac{n}{V})RT = cRT \), it is straightforward to show

\[ K_P = K_e (RT)^{(y+z)-(a+b)} \]

In general, we can write (ideal gases)

\[ \Delta G^0 = -RT \ln \left( \frac{X_Y^y X_Z^z}{X_A^a X_B^b} \right); \quad x = \frac{\text{equilibrium conc.}}{\text{standard state conc.}} \]

**Solutions**

We really are not ready to talk about solutions since molecule-molecule interactions are much stronger in solution than in gases. However, if the solutions are "ideal" (which basically means molecule molecule interaction are comparable on reactant & product sides of an overall reaction.)

\[ \Delta G^0 = -RT \ln \left( \frac{X_Y^y X_Z^z}{X_A^a X_B^b} \right) \quad \text{"ideal" solutions} \]

X could be moles/liter, moles/kg solvent, etc.
**Heterogeneous Equilibrium**

\[ C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g) \]  

(concentration) \[ C_{CH_2} < C_{CH_4} \]

Consider \( \Delta G \) for converting \( x \) moles of C(graphite), 2\( x \) moles of \( H_2 \), into \( x \) moles of \( CH_4 \).

\[
\Delta G = xM_{CH_4} - xM_C - 2xM_{H_2} = x \left[ (M_{CH_4}^0 - 2M_{H_2}^0 - M_C) + RT \ln \left( \frac{C_{CH_4}}{C_{H_2}} \right) \right]
\]

Now for a solid or pure liquid

\[
\left( \frac{\partial G}{\partial P} \right)_T = V_m \ll V_{gas}
\]

Thus, \( M_C \) won't change much in the "graphite reaction."

\[
\Delta G^0 = M_{CH_4}^0 - 2M_{H_2}^0 - M_C
\]

At equilibrium, \( \Delta G = 0 \) so

\[
\Delta G^0 = -RT \ln \left( \frac{C_{CH_4}}{C_{H_2}} \right)_{eq}
\]

This explains why solids, or pure liquids, don't enter equilibrium constant calculations.
**Aqueous Reactions**

\[ \text{reactants} + H_2O \rightarrow \text{products} + H_2O \]

Even though \( H_2O \) may be consumed or produced in the reaction, the chemical potential of \( H_2O \) usually doesn't change since \( [H_2O] \approx 55 \text{ mol/L} \). Consequently:

\[ K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} \]

with \( H_2O \) left out.
Temperature Dependence of $K_{eq}$

(Gibbs-Helmholtz Eqn.)

\[
\left( \frac{\partial G}{\partial T} \right)_p = -S
\]

since $G = H - TS$, $S = \frac{H - G}{T}$

Consider using "product rule" $\frac{d}{dx}(fg) = f \frac{dg}{dx} + g \frac{df}{dx}$

\[
\left( \frac{\partial (G/T)}{\partial T} \right)_p = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_p + G \left( \frac{\partial 1/T}{\partial T} \right)_p = -\frac{S}{T} - \frac{G}{T^2}
\]

\[
= \frac{G - H}{T^2} - \frac{G}{T^2} = -\frac{H}{T^2}
\]

It follows that $\Delta G^o = -RT \ln K_{eq}$

\[
\left( \frac{\partial (G^o/T)}{\partial T} \right)_p = -R \left( \frac{\partial \ln K_{eq}}{\partial T} \right)_p = -\frac{\Delta H^o}{T^2}
\]

\[
\left( \frac{\partial \ln K_{eq}}{\partial T} \right)_p = \frac{\Delta H^o}{RT^2}
\]

(Gibbs-Helmholtz Eqn.)

If $\Delta H^o$ is independent of $T$

$$\ln K_{eq}(T) - \ln K_{eq}(T_0)$$

$$= \int_{T_0}^{T} \frac{\Delta H^o}{RT^2} dT - \frac{\Delta H^o}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

\[
\text{slope} = \frac{\Delta H^o}{R}
\]
Also,

\[ \ln K_c^0 (T) = -\frac{\Delta G^0 (T)}{RT} = -\frac{1}{RT} (\Delta H^0 - T \Delta S^0) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]

\[ \ln K_c^0 (T) = \ln K_c^0 (T_0) + \frac{\Delta H^0}{RT} \left( \frac{T}{T_0} - 1 \right) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT_0} \]

\[ \frac{\Delta S^0}{R} = \ln K_c^0 (T_0) + \frac{\Delta H^0}{RT_0} \]

Example: \[ I_2 (g) + C_5 H_{10} (g) \rightarrow 2 HI (g) + C_5 H_{10}^+ \]

\[ \log_{10} K_p = 7.55 - \frac{4244}{T} \quad \text{(From exp.)} \]

What is \( K_p, \Delta H^0, \Delta G^0, \Delta S^0 \) at 400°C?

b) \[ \log_{10} K_p (400) = 7.55 - \frac{4244}{673} = -3.54 \quad \Rightarrow \quad K_p (400) = 2.259 \]

c) \[ \Delta G^0 = -RT \ln K_p = (8.315 \, \text{J/K mol}) (673) \ln (2.259) = -4.562 \, \text{kJ} \]

To determine \( \Delta H^0 \), begin with \( \frac{\Delta S^0}{R} \): this is \( -\frac{\Delta H^0}{R} \)

\[ \ln K_p = 2.303 \log_{10} K_p = 17.388 - \frac{11.156}{T} \]

c) \[ \Delta H^0 = -R \left( -11.156 \right) = +92.76 \, \text{kJ/mol} \]

d) \[ \Delta S^0 = R \left( 17.388 \right) = 144.58 \, \text{J/mol K} \]
Pressure dependence of \( K_{eq} \)

\[
\left( \frac{\partial G}{\partial P} \right)_T = V \\
\left( \frac{\partial A^0}{\partial P} \right)_T = \Delta V^0 \\
\left( \frac{\partial \ln K_{eq}}{\partial P} \right)_T = -\frac{\Delta V^0}{RT} \\
d \ln K_{eq} = -\frac{\Delta V^0}{RT} dP \quad (T = \text{const})
\]

For solid or liquid reactions,
\( \Delta V^0 \approx 0 \)

\( K_{eq} \) indep. of \( P \) (or nearly so)

For gas reactions,

\[
I_2(g) + C_5H_{10}(g) \rightarrow 2HI(g) + C_5H_7(g)
\]

\( \Delta V^0 \approx \frac{\partial NRT}{P} = \frac{RT}{P} \) (above example)

For general gas reactions (assuming ideal behavior)

\[
d \ln K_{eq} = -\frac{\partial NRT}{P} \frac{dP}{RT} = -\frac{\partial N}{P}
\]

\[
\ln \frac{K_{eq}(P_2)}{K_{eq}(P_1)} = -\ln \frac{P_2}{P_1}
\]
Real Gases

Compressibility \( Z = \frac{V}{V_{\text{ideal}}} = \frac{PV}{nRT} = \frac{PV_m}{RT} \)

For an ideal gas \( Z = 1 \)

Deviations from 1 \( z < 1 \) attraction occur because of intermolecular interactions \( z > 1 \) repulsion

Virial Expansion \( Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \ldots \)

Models of Real Gases

There have been many models formulated.

We shall only examine the Van der Waals model.

attraction \( P + \frac{an^2}{V^2} \) repulsion \( (V-nb) = nRT \)

\( (P + \frac{a}{nV_m^2})(V_m-b) = RT \)

Tabulated in Table 7-4
Multiply the last expression by $\frac{V_m}{RT(V_m-b)}$

\[
\frac{(P + \frac{a}{V_m})V_m}{RT} = \frac{V_m}{V_m-b} \quad \text{divide numerator and denominator by } V_m
\]

\[
\frac{PV_m}{RT} + \frac{a}{RTV_m} = \frac{V_m}{V_m-b} = \frac{1}{1-b/V_m}
\]

Now $b/V_m$ is usually very small.

Since ($x<<1$)

\[
\frac{1}{1-x} \approx 1 + x + x^2 \ldots \quad \text{arithmetic series}
\]

\[
Z + \frac{a}{RTV_m} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} \quad \text{this is } C(T)
\]

\[
Z = 1 + \left( b - \frac{a}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} \quad \text{this is } B(T)
\]

$B(T) =$ second virial coefficient $= b - \frac{a}{RT}$

$C(T) =$ third " " " $= b^2$

At sufficiently low $P$ (large $V_m$), only the leading 2 terms ($Z = 1 + B(T)/V_m$) are significant.

$B(T) = b - \frac{a}{RT}$

\[
\begin{align*}
Z & \quad \text{high } T \quad B(T) > 0 \\
& \quad \text{low } T \quad B(T) < 0
\end{align*}
\]

$T_b$ (Boyle temperature)
At the Boyle temperature

\[ 0 - \frac{a}{RT_b} = 0 \Rightarrow T_b = \frac{a}{Rb} \]

Problem. For H_2O, \( a = 5.537 \text{ dm}^3 \text{ bar/mol}^2 \), \( b = 0.305 \text{ dm}^3/\text{ mole} \).

What is \( T_b \) for H_2O?

\[ T_b = \frac{5.537 \text{ dm}^3 \text{ bar/mol}^2}{(0.083145 \text{ dm}^3 \text{ bar/molK})(0.305 \text{ dm}^3/\text{ mole})} \]

\[ = 2180 \text{ K} \]

In the VDW Equation, \( a \) and \( b \) depend on the particular gas. Can the VDW Equation be written in a way that is independent of molecular parameters?

**PV relations (T = constant)**

Take one mole of steam at 380 K initially at 1 bar pressure. At some pressure \( P^* \) (holding \( T \) constant), the steam liquifies & \( V_m \) drops dramatically. The water remains liquid as \( P \) increases further.
Repeat this process at successively higher $T$. As $T$ increases, the difference between $V_m$ (gas) and $V_m$ (lilq) decreases and at the Critical Point, vanishes.

All materials have a unique critical point characterized by specific $T_c$, $P_c$, and $V_c$.

At critical point \[ \left( \frac{\partial P}{\partial V} \right)_{T_c} = 0; \quad \left( \frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0 \]

From VDW equation, can show

\[ a = 3P_c V_c^2 \quad P_c = \frac{a}{27b^2} \]
\[ b = \frac{1}{3}V_c \quad \text{conversely} \quad V_c = 3b \]
\[ R = \frac{8P_c V_c}{3T_c} \quad T_c = \frac{8a}{27bR} \]

Substituting these back into VDW Eqn.

\[ (P_r + \frac{3}{V_r^2})(V_r - \frac{1}{3}) = \frac{8}{3} T_r \]

where \[ P_r = \frac{P}{P_c}, \quad V_r = \frac{V}{V_c}, \quad T_r = \frac{T}{T_c} \]

All gases are predicted to obey the same law "Law of Corresponding States" (Fig. 7.7)
From the data in Table 7.4, predict $P_e$, $T_e$, and $V_e$ for CO$_2$(g).

\[
a = 3.658 \text{ dm}^6 \text{ bar/mol}^2
\]
\[b = 0.0429 \text{ dm}^3 / \text{mol}
\]

\[
V_e = 3b = 0.129 \text{ dm}^3 / \text{mol} \quad (129 \text{ mL})
\]

\[
T_e = \frac{8a}{27Rb} = \frac{(29.264 \text{ dm}^6 \text{ bar/mol}^2)}{(27)(0.083145 \text{ dm}^3 \text{ bar} / \text{mol} K)(0.0429 \text{ dm}^3 / \text{mol})} = 303.9 \text{ K}
\]

\[
P_e = \frac{a}{27Rb} = 73.6 \text{ bar}
\]

**Free Energy of Real Gases**

For any pure material,

\[
\left( \frac{\partial \eta}{\partial P} \right)_T = V_m
\]

At constant $T$, \[d\eta = V_m dP\]

For ideal gases, $V_m = \frac{RT}{P}$ and we found

\[
\eta_{\text{id}} = \eta^0 + RT \ln P
\]

For real gases, it is convenient to define " fugacity " $F$, by

\[
\eta = \eta^0 + RT \ln F
\]
To obtain a useful expression for \( F \), start with

\[
d(\eta - \eta^\text{id}) = (V_m - \frac{RT}{P})dP
\]

Integrate from some very low pressure, \( P^* \), to final pressure \( P \)

\[
(\eta - \eta^\text{id}) - (\eta^* - \eta^\text{id}^*) = \int_{P^*}^{P} (V_m - \frac{RT}{P})dP
\]

Now as \( P \to 0 \), \( \eta^* \to \eta^\text{id}^* \) so

\[
\eta - \eta^\text{id} = \int_{0}^{P} (V_m - \frac{RT}{P})dP
\]

Provided our \( \eta^0 \)'s are the same

\[
\eta - \eta^\text{id} = (\eta^0 + RTdnF) - (\eta^0 + RTdnP) = \int_{0}^{P} (V_m - \frac{RT}{P})dP
\]

\[
RTdn\left(\frac{F}{P}\right) = \int_{0}^{P} (V_m - \frac{RT}{P})dP
\]

Application: At fairly low \( P \), \( P(V_m - b) \approx RT \)

\[
V_m - \frac{RT}{P} = b
\]

\[
RTdn\left(\frac{F}{P}\right) = \int_{0}^{P} b dP = bP
\]

\[
\frac{F}{P} = e^{bP/RT}
\]

Suppose \( b = 0.02 \) \( \text{liters/mole} \), \( T = 298^\circ C \), \( P = 1 \text{ bar} \)

\[
\frac{F}{P} = e^{1.02 \text{ liters/mol} \times 1 \text{ bar} \times 0.092 \text{ bar/mol} \times K^{-1} \times 298.15} = 1.0002
\]
Phases

Pure substances exist as
a) solids at low T
b) (perhaps) liquid at intermediate T
c) gases at high T

Which phase is stable at a particular T & P is determined by $\mu$.

Consider H$_2$O at 1 bar = P & variable T

\[ T = 400 \text{ K}, \text{ gas} \]
\[ T_b = 373.15, \text{ gas} \equiv \text{ liquid} \]
\[ T = 300, \text{ liquid} \]
\[ T_m = 273.15, \text{ liquid} \equiv \text{ solid} \]
\[ T = 250, \text{ solid} \]

Thermodynamic Justification

\[ (\frac{\partial^2 u}{\partial T^2})_P = -S_u \]

Also \[ (\frac{\partial^2 u}{\partial T^2})_P = -(\frac{\partial^2 u}{\partial P^2})_T \]

\[ dS_u = \frac{du}{T} = \frac{C_p u}{T} \]

Consider H$_2$O at

P = 1 bar
Pressure dependence: \( \left( \frac{\partial M_k}{\partial P} \right)_T = V_k \)

Since \( V_{\text{gas}} \gg V_{\text{liq}} \approx V_{\text{solid}} \), the gas drops quickly as \( P \) increases, but the gas and liquid drop gradually as \( P \) increases.

\[ P = 0.01 \text{ atm} \]

For \( \text{CO}_2 \), we see this behavior at \( P = 1 \text{ atm} \). For \( \text{H}_2\text{O} \), sublimation occurs at lower pressures.

At a particular \( P \), \( P_{\text{triple}} \), all three curves intersect.

\[ M_{\text{solid}} = M_{\text{liq}} = M_{\text{gas}} \]

3 phases coexist.

**Phase Diagram**

\((P-T)\) diagram for \( \text{CO}_2 \):

- Solid
- Liquid
- Gas
- Critical point
- Triple point

Example of \( \text{CO}_2 \) phase diagram:

- \( P_c \)
- \( T_c \)
- \( P_{\text{triple}} \)
- \( -56.6^\circ C \)
- \( 311^\circ C \)
In the case of a P-T diagram, V changes freely.
We can also consider a P-V diagram. (This was considered earlier in our discussion of real gases.) We hold T constant in this case.

Consider CO₂

Lever Rule - When you have two (or more) phases present, how much of each phase is present?

\[
\text{mole fraction of liquid} = \frac{xc}{xc + ax}
\]

\[
\text{mole fraction of gas} = \frac{ax}{xc + ax}
\]

Note that if \( ax > xc \), we will have mostly liquid

molar volume of biphasic mixture
A P-V-T diagram for an ideal gas. Constant pressure, constant volume, and constant temperature paths are shown as black, red, and blue curves, respectively.

Figure 8.13 shows a P-V-T diagram for a substance that expands upon melting. The usefulness of the P-V-T phase diagram can be illustrated by revisiting the isobaric conversion of a solid to a gas at a temperature above the triple point shown as process a in Figure 8.4. This process is shown as the path $a \rightarrow b \rightarrow c \rightarrow d \rightarrow e \rightarrow f$ in Figure 8.12. We can see now that the temperature increases along the segments $a \rightarrow b$, $c \rightarrow d$, and $e \rightarrow f$, all of which lie with single-phase regions, and remains constant along the segments $b \rightarrow c$ and $d \rightarrow e$, which lie within two-phase regions. Similarly, process c in Figure 8.4 is shown as the path $g \rightarrow h \rightarrow i \rightarrow k \rightarrow l \rightarrow m$ in Figure 8.13.
Understanding the Critical Point

1) For $T < T_{\text{crit}}$, $|\frac{\partial u}{\partial T}| > |\frac{\partial m}{\partial T}|$ since $S_2 < S_1$

2) $|\frac{\partial u}{\partial T}| = \frac{C_p}{T}$, but $C_p > C_p^G$ (always)

(In a liquid, work must be done against the attractive forces that are much stronger in a liquid than in a gas. To raise $T$ at constant $P$, we must overcome these attractions as well as raise kinetic energy.)

Although $u$ curves have steeper slopes at low $T$, gas and liquid slopes must become equal at sufficiently high $T$.

Clapeyron Equation

Suppose we have liquid + solid or liquid + gas at equilibrium at some $T$ and $P$:

\[ \alpha \leftrightarrow \beta \quad \mu_\alpha = \mu_\beta \]

If we only changed one variable ($T$ or $P$), all of $\alpha$ would convert to $\beta$ or vice versa. However, by changing both $T$ and $P$ in a special way, we can maintain equilibrium.
\[ d\mu = d\nu \]  
(change both \( P, q, T \))

\[-S_\alpha \, dT + V_\alpha \, dP = -S_\beta \, dT + V_\beta \, dP \]

\[ (S_\beta - S_\alpha) \, dT = (U_\beta - U_\alpha) \, dP \]

\[ \frac{\Delta S_\alpha \to \beta}{\Delta V_\alpha \to \beta} = \frac{dP}{dT} \]

\[ \Delta S_\alpha = \frac{\Delta H_\alpha \to \beta}{T} \]

Now for a phase transition

\[ \frac{dP}{dT} = \frac{\Delta H_\alpha \to \beta}{T \Delta V_\alpha \to \beta} \]

(A) \text{ Solid} \xrightarrow{\text{Liquid}} \text{L} \text{iquid} (\text{Solid}) \Delta V_\alpha \to \beta \text{ are nearly indep. of } T

\[ dP = \frac{\Delta H_\alpha \to \beta}{\Delta V_\alpha \to \beta} \, dT \Rightarrow P_2 - P_1 = \frac{\Delta H_\alpha \to \beta}{\Delta V_\alpha \to \beta} \ln \left( \frac{T_2}{T_1} \right) \]

Example: \( S_n (s, \text{gray}) \Rightarrow S_n (s, \text{white}) \)

The two solid forms of Tin are in equilibrium at 291.15 K \( \& \) \( P = 1 \text{ bar} \). If \( P \) is raised to 100 bar, what must \( T \) be to maintain equilibrium? (\( \rho (\text{gray}) = 5.75 \, \frac{\text{g}}{\text{cm}^3}, \rho (\text{white}) = 7.28 \, \frac{\text{g}}{\text{cm}^3} \), \( M = 118.7 \, \frac{\text{g}}{\text{mol}} \), \( \Delta H_\text{gray} = 2.48 \, \text{kJ/mol} \))

\[ \Delta V_\gamma = (\frac{\rho_i}{P_i} - \frac{\rho_f}{P_f}) = (118.7 \, \frac{\text{g}}{\text{mol}})(-0.037 \, \text{cm}^3/\text{g}) = -4.37 \times 10^{-3} \, \text{cm}^3 \]

\[ T_2 = T_1 \exp \left( \frac{(\Delta V_\gamma \rho_f)}{(\Delta H_\gamma \rho_f)} (P_2 - P_1) \right) = (291.15) \exp \left( \frac{-4.37 \times 10^{-3}}{2981 \, T} (99 \times 10^{-3} \, \text{atm}) \right) \]

\[ = 276.15 \, \text{K} \]
For this transition, \( T \) drops since \( \Delta U > 0 \) (melting of water also exhibits this behavior. Most substances have \( \Delta U > 0 \) and exhibit the opposite behavior.)

\( \text{Liquid} \rightarrow \text{Gas} \)

\[
\begin{align*}
&\quad \Delta U_g = U_g - U_l = \frac{RT}{P} \\
&\quad \Delta P = \frac{\Delta H_{g}}{RT} \quad \Rightarrow \quad \frac{dP}{P} = \frac{\Delta H_{g}}{RT} \frac{dT}{T} \\
&\quad \ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{g}}{RT} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\end{align*}
\]

Example: \( \Delta H_{\text{vap}} (\text{H}_2\text{O}) = 40.656 \text{ kJ/mol} \).

If a pressure cooker works at \( P = 4 \text{atm} \) and \( T_b = 373.15 \text{ K} \) at \( P = 1 \text{atm} \), what is the "working temperature" of the cooker?

\[
\ln \left( \frac{4}{1} \right) = \frac{40.656}{8.315} \left( \frac{1}{373.15} - \frac{1}{T_2} \right)
\]

Solving for \( T_2 \) gives \( 417.3 \text{ K} = 144.6^\circ \text{C} \).

Crafts Method

Makes use of Trouton's rule.

\[
\frac{\Delta H_{g}}{T} = \Delta S_{g} \approx 88 \text{ J mole}^{-1} \text{K}^{-1}
\]

(For "associated" liquids (H₂O, alcohols), \( \Delta S_{g} \approx 105 \text{ J mole}^{-1} \text{K}^{-1} \))
\[ \Delta P = \frac{\Delta^2 v \gamma P \, dT}{RT} \Rightarrow \frac{dP}{dT} = \frac{\Delta^2 v \gamma}{R} \frac{1}{T} \]

What is \( \frac{dP}{dT} \) at \( T_b \) and \( P = 1 \text{ atm} \)?

\[ \frac{dP}{dT} \propto \frac{(88 \text{ J/mole K})(1.013 \times 10^5 \text{ Pa})}{(8.315 \text{ J/mole K}) T_b} = 1.072 \times 10^6 \text{ Pa} \]

\[ = \frac{10.582 \text{ atm}}{T_b} \]

Example 1) The b.p. of benzene at 1 atm (760 mm Hg) is 353.15 K. What is \( T_b \) at 740 mm?

\[ T_b (P) = T_b (P) + (P - P_1) \frac{dT}{dP} \]

\[ = 353.25 + (740 - 760) \left( \frac{1 \text{ atm}}{760} \right) \left( \frac{353.25}{10.582 \text{ atm}} \right) \]

\[ = 352.37 \text{ K} - 88 \]

Phase Transitions

1st order
(any solid + liq or liq + gas)

\[ \left( \frac{\partial^2 S}{\partial T \partial P} \right)_T \]

\[ \frac{\partial S}{\partial T} = -SdT + VdP \]

\( G \) must be continuous at \( T_{eq} \) in order for phases to coexist.
Heat material at fixed rate

**Second Order**

Certain transitions don't require a "latent heat."

Examples - certain solid → solid crystal → plastic crystal

Adamantane
Partial Molar Quantities

Initially

\[ V_\text{tot} = n_A V_A \]

molar volume of pure A

\[ V_\text{tot} = n_A V_A \]

\[ \text{add } B \]

\[ A + B \]

\[ \Delta V_\text{tot} = \left( \frac{\partial U_\text{tot}}{\partial n_A} \right)_{n_B} n_A + \left( \frac{\partial U_\text{tot}}{\partial n_B} \right)_{n_A} n_B \]

+ deviation from ideal \( (V_B > V_B^0) \)

\[ \text{ideal} \]

slope = \( \frac{\partial U_\text{tot}}{\partial n_B} = V_B^0 = \text{molar volume of pure } B \)

- deviation from ideal \( (V_B < V_B^0) \)

\[ n_B \]

It is possible that \( V_B < 0 \)!

In general

\[ dV = V_A dn_A + V_B dn_B + \ldots \]

Suppose we hold the composition constant, & simply pour it into a beaker

\[ \text{add liquid mixture} \]

\[ \Rightarrow \]

\[ \text{empty} \]

\[ \Rightarrow \]

\[ A, B, \text{etc.} \]

\[ V = V_A n_A + V_B n_B + V_C n_C + \ldots \]

differentiate

\[ dV = V_A dn_A + V_B dn_B + \ldots + n_A dV_A + n_B dV_B + \ldots \]

\[ O = n_A dV_A + n_B dV_B \] (Gibbs-Duhem Eq.)
Generalize Expression for $G$ for a mixture. $G$ can depend on $T, P, n_A, n_B, \ldots$

\[ dG = -SdT + VdP + \left( \frac{\partial G}{\partial n_A} \right) dn_A + \left( \frac{\partial G}{\partial n_B} \right) dn_B + \ldots \]

\[ = \left( \frac{\partial G}{\partial T} \right) _{P, n_i} \left( \frac{\partial G}{\partial P} \right) _{T, n_i} \quad n_A \quad n_B \]

(chemical potentials)

Also \[ \frac{\partial^2 G}{\partial T \partial n_A} = \frac{\partial^2 G}{\partial n_A \partial T} \]

\[ \left( \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial n_A} \right) \right) = \left( \frac{\partial}{\partial n_A} \left( \frac{\partial G}{\partial T} \right) \right) \]

partial molar entropy

\[ \left( \frac{\partial n_A}{\partial T} \right) _{P, n_i} = -\left( \frac{\partial S}{\partial n_A} \right) _{P, T, n_i} = -S_A \]

compare with \[ \left( \frac{\partial G}{\partial T} \right) _P = -S \]

All thermodynamic relations developed for pure substances are applicable to mixtures provided the extensive variables ($H, S, A, F, U$) are replaced with partial molar equivalents ($H_A, S_A, \text{etc.}$)

Repeat our "uniform composition" experiment, but consider $G$ ($T \& P$ constant)

\[ dG = \sum_j \eta_j dn_j \Rightarrow G_{\text{Tot}} = \sum_j \eta_j n_j \]

differentiate \[ dG = \sum_j \left( \eta_j dn_j + n_j d\eta_j \right) \]

Subtract \[ 0 = \sum_j \eta_j d\eta_j \quad \text{Gibbs-Duhem Eqn.} \]
Consider dissolving $I_2$ in $CCl_4$. $I_2$ dissolves until solution is saturated.

Initially, $\mu_{I_2}^{solid}(CCl_4) < \mu_{I_2}^{solid}$ and solid $I_2$ dissolves. As more $I_2$ dissolves, $\mu_{I_2}^{solid}(CCl_4)$ ↑ and at some point

$$\mu_{I_2}^{solid}(CCl_4) = \mu_{I_2}^{solid} \quad \text{(saturation)}$$

Now consider $I_2$ dissolved in two immiscible solvents, $H_2O$ & $CCl_4$

Move $\delta x$ moles of $I_2$ from $CCl_4$ to $H_2O$

$$d\mu = \mu_{I_2}^{H_2O}(\delta x) + \mu_{I_2}^{CCl_4}(-\delta x) = \delta x \left[ \mu_{I_2}^{H_2O} - \mu_{I_2}^{CCl_4} \right]$$

if $\mu_{I_2}^{H_2O} < \mu_{I_2}^{CCl_4}$, $I_2$ moves from $CCl_4 \rightarrow H_2O$

if $\mu_{I_2}^{H_2O} > \mu_{I_2}^{CCl_4}$, $I_2$ moves from $H_2O \rightarrow CCl_4$

at equilibrium $\mu_{I_2}^{H_2O} = \mu_{I_2}^{CCl_4}$
Solutions

For a pure solution
(assume vapor behaves ideally)
standard state of gas

\[ \Delta G = \Delta G^0 = \Delta H + RT \ln P^0_A \]

---

Molecules are more complicated, but a few limiting cases can be considered

1) Mixture of A + B
(both molecules comparable in size), but A in excess.

\[ x_A = \text{mole fraction of A in liquid} \]
\[ x_B = \text{mole fraction of B in liquid} \approx 0 \]

On average, an A molecule is in about the same liquid environment as in pure A, but its exposure to the atmosphere is reduced by the fractional amount, \( x_A \).

Consequently

\[ P_A \approx x_A P^0_A \quad \text{(Raoult's Law)} \]

A

B molecule, on average, is surrounded almost entirely by A's and experiences a very different environment than in pure B. However, we still expect

\[ P_B \propto x_B \quad \text{(Henry's Law)} \]
The "solvent" (component in excess) obeys Raoult's Law as $x_A \to 1$

The "solute" (component in lesser amount) obeys Henry's Law as $x_B \to 0$

The graph exhibits the general behavior at all $x_A \neq x_B$.

**Negative Deviation from Ideality**
$A$ and $B$ attract each other more than $A$ attracts $A$ or $B$ attracts $B$ (example: chloroform and acetone)

**Positive Deviation from Ideality**
$A$ and $B$ repel each other (example: chloroform and ethanol)

**Ideal solutions**
Raoult's Law obeyed at all $x_A \neq x_B$

So $k_A = P_A^*$ and $k_B = P_B^*$

$$P_A = x_A \cdot P_A^*$$
$$P_B = x_B \cdot P_B^*$$
Thermodynamics of ideal solutions

\[ m_A = m_A^0 + RT \ln P_A \]
\[ = m_A^0 + RT \ln (x_A P_A^0) \]
\[ = m_A^0 + RT \ln P_A^0 + RT \ln x_A \]
\[ = m_A^0 = \text{chemical potential of pure liquid } A \]

Similarly, \[ m_B = m_B^0 + RT \ln x_B \]
\[ = m_B^0 + RT (1 - x_A) \]

Free Energy of Mixing

Take \( x_A \) moles of pure A and combine with \( x_B = 1 - x_A \) moles of pure B

\[ \Delta G_{mix} = (G_{mix} - G_{pure}) \]
\[ = (x_B m_B + x_A m_A) - (x_B m_B^0 + x_A m_A^0) \]
\[ = x_B (m_B - m_B^0) + x_A (m_A - m_A^0) \]
\[ = RT (x_B \ln x_B + x_A \ln x_A) \]

What is \( \Delta H_{mix} \)?

From Gibbs-Helmholtz Eqn.
\[ \frac{\partial \Delta G_{mix}}{\partial T} = -\frac{\Delta H_{mix}}{T^2} \]

\[ -\frac{\Delta H_{mix}}{T^2} = 2 \left[ \frac{RT}{T} (x_B \ln x_B + x_A \ln x_A) \right] = 0 \]

\[ \Delta H_{mix} = 0 \quad (\text{ideal solution}) \]
Determination of solute molecular weight from changes in partial pressure of solvent.

Although most solutions are not ideal, the solvent must obey Raoult's Law in the limit $x_A \to 1$ ($x_B \to 0$).

$$P_A = x_A P_A^*$$

Suppose we add $m_B$ gms of solute to $m_A$ gms of solvent ($m_B \ll m_A$). Let $M_A$ and $M_B$ denote molecular weights of $A$ and $B$.

The partial pressure of the solvent drops from $P_A^*$ to $P_A$ after the solute is added.

$$\Delta P_A = P_A^* - x_A P_A = P_A^*(1 - x_A) = x_B P_A^*$$

$$x_B = \frac{n_B}{n_B + n_A} \approx \frac{n_B}{n_A} = \left(\frac{m_B}{M_B}\right) \left(\frac{M_A}{m_A}\right)$$

$$\Delta P_A = \frac{m_B M_A}{m_A M_B} P_A^*$$

$$M_B = \left(\frac{m_B}{m_A}\right) M_A \left(\frac{P_A^*}{\Delta P_A}\right)$$
One gm of an unknown material (assumed nonvolatile) is dissolved in 200 gm of 
CCl₄ \( (M_A = 153.81 \text{ gm/mole}) \) and \( P_A \) drops 
from 76.7 torr to 75.1 torr. What is \( M_B \)?

\[
M_B = \left( \frac{1 \text{ gm}}{200 \text{ gm}} \right) \left( 153.81 \text{ gm/mole} \right) \left( \frac{76.7 \text{ torr}}{1.6 \text{ torr}} \right) = 36.87 \text{ gm/mole}
\]

**Solutions in general**

\[
U_A = U_A^0
\]

\[
U_A = U_A^0 + RT \ln P_A = U_A^0 + RT \ln P_A^0 - RT \ln P_A^0 + RT \ln P_A
\]

\( U_A^0 \) = chemical potential of pure liquid \( A \)

\[
= U_A^0 + RT \ln \left( \frac{P_A}{P_A^0} \right) = U_A^0 + RT \ln a_A = U_A^0 + RT \ln \chi A A
\]

\( \chi A A \) = activity coefficient

If the solution is ideal or \( x_A \approx 1 \), \( \chi A = 1 \)

Problem) 190 gm of sucrose \( (M = 342.3 \text{ gm/mole}) \) 
has negligible vapor pressure when 
dissolved in 1 kg of water. If 
the vapor pressure of pure water at \( 20^\circ \text{C} \) 
= 2.339 kPa \( \Delta \) that of the solution is 
2.269 kPa, calculate \( a \) and \( \chi \) for 
water.
\[a_{H_2O} = \frac{1}{P_{H_2O}} = \frac{2.691}{2.339} = 0.970\]

\[n_{H_2O} = \frac{1000 \text{ gm}}{(18 \text{ gm/mole})} = 55.56 \text{ moles}\]

\[n_{\text{sucrose}} = \frac{190 \text{ gm}}{(342.3 \text{ gm/mole})} = 0.55 \text{ moles}\]

\[x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{\text{sucrose}}} = 0.990\]

\[\gamma_{H_2O} = \frac{a_{H_2O}}{x_{H_2O}} = \frac{0.970}{0.990} = 0.980\]

**Standard States Reconsidered**

(component A)

Solvent - standard state is pure liquid

(component B)

Solute - convenient to choose a different S.S.

\[M_B = M_B^0 + RT \ln a_B\]

S.S. to be determined

We want to choose solute standard state such that \(\gamma_B \approx 1\) as \(x_B \to 0\)

\[M_B = M_B^0 + RT \ln x_B\] (valid when \(x_B \to 0\))

In the limit of low conc., we expect each B molecule to be surrounded, on average, by A molecules.

Also

\[P_B = \gamma_B x_B\]  
**Henry's Law**

\[\gamma_B\]  
**Henry's constant**
In our solution were cases, \( k_B = P_B^0 \). In general, however, \( k_B \neq P_B^0 \).

\((k_B \to 0)\) \( \mu_B = \mu_B^0 + RT \ln \frac{P_B}{P_B^0} = \mu_B^0 + RT \ln \frac{k_B x_B}{P_B} \)

\[ = \left( \mu_B^0 + RT \ln \frac{k_B}{P_B} \right) + RT \ln x_B \]

This is \( \mu_B^H \)

\[ \mu_B^H = \mu_B^0 + RT \ln \frac{k_B}{P_B} = \mu_B^0 + RT \ln k_B \]

\[ \uparrow \text{chemical potential of pure } B \text{ if it obeyed Henry's Law over entire range.} \]

Problem) \( O_2 \) \& \( N_2 \) dissolve in \( H_2O \) to a limited extent. (This is how fish get \( O_2 \).)

At \( 0^\circ C \), Henry's law applies

\[ k_{N_2} = 7.58 \times 10^{-4} \text{ bar} \]

\[ k_{O_2} = 3.88 \times 10^{-4} \text{ bar} \]

The m.w. of water is 18gm/mole \& air consists of 80% \( N_2 \) \& 20% \( O_2 \). At \( P_{tot} = 1 \text{ bar} \), calculate the molality of \( N_2 \) \& \( O_2 \) in water.

You can assume Henry's law is obeyed.

\[ \mu_B^0 = \mu_B^0 \]

\[ \mu_B^0 + RT \ln \frac{P_B}{P_B^0} = \mu_B^H + RT \ln x_B \]

\[ \Delta \mu_B^0 + RT \ln \frac{x_B P_{tot}}{P_{tot}^0} = \Delta \mu_B^0 + RT \ln x_B + RT \ln \frac{k_B x_B}{P_B} \]

\[ RT \ln (x_B P_{tot}) = RT \ln (k_B x_B) \]

\[ x_B^2 = \frac{x_B^2 P_{tot}}{k_B} \]

\[ x_{N_2} = \frac{0.80(1 \text{ bar})}{1.06 \times 10^{-5}} = 0.02 \times 10^{-5} \]

\[ x_{O_2} = \frac{0.20(1 \text{ bar})}{5.15 \times 10^{-6}} = 3.88 \times 10^{-4} \]
\[ n_s = \text{moles solvent} = \frac{m_s}{M_s} = \frac{1000 \text{ g mol}}{18 \text{ g mol/mole}} = 55.6 \text{ moles kg solv.} \]

\[ n_{o_2} = \text{moles O}_2/\text{kg solv.} \]

\[ m_{o_2} = n_{o_2} = x_{o_2} \cdot n_{\text{Tot}} \]

\[ = x_{o_2} (n_{o_2} + n_{n_2} + n_s) \approx x_{o_2} n_s = 55.6 \times 0.2 \]

\[ m_{o_2} = (55.6 \frac{\text{moles}}{\text{kg solv}})(5.15 \times 10^{-6}) = 2.84 \times 10^{-4} \frac{\text{moles}}{\text{kg solv}} \]

\[ m_{n_2} = \ldots 5.87 \times 10^{-9} \frac{\text{moles}}{\text{kg solv}}. \]
Culligative Properties

Freezing Point Depression \{ \text{depend on solute number concentration} \}
Boiling Point Elevation \{ \text{valid for } x_A \ll 1 \}
Osmotic Pressure

Freezing Point Depression - adding solute reduces \( T_m \) of solvent. (Salt reduces melting pt. of ice.)

\[
M_{A, \text{solid}}(T, P) = M_{A, \text{liq}}(T, P, x_A) = M_{A}^{\circ}(T, P) + RT \ln x_A
\]

As B is added, the \( RT \ln x_A \) term causes \( M_{A}^{\circ} \) to drop and this reduces the melting temp of A from \( T_m^\circ \) to \( T_m \)

\[
\ln x_A = \frac{M_{A, \text{solid}}(T, P) - M_{A}^{\circ}(T, P)}{RT} = \frac{\Delta G_{\text{Fusion}}(A)}{RT}
\]

Now

\[
-\frac{\Delta H_{\text{Fus}}(A)}{T^2} = \frac{\partial (\Delta G_{\text{Fus}}(A)/T)}{\partial T} = -R \frac{\partial \ln x_A}{\partial T}
\]

\[
\frac{\partial \ln x_A}{\partial T} = \frac{\Delta H_{\text{Fus}}(A)}{RT^2}
\]

\[
\int_{T_m^\circ}^{T_m} \frac{\partial T}{T^2} = \int_{x_A=1}^{x_A} \frac{\Delta H_{\text{Fus}}(A)}{R} \int_{T_m}^{T_m^\circ} \frac{dT}{T^2}
\]

\[
\ln x_A - \ln 1 = \ln x_A = -\frac{\Delta H_{\text{Fus}}(A)}{R} \left( \frac{1}{T_m^\circ} - \frac{1}{T_m} \right) = \frac{\Delta H_{\text{Fus}}(A)}{RT_m T_m^\circ} (T_m - T_m^\circ)
\]
\[ \ln \left(1 - x_B\right) = -x_B - \frac{1}{2} x_B^2 \quad \Rightarrow \quad \ln \left(1 - x_B\right) = -x_B \quad (x_B \ll 1) \]

\[ \ln(1 - 0.001) = -0.001 - 5 \times 10^{-7} \]

\[ \ln 0.999 = -1.0005 \times 10^{-3} \approx -0.01 \]

Now, \[ \ln \left(1 - x_B\right) = -x_B - \frac{1}{2} x_B^2 \]

Also, \[ x_B = \frac{\Delta H_{fus}(m)}{R T_m^2} \Delta_{fus} T \]

\[ x_B \times \frac{m_B}{m_A} = \frac{m_B}{M_A} = m_B M_A \]

\[ \Delta_{fus} T = \frac{M_A R T_m^2}{\Delta H_{fus}(m)} \]

\[ m_B = K_f m_B \]

\[ (\text{molality of B}) \]

\[ K_f = \frac{m_B M_A}{\Delta H_{fus}} \]

\[ = \frac{(0.18 \text{ kg/mole})(1.315 \frac{T}{\text{mol.K}})(273.15 \text{K})}{6009 \text{ J/mole}} \]

\[ = 1.858 \text{ kg K/mol} \]

Suppose you add 1 mole of sucrose to 1 kg liter of water. What is \( \Delta_{fus} T \)?

\[ \Delta_{fus} T = K_f m_B = (1.858 \text{ kg K/mol})(1 \text{ mole}) = 1.858 \text{ K} \]

Suppose we added 1 mole (58.44 gm) of NaCl to 1 kg water. At first glance, you might expect \( \Delta_{fus} T = 1.86 \text{ K} \). Actually, it's twice this! Why?
Boiling Point Elevation

A treatment identical to that just considered gives
\[ \Delta_{\text{vap}} T = T_b - T_b^0 = K_b m_B \]
where \( K_b \) is the molality of solute.

\[ K_b = \frac{M_A R T_b^0}{\Delta H_{\text{vap}}(A)} \]

Osmotic Pressure

A semipermeable membrane allows \( A \) to pass, but not \( B \).

A tends to flow into the left side compartment through the semipermeable membrane to equalize the concentration of \( A \).

This leads to a pressure difference, \( \pi \), between the two sides.

\[ m_A^{\text{left}} = m_A^{\text{right}} \]

\[ m_A^0(T, P + \pi) + RT \ln x_A = m_A^0(T, P) \]

Now \( \left( \frac{\partial V}{\partial P} \right)_T = V \equiv \left( \frac{\partial m_A}{\partial P} \right)_T = V_A \Rightarrow \Delta m_A = V_A dP \)

\[ \therefore m_A^0(T, P + \pi) = m_A^0(T, P) + V_A \pi \]

\[ m_A^0(T, P) + \pi V_A + RT \ln x_A = m_A^{\text{right}}(T, P) \]

\[ \pi V_A = -RT \ln x_A = -RT \ln (1 - x_B) \approx x_B RT \]
\[ P = \frac{X_B RT}{V_A} = \frac{RT}{V_A} \left( \frac{n_B}{n_A + n_B} \right) \times \frac{RTn_B}{n_A V_A} = \frac{RT}{V_M} \frac{W_B}{\text{mass of } B} \]

\[ M_B = \frac{W_B RT}{V} \]

Example: 1 gm of an unknown per liter of water produces an osmotic pressure of 10 mm Hg. What is \( M_B \) (\( T = 20^\circ C \))

\[
M_B = \frac{(1.00 \text{ kg})(0.082 \frac{\text{Ltre atm}}{\text{mole K}})(293.15 \text{ K})}{(10 \text{ mm Hg}) \left( \frac{1 \text{ atm}}{760 \text{ mm Hg}} \right)(1 \text{ Ltre})} = 1.83 \text{ kg/mole} \]

\[ = 1830 \text{ gm/mole} \]

Osmotic pressure is a useful means of determining molecular weights in the range of 1000 to 10,000 gm/mole.
Phase diagrams of mixtures

A) Ideal Solutions (binary)

\[ P_A = x_A^o P^o \]
\[ P_B = x_B^o P_B^o = (1-x_A^o) P_B^o \]
\[ P_{tot} = P_A + P_B = P_B^o + x_A^o (P_A^o - P_B^o) \]

Suppose \( P_A^o = 200 \text{ torr}, \ P_B^o = 100 \text{ torr}, \ x_A^o = 0.3 \)

\[ P_t = 100 + 0.3(200-100) = 130 \text{ torr} \]

What is composition of vapor?

\[ x_A^v = \frac{P_A}{P_{tot}} = x_A^o \left( \frac{P_A^o}{P_{tot}} \right) = 0.3 \left( \frac{200}{130} \right) = 0.465 \]

Note that \( x_A^v \neq x_A^o \). In general, the more volatile component (A in this example) will be more concentrated in the vapor phase.

1) Starting at \( P_1 \), all liquid
2) As \( P \) is reduced to \( P_2 \), vapor starts to appear \( (x_A^v = 0.3, x_A^v = 0.465) \)
3) As \( P_B \), more liquid evaporates. Since vapor is richer in \( A \), \( x_A^v \) drops.
4) At \( P_4 \), the last of the liquid evaporates.
5) At \( P_5 \), all gas.
**Nonideal Liquids**

\[ p \quad \text{vapor} \]

- **Ethanol** + **Chloroform**
  - + deviation from ideality

\[ T \quad \text{vapor} \]

- **Ethanol** + **Chloroform**
  - - deviation from ideality

\[ O = \text{denotes "azeotrope"} \]

**T vs. composition phase diagrams are also useful.**

- **Ethanol** + **Chloroform**
  - **Acetone** + **Chloroform**

**More complex phase diagrams are seen as the two species become less compatible.**

- **Ethanol** & **Chloroform** (miscible)
- **Aniline** & **Water** (immiscible at low T)
- **Benzene** & **Water** (immiscible to pt. of vap.)
Exercise)

Consider what happens to the composition of the system as you raise $T$ following paths $a$, $b$, and $c$

Other phase diagrams

Forms a particularly stable $AB_2$ complex

$(A+AB_2)$ nearly ideal behavior

$(AB_2+AB)$

Azeotropes indicate "unstable" ratios

Regions where solid partitions into 2 different solid phases.
Electrolyte Solutions

When a salt dissolves in aqueous solution

\[ \text{NaCl}(s) \leftrightharpoons \text{Na}^+(aq) + \text{Cl}^-(aq) \]

\( \Delta H \) can be < 0 or > 0

Solutions are non-ideal. Solvation of ions involves a lot of energy.

As for any reaction we can write

\[ \Delta H_{\text{solv}}^0 = \Delta H_{\text{f}}^0(\text{Na}^+, \text{aq}) + \Delta H_{\text{f}}^0(\text{Cl}^-, \text{aq}) - \Delta H_{\text{f}}^0(\text{NaCl}, \text{s}) \]

As before, "standard state" is at

\[ T = 298.15 \text{ K} \]
\[ P = 1 \text{ bar} \]

all species at unit "activity"
\[ \text{Na}(s) \rightarrow \text{Na}^+(aq) \quad \Delta H_f^\circ(\text{Na}^+, \text{aq}) \]
\[ \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Cl}^-(aq) \quad \Delta H_f^\circ(\text{Cl}^-, \text{aq}) \]

It is useful to remind yourself exactly what these standard state enthalpies of formation refer to.

Although it is possible to measure \( \Delta H^\circ \) solv experimentally (or at least under conditions different from STP which are subsequently corrected to STP), it is never possible to measure \( \Delta H^\circ \) of ionic species directly!

This is because ions are always paired. (Charge neutrality)
Can we obtain $\Delta H^0_s$ of ions by considering a combination of reactions? Let's suppose we want to find $\Delta H^0_s (Na^+, ag)$ and consider:

\[NaCl(s) \rightleftharpoons Na^+(ag) + Cl^-(ag)\]

\[K^+(ag) + Cl^-(ag) \rightleftharpoons KCl(s)\]

\[\Delta H^0_{solv}(NaCl) = \Delta H^0_s(Na^+) + \Delta H^0_s(Cl^-) - \Delta H^0_s(NaCl)\]

\[\Delta H^0_{solv}(KCl) = -\Delta H^0_s(K^+) - \Delta H^0_s(Cl^-) + \Delta H^0_s(KCl)\]

If we add, we do get rid of $\Delta H^0_s(Cl^-)$, but:

\[\Delta H^0_{solv}(NaCl) - \Delta H^0_{solv}(KCl)\]

\[= (\Delta H^0_s(Na^+) - \Delta H^0_s(K^+)) - (\Delta H^0_s(NaCl) - \Delta H^0_s(KCl)\]

unknown

we now have introduced another unknown, $\Delta H^0_s(K^+, ag)$
Since heats of reactions (or free energies) always involve differences, a pragmatic way of dealing with this paradox is to arbitrarily assign a \( \Delta H^0 \) or \( \Delta G^0 \) of a single ion.

Today, the following convention is usually followed:

\[ \Delta G^0_{\text{f}}(H^+, \text{aq}) = 0 \]

With this convention,

\[ S^0_{\text{f}}(H^+, \text{aq}) = \left( \frac{\partial \Delta G^0_{\text{f}}(H^+, \text{aq})}{\partial T} \right)_P = 0 \]

\[ \Delta H^0_{\text{f}}(H^+, \text{aq}) = \Delta G^0_{\text{f}}(H^+, \text{aq}) - TS^0_{\text{f}}(H^+, \text{aq}) = 0 \]

With these, all \( S^0_{\text{f}} \)'s, \( \Delta G^0_{\text{f}} \)'s, and \( \Delta H^0_{\text{f}} \)'s of all ions can be determined.
Consider the reaction

\[ \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \]

\[ \Delta H^0 = \Delta H_f^0(H^+) + \Delta H_f^0(Cl^-) - \frac{1}{2} \Delta H_f^0(H_2) - \frac{1}{2} \Delta H_f^0(Cl_2) \]

can be measured:

\[ \Delta H^0 = \Delta H_f^0(Cl^-, \text{aq}) = -167.2 \quad \text{kJ/mol} \]

Return now to the reaction

\[ \text{NaCl(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \]

\[ \Delta H^0 = +3.90 \quad \text{kJ/mol} \]

\[ = \Delta H_f^0(\text{Na}^+) + \Delta H_f^0(Cl^-) - \Delta H_f^0(\text{NaCl}) \]

\[ \Rightarrow \quad \Delta H_f^0(\text{Na}^+, \text{aq}) = 3.90 + 167.2 - 411.2 \]

\[ = -240.1 \quad \text{kJ/mol} \]

Exercise: What is \( \Delta H_f^0(K^+, \text{aq}) \) given earlier in \( \text{So} \).
Entropies of formation of ions, $S_f^0$

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G_f^0(H^+) + \Delta G_f^0(Cl^-) - \frac{1}{2} \Delta G_f^0(H_2) - \frac{1}{2} \Delta G_f^0(Cl_2)$$

$$= 0 + (-131.2) - \frac{1}{2}(10) - \frac{1}{2}(0)$$

$$= -131.2$$

$$-131.2 = \Delta H_f^0(Cl^-(aq)) - T \left[ S_f^0(Cl^-,aq) \right.$$  

$$- S_f^0(H_2,g)/2 - S_f^0(Cl_2,g)/2 \right]$$

At 298.15 K

$$S_f^0(Cl^-,aq) = \frac{(-131.2 + 167.2) + 1000}{298.15}$$

$$+ \frac{1}{2} (130.7 + 223.1) = + 56.2 \frac{J}{mole K}$$

$S_f^0$'s for ions are summarized in Table 10.1
For certain ions, \( S^\circ_f < 0 \).

(This might appear to contradict the 3rd Law, but keep in mind, ions always come paired.)

What is the absolute entropy of \( 1 \text{N Na}^+(aq) \)?

\[
S^\circ_f (\text{Na}^+(aq)) = S^\circ_f (\text{Na}^+) + S^\circ_f (F^-)
\]

\[
= +59.0 - 13.8 = +45.2 \text{ J/mole K}
\]

\( \text{CaCl}_2 (aq) \)

\[
S^\circ_f (\text{CaCl}_2(aq)) = S^\circ_f (\text{Ca}^{2+}) + 2S^\circ_f (\text{Cl}^-)
\]

\[
= -53.1 + 2(56.5)
\]

\[
= +59.90 \text{ J/mole K}
\]

Absolute entropies of aquated salts (both \( + \) and \(-\) ions) are always \( > 0 \).
Heats, Free Energies of Solvation

\[ \text{Na}^+(g) \longrightarrow \text{Na}^+(aq) \]

\[ \Delta H^\circ_{\text{solution}}(\text{Na}^+) = -240.1 \, \text{kJ/mol} \]

\[ = \Delta H_f^\circ(\text{Na}^+|aq) - \Delta H_f^\circ(\text{Na}^+, g) \]

\[ \text{Na}(s) \longrightarrow \text{Na}(g) \quad \Delta H = 107.5 \, \text{kJ/mol} \]

\[ \text{Na}(g) \longrightarrow \text{Na}^+(g) \quad \Delta H^\circ = 495 \, \text{kJ/mol} \]

\[ \Delta H_f^\circ(\text{Na}^+, g) = +602.5 \, \text{kJ/mol} \]

\[ \therefore \Delta H^\circ_{\text{solution}}(\text{Na}^+, aq) = -842.60 \, \text{kJ/mol} \]

These are very exothermic and reflect the substantial effect of solvation on the energetics of ions in solution.
Born Free Energies

\(\omega = \text{electrical work of creating a charge, } e^2, \text{ of radius } R \text{ in a medium of dielectric constant, } \varepsilon_r. \text{ (Born Free Energy)}\)

\(\omega = \frac{1}{2} e^2 \Phi = \frac{e^2 \Phi}{8\pi\varepsilon_0 \varepsilon_r R}\)

\(\Phi = \text{electric potential at distance } R \text{ from point charge, } e^2\)

\[\Phi = \frac{e^2}{4\pi\varepsilon_0 \varepsilon R} \text{ (Coulomb's Law)}\]
\[ \Delta G^0_{\text{solv}} = \text{free energy change of taking one mole from gas} \left( e_r = 1 \right) \text{to water} \left( e_r = 6.0 \approx 80 \right) \]

\[ \Delta G^0_{\text{Born}} = \frac{e^2 e^2 N}{8 \pi \varepsilon_0 R} \left( \frac{1}{e_r} - 1 \right) \]

Suppose \( e_r = 80.36 \) (20°C, H₂O)

\[ R = 1 \text{Å} = 10^{-10} \text{m} \]

\[ \frac{N e^2}{8 \pi \varepsilon_0 R} = \frac{(1.602 \times 10^{-19} \text{Coul})^2 (6.02 \times 10^{23}) \left( 25.13 \right) \left( 8.854 \times 10^{-12} \text{Coul}^2 / \text{Jm} \right) (10^{-10} \text{m})}{694.29 \frac{\text{kJ}}{\text{mole}}} = 694.29 \frac{\text{kJ}}{\text{mole}} \]

\[ \Delta G^0_{\text{Born}} = 694.29 \left( \frac{1}{80.36} - 1 \right) = -694 \frac{\text{kJ}}{\text{mole}} \]

For \( e = +1 \)

In general

\[ \Delta G^0_{\text{Born}} = \frac{694.29}{R} \left( \frac{1}{e_r} - 1 \right) e^2 \]

(in kJ/mole) \[ \uparrow \]

(in Å) \[ \uparrow \]
Good agreement with experiment is found with the following modifications:

\[ R = R_{\text{crystal}} + 0.085 \text{ nm} \text{ + ions} \]
\[ - 0.100 \text{ nm} \text{ - ions} \]

At 25°C

\[ \Delta G^{\circ}_{\text{Born}} (H^+_1, \text{aq}) = -1050 \text{ kJ/mole} \]
\[ \Delta H^{\circ}_{\text{Born}} (H^+_1, \text{aq}) = -1090 \text{ kJ/mole} \]
\[ S^{\circ}_{\text{Born}} (H^+_1, \text{aq}) = -130 \text{ J/mole K} \]

To calibrate Born enthalpy, free energy, and entropy with thermodynamic solutions:

\[ \Delta G^{\circ}_{\text{solv}} = \Delta G^{\circ}_{\text{Born}} + 1050 \frac{\Delta T}{\text{mole}} \]
\[ \Delta H^{\circ}_{\text{solv}} = \Delta H^{\circ}_{\text{Born}} + 1090 \frac{\Delta T}{\text{mole}} \]
\[ S^{\circ}_{\text{solv}} = S^{\circ}_{\text{Born}} + 130 \text{ J/mole K} \]
Debye-Hückel Theory

Consider reaction

\[ A_{v+} B_{v-} \rightarrow v_+ A^{z+} + v_- B^{z-} \]

(molality) \( m \), \( m_+ = v_+ m \), \( m_- = v_- m \)

\( m \) = molality of salt that dissolves

For dilute aqueous solutions

\( m_i \approx c_i \) (moles/liter)

Also \( |v_+ z_+| = |v_- z_-| \) (charge neutrality)

Examples

\[ \text{NaCl} \rightarrow \text{Na}^{+} + \text{Cl}^{-} \]

\( m = .001 \), \( m_+ = .001 \), \( m_- = .001 \)

\( z_+ = +1 \), \( z_- = -1 \)

\( v_+ = v_- = 1 \)

\[ I = \text{ionic strength} \]

\[ = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} (0.001(1)^2 + 0.001(-1)^2) \]
MgCl$_2$ → Mg$^{2+}$ + 2Cl$^-$

$m_\text{Mg} = .001$
$m_\text{Cl} = .001$
$m_\text{e} = .002$
$z_+ = +2$
$z_- = -1$

$v_+ = 1$
$v_- = 2$

$v_+ z_+ + v_- z_- = 1(2) + 2(-1) = 0$

$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$

$= \frac{1}{2} (.001(4) + .002(-1)^2)$

$= .003$

**Electrical Potential in Vicinity of a Ion**

For an isolated ion of charge $z_i e$ at a radius $R_i$ in water, the electric potential at a distance $r$ is

$\phi_{\text{isolated}}(r) = \frac{z_i e}{4\pi\varepsilon_0 e_r}$
In a solution, however, counterions (ions of opposite charge from central ion) tend to concentrate near the central ion. This modifies $\phi(r)$. The Poisson-Boltzmann Equation needs to be solved

$$\nabla^2 \phi(r) = -\frac{1}{\varepsilon \varepsilon_0} \rho(r)$$

charge density

$$= -\frac{N\mu e}{\varepsilon \varepsilon_0} \sum_i m_i z_i e^{-z_i e \phi(r)/k_B T}$$

For dilute solutions

$$e^{-z_i e \phi(r)/k_B T} \ll 1$$

$$e^{-2i e \phi/\kappa_B T} \approx 1 - \frac{2i e \phi}{\kappa_B T}$$
\[ \sum_{i} \xi_{i} m_{i} e^{-2 \xi_{i} e \phi / k_{B} T} \]
\[ \approx \sum_{i} \xi \xi_{i} m_{i} - \frac{e \phi}{k_{B} T} \sum_{i} \xi_{i} m_{i} \]
\[ = -\frac{2e \phi}{k_{B} T} I \]

Substituting this into (1)

(3) \[ \nabla^{2} \phi(r) = -\chi^{2} \phi(-) \]
\[ \chi^{2} = \frac{2 N_{A} \epsilon_{0} e^{2}}{\epsilon_{0} e_{r} k_{B} T} I \]

In water at 25°C
\[ \chi = 3.29 \times 10^{9} \sqrt{I} \]
\[ \uparrow \text{ in m}^{-1} \]
\[ \Sigma \text{ in moles/liter} \]
\[ \chi \text{ is called the Debye-Hückel screening parameter and has units of 1/length.} \]
Now return to (4) and consider behavior at small $kr$:

$$\phi(r) \approx \frac{Z_i e}{4\pi\varepsilon_0 kr} e^{-kr} \approx \frac{Z_i e}{4\pi\varepsilon_0 kr} - \frac{Z_i e K}{4\pi\varepsilon_0 r}$$

The first term represents the potential of the ion itself and the second term is the potential produced by neighboring ions.

This latter contribution is of interest to us since it is the concentration of counter ions near the central ion that is responsible for thermodynamic non-ideality:

$$\phi' = -\frac{Z_i e K}{4\pi\varepsilon_0 kr} \quad (5)$$

Suppose all ions are initially uncharged and we gradually charge them.
\[ z_i^* = z_i \delta S \]

and (5) becomes
\[ \phi^* = -\frac{z_i e e_x}{4\pi \varepsilon_0 \varepsilon_r} \]

"Turning up" the charge by an amount \( d\delta S \) is equivalent to raising the charge on the central ion by \( 4\pi e dS \). The electric work per ion is
\[ dW_i = \phi^* z_i e dS \]
\[ = -\left( \frac{e^2 e_x}{4\pi \varepsilon_0 \varepsilon_r} \right) z_i^2 \delta S dS \]

Suppose we have 1 liter or 1 kg of solvent. The total work of charging all ions is
\[ dW_{elec} = N_{av} \sum_i e_i dW_i \]

\[ \text{molality} \times \text{molarity} \]

Charging up from \( S = 0 \) to 1
\[ W_{elec} = 6.01 = -\frac{N_{av} e^2 e_x}{8\pi \varepsilon_0 \varepsilon_r} \sum_i z_i \]
\[ \rightarrow \text{electric free energy} \]
\[ m_j = \frac{\partial G_j}{\partial n_j} \approx \frac{\partial G_j}{\partial m_j} \]

\[ = -\frac{N_{\text{Av}} e^2 x_j^2}{8\pi\varepsilon_0\varepsilon_r} \quad (6) \]

In practice, we define the activity \( x_j \) (Henry standard state):

\[ m_j = m_j + RT \ln a_j \]

\[ = m_j^\text{H} + RT \ln m_j + RT \ln Y_j \]

ideal part \quad electric part

and cannot separate ions individually. Consider a single salt:

\[ A_j^+ + B_j^- \rightleftharpoons u^+ A^2+ + u^- B^2- \]

\[ M_{\text{salt}} = u^+ M^+ + u^- M^- \equiv uM^\pm \quad (8) \]

\[ u = u^+ + u^- \]

\[ M^\pm = \text{mean ionic chemical potential} \]
From (6) and (7)

\[ \ln Y_i = -\frac{N_a e^2 x_i}{8\pi \varepsilon_0 \varepsilon_r RT} z_i^2 \]

From (7) and (8)

\[ u \ln Y_\pm = u_+ \ln Y_+ + u_- \ln Y_- \]  \hspace{1cm} (9)

\[ \ln Y_\pm = -\frac{N_a e^2 x}{8\pi \varepsilon_0 \varepsilon_r RT} \left( \frac{u_+ z_+^2 + u_- z_-^2}{u_+ + u_-} \right) \]

\[ = -\frac{N_a e^2 x}{8\pi \varepsilon_0 \varepsilon_r RT} \left| z_+ - z_- \right| \]

In water at 25°C this becomes

\[ \log_{10} Y_\pm = -0.5092 \left| z_+ - z_- \right| \sqrt{I} \]  \hspace{1cm} (10)

From (9) we also have

for the mean activity coefficient

\[ \ln Y_\pm^u = \ln Y_+^u + \ln Y_-^u \]

\[ = \ln Y_+^u + Y_-^u \]

\[ Y_\pm = (Y_+^u + Y_-^u)^{1/2} \]
Solubility of Weakly Dissociating Salts

\[ A_{u^+}B_{u^-} \rightleftharpoons u_+A^{2+} + u_-B^{u^-} \]

\[ K_{sp} = a_+ a_- = (m_+ u_+) (Y_+ u_+) = (m_+ u_-) Y_+ \]

Example: \( K_{sp} \) for AgCl is \( 1.8 \times 10^{-10} \)

A) How many gm AgCl dissolve in 1 Kg of distilled water?

\( \log Y_+ = -0.5092 \) \( 1.2_{+2} \sqrt{E} = 0 \)

\[ Y_+ = 1.0 \]

Also, \( u_+ = u_- = 1 \)

\[ m_+ = m_- = m_0 = \text{AgCl dissolved} \]

\[ 1.8 \times 10^{-10} = K_{sp} = m_0^2 Y_+ = m_0^2 \]

\[ m_0 = 1.34 \times 10^{-5} \text{ moles} \]
\[ c \cdot \text{AgCl} \]

mass = \((143.32 \text{ \text{g/mol}})(1.34 \times 10^{-5})\)  
\(= 1.92 \times 10^{-3} \text{ gm.} \)

B) Repeat for \(I = 0.02 \text{ mol/L} \) for

\[ \log_{10} Y_+ = -0.5092/2.31 \sqrt{I} \]
\(= -0.0720 \)
\[ Y_+ = 0.9305 \]
\[ 1.8 \times 10^{-10} = n_0^2 Y_+^2 \]
\(= n_0^2 (0.866) \)
\[ n_0 = 1.44 \times 10^{-5} \]

mass of AgCl dissolving in 1 L of solution  
\(= (143.32)(1.44 \times 10^{-5}) \)
\(= 2.07 \times 10^{-3} \text{ gm} \)

Solubility increases as added salt increases.
Electrochemistry is basically the chemistry of electron transfer.

\[ Cu^{+2}(aq) + Zn \rightarrow Cu + Zn^{+2}(aq) \]

This is a spontaneous process so \( \Delta G < 0 \).
Also \( \Delta G \leq \Delta W_{\text{non PV}} \) at constant \( T \) and \( P \).

Scientists (like Volterra, late 1700's) used reactions like this to construct the first batteries.
Can we "harness" this reaction to do useful work?

Salt Bridge - essential to maintain charge neutrality (complete electric circuit)

Shorthand notation

Zn(s) | ZnSO₄(ag) || CuSO₄(ag) | Cu(s)
(anode) (cathode)
cross-sectional area = A

Consider a wire (shown above) with voltage \( \Delta \phi \) applied across it:

\[ \Delta \phi = i R \delta \]  (Ohm's Law)

\( R \) in volts, \( \delta \) in current (in amperes = coul/sec)

Also \( R = \frac{\rho}{\Delta A} \)

\( \rho \) is resistivity (depends on material (Cu, Ag, etc.) but not geometry)

In our "battery" (previous page) current flows so there must be a \( \Delta \phi \).
Now consider 2 "batteries" that are identical to each other in all respects except in $l$ (length of wire between anode and cathode).

\[ \Delta \phi \text{ same for both} \]

\[ R_{II} = 2R_I \]

\[ i_{II} = \frac{1}{2} i_I \]

**Important Point**

$\Delta \phi$ depends on fundamental chemistry of particular electron transfer reaction. In this case $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$ is unimportant.

other
Current is amount of charge moved
\[ i = \frac{dQ}{dt} = \frac{d}{dt} (-n \, \text{mol} \, \text{e}^{-}) = -F \frac{dn}{dt} \]
moles electrons
\[ F = \text{Avogadro's number} = (6.02 \times 10^{23})(1.602 \times 10^{-19} \text{ coul}) \]
(Faraday) = 96,485 coul/mole

In the Zn/Cu cell, suppose \( \Delta \phi = 1 \text{ volt} \) and \( R = 100 \text{ ohm} \). How many \( \text{gm} \) of Cu will form on the Cu electrode in 1 hour?

\[ i = \frac{\Delta \phi}{R} = 0.01 \text{ volt} \, \text{ohm}^{-1} = 0.01 \text{ amp} = 0.01 \text{ coul/sec} \]

\[ Q = \text{amt charge moved} = i \cdot t = 36 \text{ coul} \]
\[ n = \text{mol} \, \text{e}^{-} \, \text{moved} = \frac{Q}{F} = 3.733 \times 10^{-4} \]

moles Cu formed = \( \frac{1}{2} \) moles e-
\[ = 1.866 \times 10^{-4} \text{ mol/ces} \]

\[ \text{gm Cu formed} = (1.866 \times 10^{-4} \text{ mol/ces}) \times (63.55 \text{ g/mole}) = 0.0117 \text{ gm} \]
**Electrical Work**

\[ dW_{\text{non-exp}} = \Delta \phi \, dQ = -\int \phi \, d\mu \]

A "battery" is any electrical cell that can push current through a wire.

Suppose we now use another battery (variable voltage) to oppose the current flow of our cell.

If we adjust our variable voltage to just match \( \Delta \phi \), no current flows. This corresponds to a reversible electric engine!

\[ dW_{\text{rev}} = -F \, \phi \, d\mu = \Delta G \]

\[ \text{cathode} \quad \text{anode} \]

\[ = (\mu^- - \mu^+) \, d\mu \]
\[-F \delta \phi = -F(\phi^{\text{cath}} - \phi^{\text{an}})\]

\[= \mu_{e^{\text{cath}}} - \mu_{e^{\text{an}}}\]

Within an additive constant \(\mu_e = -\delta \phi\)

Now consider the reversible conversion of \(dx\) moles of \(Zn\) to \(Zn^{+2}\) (anode) and \(Cu^{+2}\) "Cu" (cathode).

Anode: \(Zn \rightarrow Zn^{+2}(aq) + 2e^-\)

\[dG_{\text{anode}} = (-2\delta \phi + M_{Zn^{+2}} - M_{Zn})dx\]

\[M_{Zn^{+2}} = M_{Zn} + RT \ln a_{Zn^{+2}}\]

The potential of the electrons are raised (by variable voltage battery) to \(\phi_e\) as their brought to cathode

Cathode: \(Cu^{+2} + 2e^- \rightarrow Cu\)

\[dG_{\text{cathode}} = (M_{Cu} - M_{Cu^{+2}} + 2\delta \phi)\]

\[M_{Cu^{+2}} = M_{Cu} + RT \ln a_{Cu^{+2}}\]
Since the whole process is reversible

\[ \Delta G^0 = \Delta G_{\text{anode}} + \Delta G_{\text{cathode}} \]

\[ = 8 \times (\Delta G^0 + RT \ln \frac{a_{3n^2}}{a_{Cu^{2+}}}) \]

\[ \Delta G^0 = M_{Cu} - M_{Zn} + M_{Cu^{2+}} - M_{Zn^{2+}} \]

\[ -2 \overline{F} (\overline{\psi} - \overline{\psi}_A) = \Delta G^0 + RT \ln \frac{a_{3n^2}}{a_{Cu^{2+}}} \]

To emphasize we are dealing with a reversible electrochemical cell, \( \Delta G^0 \) is represented by \( E \).

In general

\[ -n \overline{F} E = \Delta G^0 + RT \ln K \]

mols e\(^-\) transferred

If our species are at unit activity, \( K \rightarrow 1 \) and

\[ -n \overline{F} E^0 = \Delta G^0 \]

\( ^0 \) indicates all species at unit activity
All electrochemical reactions involve an oxidation (at anode) and a reduction (at cathode). It is convenient to write

\[ E^0 = E^0_{\text{reduction}} + E^0_{\text{oxidation}} \]

(cathode) (anode)

However, an oxidation is just a reduction in reverse.

The convention is to define all half cell reactions as reduction reactions. Following this convention

\[ E^0 = E^0_{\text{cathode}} - E^0_{\text{anode}} \]

reduction half cell reactions.

Important note

Since \( E^0 \)'s are intensive variables, they are independent of stoichiometry.
Consider the reaction

\[ 2\text{MnO}_4^{-2} (aq) + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2^- + 4\text{OH}^- + \text{O}_2 (g) \]

Calculate \( E^0 \) and \( K_c \)

From Table 11.2, relevant half cell reactions are

\[ 2\text{MnO}_4^{-2} + 4\text{H}_2\text{O} + 4e^- \rightarrow 2\text{MnO}_2^- + 8\text{OH}^- \quad E_1^0 \]

\[ 4e^- + \text{O}_2 (g) + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^- \quad E_2^0 \]

From Table, \( E_1^0 = +.600 \)

\( E_2^0 = +.401 \)

Reversing the 2nd reaction & adding it to the first gives the desired reaction

\[ E^0 = E_1^0 - E_2^0 = .199 \text{ Volts} \]

\[
\ln K = \frac{\Delta G^0}{RT} = + \frac{nF E^0}{RT} = \left( \frac{\text{coulamp} \times \text{Volt}}{\text{Joule}} \right) \]

\[
= (4)(76.485 \text{ coul})(.199 \text{ volt}) \]

\[
= \frac{1.314 \text{ J}}{298.15} = 30.98 \]

\[ K = 2.96 \times 10^{13} \]
The two half-reactions (written as reductions) can be written as follows:

Right electrode: \( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \) \( E^0_+ = 0.771 \text{ V} \)

Left electrode: \( \text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^- \) \( E^-_c = 0.222 \text{ V} \)

The electrode potentials are

\[
E_+ = 0.771 - 0.05916 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right)
\]

\[
E_- = 0.222 - 0.05916 \log([\text{Cl}^-])
\]

and the cell voltage is the difference \( E_+ - E_- \):

\[
E = \left( 0.771 - 0.05916 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \right) - \left( 0.222 - 0.05916 \log([\text{Cl}^-]) \right) = 0.197
\]

Figure 15-1 A galvanic cell that can be used to measure the quotient \( [\text{Fe}^{2+}] / [\text{Fe}^{3+}] \) in the right half-cell. The Pt wire is the indicator electrode, and the entire left half-cell plus salt bridge (enclosed by the dashed line) can be considered a reference electrode.

Pt electrode serves as site for \( \text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \)

Suppose \( E = 0.435 \), what is \( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \)?

\[
E = 0.435 = 0.771 - 0.05916 \log_{10} \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} - 0.197
\]

\[
0.05916 \log_{10} \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0.771 - 0.197 - 0.435 = 0.139
\]

\[
\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 22.4
\]
Have you noticed that the electrodes we talk about in theory never look like the electrodes you actually use in the lab? Modern electrodes are alot more sophisticated, but the fundamental chemistry is the same. Above is the streamlined version of the previous transparency.

A common electrode

Basic chemistry

\[ \frac{1}{2} \text{Hg}_2 \text{Cl}_2 (s) + e^- \rightarrow \text{Hg}(l) + \text{Cl}^- (aq) \]

\[ E_0 = .268 \text{ V} \]

\[ E(\text{sat. Cl}^-) = .241 \text{ V} \]
Electrochemical Series

\[ \text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn} (s) \quad E^0 = -0.762 \]
\[ \text{Ag}^+ (aq) + e^- \rightarrow \text{Ag} (s) \quad E^0 = +0.800 \]
\[ \text{Au}^+ (aq) + e^- \rightarrow \text{Au} (s) \quad E^0 = 1.692 \]

For reduction of \( \text{MnO}_4^- \) to \( \text{Mn}^{2+} \) in acidic media,
\[ \text{MnO}_4^- + 8H^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4H_2O \quad E^0 = +1.51 \]

Some metal (Zn, Ag, or Au) needs to act as a reducing agent

\[ E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = 1.51 - E^0 \]

If \( E_{\text{cell}} > 0 \), \( \Delta G < 0 \) and the reaction occurs.

This will be true for Zn and Ag, but not Au.
Battery Efficiency

\[
\text{max } \Delta G^\circ = -\Delta G^\circ
\]

Free energy change

(example convert 1 mole of Zn(s) and Cu^{+2}(aq) (a = 1) to 1 mole of Cu(s) and Zn^{+2} (a = 1)

\[
\Delta G^\circ = -212.6 \text{ kJ}
\]

\[
\Delta H^\circ = -218.7 \text{ kJ}
\]

Defining the efficiency of a battery

\[
\eta = \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{212.6}{218.7}
\]

\[
\eta = 97.2\%
\]

This is much better than heat engines!
Kinetics

Thermodynamics can tell us if a chemical reaction might occur.

Rates measured by monitoring concentrations of reactants/end products

\[ \text{[N}_2\text{O]} \]
\[ \text{[N}_2\text{]} \qquad 2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2 \]
\[ \text{[O}_2\text{]} \]
\[ \text{[O]} \]

Trace quantities (O in above example) can provide valuable information about the mechanism of the reaction.

Series of elementary reactions involved in overall reaction

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \] \quad \{ \text{elementary reactions} \}
\[ \text{O} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 \]
\[ 2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2 \] \quad \text{net}
Rates of Reaction

\[ aA + bB \rightarrow yY + zZ \]

Rate = \( R = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{y} \frac{d[Y]}{dt} + \frac{1}{z} \frac{d[Z]}{dt} \)

--- for reactants ----

--- for products ---

Example: \( 2N_2O \rightarrow 2N_2 + O_2 \)

\[ R = -\frac{1}{2} \frac{d[N_2O]}{dt} + \frac{1}{2} \frac{d[N_2]}{dt} = \frac{d[O_2]}{dt} \]

Because of intermediates, these conditions are not strictly valid. However, since intermediates are usually unstable and present in very low concentrations, it is an excellent approximation.

Variation in \( P_{\text{tot}} \) in gas phase reaction (\( V \text{ constant} \))

\[ aA + bB \rightarrow yY + zZ \]

\[ P_{\text{tot}} = P_A + P_B + P_Y + P_Z \quad \text{partial pressures} \]

\[ \frac{dP_{\text{tot}}}{dt} = \frac{dP_A}{dt} + \frac{dP_B}{dt} + \frac{dP_Y}{dt} + \frac{dP_Z}{dt} \]

But \[ P_A = \frac{nART}{V} = [A]RT \]
\[
\frac{dP_t}{dt} = RT \left[ \frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[Y]}{dt} + \frac{d[Z]}{dt} \right] \\
-av - bu + yu + zu
\]

(let \( v \) denote rate (to avoid confusion with gas constant, \( R \))

\[
\frac{dP_t}{dt} = RTv(y+z-a-b)
\]

\[
\therefore \quad v = \frac{1}{RT(y+z-a-b)} \frac{dP_t}{dt}
\]

Example: \( 2N_2O \rightarrow 2N_2 + O_2 \)

\( a=2, b=0, y=2, z=1 \)

\[
\therefore \quad v = \frac{1}{RT} \frac{dP_t}{dt}
\]

(measurable)

**Rate Laws**

Rates depend on: \( T \), concentrations, presence of catalyst

.......

We can usually write

\[
v = f(T, P_t, [A], [B], ...)
\]

Oftentimes, rates can be written

\[
v = A(T) [A]^a [B]^b ....
\]
\( k(T) \) = rate constant
\( \alpha \) = reaction order with respect to A
\( \beta \) = reaction order with respect to B
Etc.

\( \alpha + \beta + \ldots \) = overall reaction order

In general, there is no connection between \( \alpha \) and \( \beta \) and stoichiometry.

In the example, \( 2N_2O \rightarrow 2N_2 + O_2 \), you might expect the reaction rate would be second order with respect to \( N_2O \). This, however, is not the case.

We shall see later that reaction mechanism and reaction order are interrelated.
Determination of Reaction Order

A) Differential rate laws (Works well for slow reactions.)

\[ A + B + C \rightarrow \text{products} \]

\[ v = k [A]^x [B]^y [C]^z \]

<table>
<thead>
<tr>
<th>( [A]_0 )</th>
<th>( [B]_0 )</th>
<th>( [C]_0 )</th>
<th>( v_{\text{Initial}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) .10</td>
<td>.10</td>
<td>.10</td>
<td>.05</td>
</tr>
<tr>
<td>2) .20</td>
<td>.10</td>
<td>.10</td>
<td>.10</td>
</tr>
<tr>
<td>3) .10</td>
<td>.20</td>
<td>.10</td>
<td>.05</td>
</tr>
<tr>
<td>4) .10</td>
<td>.10</td>
<td>.20</td>
<td>.20</td>
</tr>
</tbody>
</table>

Comparing 1) and 2), doubling \([A]_0\), doubles \(v\), \(\Rightarrow x = 1\)

Comparing 1) and 3), doubling \([B]_0\), does not change \(v\), \(\Rightarrow y = 0\)

Comparing 1) and 4), doubling \([C]_0\), increases \(v\) by factor of \(\sqrt{y}\), \(\Rightarrow z = 2\)

Consequently

\[ v = k [A][C]^2 \]
Integrated Rate Laws

1) First order \[A \rightarrow \text{products}\]

Examples: radioactive decay, unimolecular decomposition

\[ v = -\frac{d[A]}{dt} = k[A] \]

\[ + \frac{d[A]}{[A]} = -k \, dt \]

Integrate this from \( t=0 \) to \( t=t \) and \([A] = [A]_0\) to \([A]\)

\[ \ln \frac{[A]}{[A]_0} = -kt \]

\[ A = [A]_0 e^{-kt} \]

Half life - time it takes \([A]\) to drop to \([A]_0/2\).

For first order reactions

\[ \frac{1}{2} [A]_0 = [A]_0 e^{-kt_{1/2}} \]

\[ \ln \frac{1}{2} = -kt_{1/2} \Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \]
Note that $t_{1/2}$ is independent of amount of starting material. This is only true for 1st order reactions.

Example:

$^{14}$C decays with $t_{1/2} = 5760$ years. Living matter maintains enough $^{14}$C to produce 15.3 disintegrations per minute per gram of C present.

A small bone from a mammoth found in Alaska produces 0.8 disintegrations/min. Carbon analysis shows there is 0.15 gm of C in the sample. When did the mammoth die?

\[
\frac{0.8 \text{ dis/min}}{0.15 \text{ gm}} = 5.33 \frac{\text{dis}}{\text{min.gm}} = C
\]

\[
c = c_0e^{-kt} = c_0e^{-0.693t/t_{1/2}}
\]

\[
5.33 \rightarrow \frac{\text{dis/min.gm at death}}{\text{dis/min.gm}} = 15.3
\]

\[
\ln \frac{c}{c_0} = -\frac{0.693}{t_{1/2}} t
\]

\[
t = -\frac{t_{1/2}}{0.693} \ln \frac{c}{c_0} = -\frac{5760 \text{ years}}{0.693} \ln \left( \frac{5.33}{15.3} \right)
\]

\[
= 8760 \text{ years}
\]
Second Order Reactions

\[ A + B \rightarrow 2x \]

Initial \((t=0)\)

\[
\begin{align*}
& a_0 \quad b_0 \\
& a_0 - x \quad b_0 - x
\end{align*}
\]

time = \( t \)

\[
\begin{align*}
\frac{d[A]}{dt} &= -\frac{d[B]}{dt} + \frac{d[x]}{dt} \\
&= k[A][B] \\
&= k(a_0 - x)(b_0 - x)
\end{align*}
\]

\[
\frac{dx}{dt} = k(a_0 - x)(b_0 - x) \Rightarrow \frac{dx}{(a_0 - x)(b_0 - x)} = kdt
\]

2 cases

\( a_0 = b_0 \) \((2A \rightarrow 2, \text{ for example})\)

\[
\int_0^{x_f} \frac{dx}{(a_0 - x)^2} = \int_0^{t_f} kdt = kt_f
\]

Let \( y = a_0 - x, \ dy = -dx \)

\[
k t_f = -\int_0^{a_f} \frac{dy}{y^2} = -y^{-2+1} \bigg|_{a_f}^{a_0} = \frac{1}{a_f} - \frac{1}{a_0}
\]

Let \( a_f \rightarrow a, t_f \rightarrow t \)

\[
\frac{1}{a} = \frac{1}{a_0} + kt
\]

\[
\frac{1}{a} \quad \text{slope} = k
\]
Half-life) When \( t = t_{1/2} \), \( a = \frac{1}{2}a_0 \)

\[
\frac{2}{a_0} = \frac{1}{a_0} + k t_{1/2}
\]

\( t_{1/2} = \frac{1}{k a_0} \)

Note that \( t_{1/2} \) depends on \( a_0 \)!

Example) Suppose the reaction

\[
\text{CH}_3\text{COH} + \text{CH}_3\text{COH} \rightarrow \text{CH}_3\text{CO}^\cdot \text{CH}_3 + \text{H}_2\text{O}
\]

is 2nd order in acetic acid with \( k = 10^{-3} \text{ liter/mole sec.} \) IF \( a_0 = 0.01 \text{ moles/liter} \)

\[
t_{1/2} = \frac{1}{(10^{-3} \text{ liter/mole sec})(0.01 \text{ mole/liter})} = 10^5 \text{ sec} = 27.8 \text{ hours}
\]

IF \( a_0 = 0.005 \text{ moles/liter} \)

\[
t_{1/2} = 2 \times 10^5 \text{ sec} = 55.5 \text{ hours}
\]

As reaction proceeds, \( t_{1/2} \) increases.
Case 2) \( a_0 = b_0 \)
(This occurs when A and B are different reactants at different starting concs.)

\[
\begin{align*}
\Delta T_f &= \int_0^x \frac{dx}{(a_0-x)(b_0-x)} \\
&= \frac{1}{b_0-a_0} \int_0^x \left( \frac{1}{a_0-x} - \frac{1}{b_0-x} \right) dx \\
&= \frac{1}{b_0-a_0} \left[ -\int \frac{dy}{a_0} + \int \frac{dy}{b_0} \right] \\
&= \frac{1}{b_0-a_0} \left[ \ln \frac{b_0}{a_0} - \ln \frac{a_0}{b_0} \right] = \frac{1}{b_0-a_0} \ln \left( \frac{b_0 a_0}{b_0-a_0} \right)
\end{align*}
\]

Applications

Suppose \( a_0 \gg b_0 \) (one species is \( \text{H}_2\text{O} \) and \( a_0 = 55 \text{ moles / liter} \))

\[
\begin{align*}
a_0 &= 55 \text{ M} \\
b_0 &= 0.1 \text{ M} \\
b \text{ lies between 0 and 0.1} \\
a \text{ " " 55 and 55.9}
\end{align*}
\]

To a good approx. \( a \approx a_0, b - a, x - a_0 \)

\[
\Delta T_f = -\frac{1}{a_0} \ln \left( \frac{b_0}{b} \right) \Rightarrow b_0 = b_0 e^{-a_0 \Delta T_f}
\]
Reaction is "pseudo first order" in B

Effective rate constant = $a_0 \cdot k$

This is called "swamping out"

**Coupled Reactions**

Consider the overall react.

$$X \rightarrow B$$

Suppose, however, the actual mechanism involves 2 steps

$$X \xrightarrow{k_1} Y \quad (Y = \text{intermediate})$$

$$Y \xrightarrow{k_2} P$$

$$\frac{d[X]}{dt} = -k_1[Y] \Rightarrow [X] = [X]_0 e^{-k_1 t}$$

Also

$$\text{Rate} = \frac{d[Y]}{dt} = k_2[Y]$$

In order to solve these, we need to know how $[Y]$ varies with time.

From mechanism,
\[
\frac{dY}{dt} = A_1(x) - A_2(Y) \quad \text{depend on} \quad t
\]

\[
= A_1(x_0) e^{-A_1 t} - A_2(Y)
\]

This is a more complicated differential equation than the 1st and 2nd order reactions considered previously. This one is solvable.

There are programs available that can solve D.E.Q.'s such as this. One program is \textsc{Mathematica}. The command required to solve this is

\[
\text{DSolve}[y'[t] == A_1 x_0 \exp[-A_1 t] \leq -A_2 y[t], y[t], t]
\]

The general solution is

\[
Y = c e^{-A_2 t} + \frac{A_1(x_0)}{A_2 - A_1} e^{-A_1 t}
\]

integration constant \( \frac{A_1(x_0)}{A_2 - A_1} \).

The constant \( c \) depends on starting conditions. In our example, suppose \( Y = 0 \) (no intermediate present at \( t = 0 \)).

\[
0 = c + \frac{A_1(x_0)}{A_2 - A_1} \Rightarrow c = -\frac{A_1(x_0)}{A_2 - A_1}
\]
\[
\begin{align*}
(Y) &= \frac{A_1(x)}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \\
\frac{(Y)}{(X)} &= \frac{A_1}{k_2 - k_1} \left( 1 - e^{-(k_2 - k_1) t} \right)
\end{align*}
\]

There are 2 cases we need to consider:

**Case 1**) \( k_2 < k_1 \) \( \rightarrow \) \( X \) more stable than \( Y \)

\[
\frac{(Y)}{(X)} = \frac{A_1}{k_1 - k_2} \left( e^{\frac{(k_1 - k_2) t}{k_1 - k_2}} - 1 \right)
\]

\( \frac{A_1}{k_1 - k_2} \approx -\infty \quad (t \rightarrow \infty) \)

**Case 2**) \( k_2 > k_1 \) \( \leftarrow \) \( X \) more stable than \( Y \)

\[
\frac{(Y)}{(X)} = \frac{A_1}{k_2 - k_1} \left( 1 - e^{\frac{(k_2 - k_1) t}{k_2 - k_1}} \right)
\]

\( \frac{A_1}{k_2 - k_1} \approx \infty \quad (t \rightarrow \infty) \)

- **diverges**
- **t**
- **All X decays  Y**
- \( \frac{A_1}{(k_2 - k_1)} \quad \frac{A_1(x)}{k_2 - k_1} \)

\( \frac{A_1}{(k_2 - k_1)} \approx \) steady state value
The most common situation is for Y to be a reactive intermediate with \( k_2 \gg k_1 \).

Example

Radon gas, \( Rn \), decays with lifetime 3.82 days. It is formed from the radioactive decay of Radium, \( Ra \). The coupled decay reactions are

\[
Ra \rightarrow Rn \quad t_{1/2} = 1590 \text{ yrs}
\]

\[
Rn \rightarrow \text{products} \quad t_{1/2} = 3.82 \text{ days}
\]

(a) What are \( k_1 \), \( k_2 \), and \( \lambda_2 \)?

\[
\lambda_1 = \frac{0.693}{1590 \text{ yrs}} \times \frac{365.25 \text{ days}}{y} = 1.193 \times 10^{-6} \text{ day}^{-1}
\]

\[
\lambda_2 = \frac{0.693}{3.82 \text{ days}} = 0.1814 \text{ day}^{-1}
\]

(Note that \( \lambda_2 \gg \lambda_1 \).)

(b) What is the "steady state" conc. of \( Rn \) relative to \( Ra \)?

\[
\left( \frac{[Rn]}{[Ra]} \right)_{ss} = \frac{\lambda_1}{\lambda_2 - \lambda_1} = \frac{1.193 \times 10^{-6}}{0.1814} = 6.58 \times 10^{-6}
\]
(c) Suppose there is a small amount of Ra in the drywall of a house. Suppose we start with no Ra at t=0 and then stop ventilating the house. How long does it take for (Ra) to reach 90% of its steady state value?

\[
(1 - e^{-(k_2-k_1)t}) = 0.90
\]
\[
e^{-(k_2-k_1)t} = 0.10 \times e^{-k_2t}
\]
\[
t = 12.67 \text{ days}
\]

**Steady State Approximation**

Most reactive intermediates reach "steady state" values early in the course of a reaction. Let \( Y \) denote a reactive intermediate in any mechanism (and not just the "two step" mechanism of the previous example). For reactive intermediates, the steady state approx. says

\[
0 = \frac{d(Y)}{dt}
\]
Example) Consider reactants $A + B \xrightleftharpoons[k_2]{k_1} X \xleftarrow{k_{-1}}$ encounter complex $X \xrightarrow{k_2} P \leftarrow$ product

rate = \frac{d(P)}{dt} \quad \text{or} \quad \frac{d(X)}{dt} = k_1(A)(B) - k_{-1}(X)

Apply "steady state approximation" to $X$

0 = \frac{d(X)}{dt} \Rightarrow (X) = \frac{k_1(A)(B)}{k_2 + k_{-1}}

V = rate = k_2(x) = \frac{k_1(A)(B)}{k_2 + k_{-1}}

Note that the reaction is second order (overall) of first order with respect to reactants $A$ and $B$.

There are several special cases we'll consider next.
Case 1) \( k_{-1} \gg k_2 \)

(Far more likely \( X \) will revert to reactants than advance to product.)

\[
U \approx k_2 \frac{k_1}{k_{-1}} (A)(B) \tag{1}
\]

If reaction didn't occur at all

\[
A + B \xrightarrow{\cancel{X}} X
\]

At equilibrium

\[
0 = \frac{d[X]}{dt} = k_1 (A)(B) - k_{-1} (X)
\]

\[
K_{eq} = \frac{(X)}{(A)(B)} = \frac{\text{out}}{\text{in}}
\]

Use this in \( \#1 \) above

\[
U = k_2 K_{eq} (A)(B)
\]

The reaction is overall 2nd order (this is called bimolecular) and

\[
K_{eq} \approx k_2 K_{eq} \frac{k_1}{k_{-1}}
\]
Case 2) \( k_{-1} \gg k_2 \)

(Far more likely X will convert to product rather than revert to reactants)

\[ v = \frac{k_{-1} k_2}{k_2} (A)(B) = k_{-1} (A)(B) \]

Reaction is bimolecular, but with \( k_{\text{eff}} = k_{-1} \)

**Activation Energies**

The easiest way to interpret the above 2 cases is in terms of activation energy

\[ E^* = \text{activation energy} \]

\[ \frac{E^*}{k_B T} \gg 1, \quad k_{-1} \gg k_2 \]

\[ \ll 1, \quad k_2 \gg k_{-1} \]
Diffusion Controlled Reaction (in solution)

\[ \langle x_A^2 \rangle = 2D_A t \]
\[ \langle x_B^2 \rangle = 2D_B t \]

\[ k_1 = 4\pi (D_A + D_B) \frac{r_A}{r_A + r_B} (1000 \, \text{N} \cdot \text{Av}) \]

\[ \frac{2}{\text{mole sec}} \]
\[ \text{m}^2/\text{sec} \]

\[ D_A = \frac{k_B T}{6\pi \eta r_A} \]

Estimate DCR rate, \( k_1 \), for protein (\( r_A = 20\,\text{Å} \)) and substrate (\( r_B = 3\,\text{Å} \)) in water at 20°C (\( \eta = 0.01 \) poise = 0.01 gm/cm sec). Also take \( r_A = r_A + r_B \)

\[ D_A + D_B = \frac{k_B T}{6\pi \eta} \left( \frac{1}{r_A} + \frac{1}{r_B} \right) = \ldots 8.23 \times 10^{-10} \, \text{m}^2/\text{sec} \]

\[ k_1 = \frac{1}{4\pi} \left( 8.23 \times 10^{-10} \, \text{m}^2/\text{sec} \right) \left( 23 \times 10^{-10} \, \text{m} \right) \left( 6.02 \times 10^{23} \right) \frac{\text{mole}}{\text{sec}} = 1.93 \times 10^{10} \]
This is actually an "upper bound" on reactions in solution. It would be physically impossible for a reaction to proceed faster than this in solution.

\[
\begin{array}{cccc}
\text{Enzyme} & \text{substrate} & A_v (\text{mole/sec}) \\
\text{acetylcholinesterase} & \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array} + \text{CH}_3 & 1.1 \times 10^{10} \\
\text{superoxide dismutase} & \text{O}_2 & 2 \times 10^9 \\
\text{chymotrypsin} & \text{proflavin} & 1.1 \times 10^8 \\
\text{lactate dehydrogenase} & \text{NADH} & 5.5 \times 10^7
\end{array}
\]

In the fastest of these reactions the reactions are nearly diffusion controlled. Hence, the catalyst effectively reduces $E^*$ to almost nothing.
Temperature Dependence of Elementary Reactions

Elementary reactions are frequently described by the Arrhenius rate expression

$$A(T) = Ae^{-E^* / RT}$$

This can be verified by studying the temperature dependence of $A(T)$

$$\ln A(T) = \ln A - \frac{E^*}{RT}$$

- intercept $= \ln A$
- slope $= -\frac{E^*}{R}$
Complex Mechanisms

The reaction

\[ \text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl} \]

is believed to occur by the following mechanism:

\[ \text{Cl}_2 + h\nu \rightarrow 2 \text{Cl} \cdot \]

\[ \text{Cl}^- + \text{CHCl}_3 \rightarrow \text{HCl} + \cdot \text{CCl}_3 \]

\[ \cdot \text{CCl}_3 + \text{Cl}_2 \rightarrow \cdot \text{CCl}_4 + \cdot \text{Cl} \]

\[ 2 \text{Cl}^- \rightarrow \text{Cl}_2 \]

1. \[ \nu = \frac{d(\text{HCl})}{dt} = A_2 (\text{Cl}) (\text{CHCl}_3) \]

2. \[ \nu = \frac{d(\text{CCl}_4)}{dt} = A_3 (\cdot \text{CCl}_3) (\cdot \text{Cl}) \]

Also assume

\[ A_1 (\text{Cl}_2) = 2I_n \]

The problem with the rates (\(\nu\)'s) above is they contain reactive intermediates.
Apply SSE to \( \text{Cl}_2 + \text{CCL}_3 \)

\[
0 = \frac{d(c(e))}{dt} = 2I_a - 2k_1(c(e))^2 - k_2(c(e))(c\text{HCl}) \\
+ k_3(c\text{Cl}_3 \times c(e))
\]

\[
0 = \frac{d(c(c\text{Cl}_3))}{dt} = k_2(c(e))(c\text{HCl}) - k_3(c\text{Cl}_3 \times c(e))
\]

Add \& solve for \( c(e) \)

\[
(c(e)) = \sqrt{\frac{I_a}{k_1}}
\]

Now use this in \# above \& solve for \( c(c\text{Cl}_3) \)

\[
k_3(c\text{Cl}_3 \times c(e)) = k_2 \sqrt{\frac{I_a}{k_1}} (c\text{HCl})
\]

\[
(c\text{Cl}_3) = \frac{k_3}{k_2} \sqrt{\frac{I_a}{k_1}} \frac{(c\text{HCl})}{(c(e))}
\]

From \#1 \( v = k_2 \sqrt{\frac{I_a}{k_1}} (c\text{HCl}) \)

From \#2 \( v = k_3 (c(e)) \frac{k_2}{k_3} \sqrt{\frac{I_a}{k_1}} \frac{(c\text{HCl})}{(c\text{Cl}_3)} \)

\[ k_{\text{eff}} = k_2 \sqrt{\frac{2I_a}{k_1}} (c\text{HCl}) \]
Despite a complex mechanism, the overall rate law is quite simple — first order in the reactant, CHCl₃.

Despite the apparent simplicity of the overall rate, a sense of the greater complexity of underlying mechanism can be grasped by considering the T-dependence of overall rate. Write

$$k_{\text{eff}} = A_{\text{eff}} e^{-E_{\text{eff}} / RT}$$

but

$$k_{\text{eff}} = I_a k_2 k_4^{-1/2}$$

$$= I_a^{1/2} (A_2 e^{-E_2 / RT})(A_4 e^{-E_4 / RT})^{-1/2}$$

$$= I_a^{1/2} A_2 A_4^{-1/2} \text{ Exp} \left[ -\frac{1}{RT} (E_2 - \frac{1}{2} E_4) \right]$$

$$\frac{A_{\text{eff}}}{E_{\text{eff}}}$$

If $E_4 > 2E_2$, the rate of the overall reaction would actually 

decrease with increasing $T$!
Chem 4110/6110
Physical Chemistry
Quiz # 1

Name: _____________________________

(Quiz is closed book, but one 8.5 by 11 inch sheet of notes can be used.)

(6) 1. The pressure of a gas in a manometer exceeds atmospheric pressure and supports a column of Hg 142 mm in height relative to the atmosphere. If atmospheric pressure is 749 mm Hg, the gas pressure (in mm Hg) is:

(a) 142 (b) 607 (c) 749 (d) 891

(6) 2. According to kinetic theory, what factor(s) determine the total energy of one mole of an ideal gas?

(a) the pressure (b) the temperature
(c) the mass of atoms comprising the gas
(d) all of the above

(6) 3. Consider gaseous samples of He (M = 4gm/mole) and Ar (M = 40 gm/mole) at the same T & P. If the effusion rate of Ar through a porous plug is 3 mmoles/min, the corresponding effusion rate for He will be (in mmoles/min)

(a) .95 (b) 3.00 (c) 3.16 (d) 9.49

(8) 4. The effective molecular weight of air is 28.8 gm/mole. Consider a building that occupies a volume of 1000 m³. Ignoring the volume of solid objects within, compute the mass of air within the building at 25 degrees C and 1 atm. You can assume the air behaves ideally.
5. Let $M$ be the mass (in grams) of air you computed in the previous problem. The heat capacities of ideal diatomic gases are $C_v = 5 \text{ cal/mole K}$ or $C_p = 7 \text{ cal/mole K}$. Ignoring the heat capacities of other objects within the building, the amount of heat (in cal) required to raise its temperature by 4 degrees C at a constant external pressure of would be approximately.

(a) $M \times 4 \times 5/28.8$  (b) $M \times 4 \times 7/28.8$
(c) $M \times 4 \times 5$  (d) $M \times 4 \times 7$

6. The van der Waals paramters for methane ($\text{CH}_4$) are $a = 0.2283 \text{ Pa m}^6\text{ mole}^{-2}$ and $b = 4.28 \times 10^{-5} \text{ m}^3\text{ mole}^{-1}$. The Boyle temperature of methane (in K) is

(a) 22.83  (b) 428  (c) 642  (d) 5334

7. The standard state enthalpies of formation of $\text{C(graphite)}$ and $\text{C(diamond)}$ are 0.00 and 1.90 $\text{kJ/mole}$. At one atmosphere pressure, the amount of heat absorbed by 2 moles of carbon in the transformation $\text{C(graphite)} \rightarrow \text{C(diamond)}$ would be (in kJ)

(a) -3.80  (b) -1.90  (c) +1.90  (d) +3.80

8. (Explain in 30 words or less.) Why is the standard state enthalpy of $\text{C(graphite)}$ 0.00 in the previous problem?

(End of Quiz 1)

Chem 4110/6110
Physical Chemistry
Quiz # 2

Name: ____________________________

(Quiz is closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. A reversible Carnot engine operates between a high temperature reservoir of 60 °C and a low temperature reservoir of 20 °C. The efficiency of the engine is

(a) -0.333  (b) 0.00  (c) +0.120  (d) +0.333

2. NaCl(s) (58.44 gm/mole) has a molar heat capacity ($C_p$) of 46 J/mole K and this heat capacity is independent of temperature to a good approximation. What is the amount of heat (in J) required to raise 10 gm of NaCl(s) from 25 °C to 50 °C?
(a) 43.  (b) 197.  (c) 1150  (d) 2690

(6) 3. What is the entropy change of the NaCl(s) in the previous problem (in J/K)?
(a) -6.34  (b) 6.34  (c) 3.704  (d) 5.456

(6) 4. The boiling point of CHCl₃ is 61 °C and its enthalpy of vaporization at that temperature is +29.4 kJ/mole K. The entropy change of one mole of CHCl₃ on going from the gas phase to the liquid phase at 61 °C is (in J/K)?
(a) -482.  (b) -88.0  (c) +88.8  (d) +482.

(6) 5. is equal to
(a) -P  (b) +P  (c) -S  (d) +S

(6) 6. According to the Third Law of Thermodynamics, the absolute entropy of any material at absolute zero is 0. If the molar heat capacity of a metal at low temperatures equals cT³, the absolute molar entropy of the metal at low temperatures equals
(a) 3cT²  (b) cT³  (c) cT³/3  (d) cT⁴/4
(6) 7. $\Delta G_{\text{sys}} < 0$ for spontaneous processes only under the following conditions

(a) $V$ and $T$ are constant
(b) $P$ and $T$ are constant
(c) Only if our system is isolated from the surroundings
(d) The process is carried out reversibly

(8) 8. One mole of an ideal gas expands adiabatically and irreversibly against a vacuum (no work is done). The final volume of the gas is twice the initial volume. If the initial temperature of the gas is $T$, what is

(i) the final temperature,
(ii) the entropy change of the gas?

(End of Quiz 2)

Chem 4110/6110
Physical Chemistry
Quiz # 3

Name: 

(Quiz is closed book, but one 8.5 by 11 inch sheet of notes can be used.)

(6) 1. The (pressure) equilibrium constant, $K_P^0$, for the reaction involving ideal gases

$$A + 2B \rightarrow C$$

at 25 °C and a total pressure of 1 atmosphere is 1000. What is $\Delta G^0$ (in kJ/mole)?

(a) $-1.434$  (b) $-0.624$  (c) $-17.13$  (d) $+17.13$

(6) 2. Suppose we start with one mole of A and two moles of B (same conditions as in the previous problem) and let $x$ represent the number of moles of A remaining at equilibrium. Which relationship below corresponds to $K_P^0$?

(a) $(1-x)/(4x^3)$  (b) $(1-x)(1+2x)^2/(4x^3)$
(c) $x/(4(1-x)^3)$  (d) $x(3-2x)^2/(4(1-x)^3)$

(6) 3. Suppose the reaction considered in the previous two problems was carried out at a total external pressure of $P$ (in atmospheres) instead of just one atmosphere. In that case, your answer to problem (2) above would have to be
(a) multiplied by $P$  
(c) divided by $P$

(b) multiplied by $P^2$  
(d) divided by $P^2$

4. Suppose the reaction in Problem (1) was carried out with a great excess of B (say 1000 moles of B per mole of A initially). If the total pressure is 1 atmosphere the equilibrium partial pressures $P_A$, $P_B$, and $P_C$ will be approximately (in atm)

(a) $10^{-6}$, $10^{-3}$, 1.0
(b) $10^{-6}$, 1.00, $10^{-3}$
(c) 0.001, 0.002, 0.003
(d) $10^{-3}$, 1.00, $10^{-6}$
(6) 5. At 30 °C and a total pressure of 1 atmosphere, $K_P^0$ in Problem (1) equals 1100. Provided $\Delta H^0$ doesn’t change significantly in this temperature interval, estimate $\Delta H^0$ (in kJ/mole)

(a) -7.3  (b) -14.3  
(c) +7.3  (d) +14.3  

(6) 6. The practical equilibrium constant, $K_c$, for the reaction

$$2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$$

is .0271 mole/liter at 1100 K. What is $K_P$ at the same temperature?

(a) .0271  (b) 1.43  
(c) 2.48  (d) 248.0  

(6) 7. At a particular temperature and pressure, the chemical potentials of the pure phases of a particular substance are

$$\mu_{\text{liquid}} < \mu_{\text{solid}} = \mu_{\text{gas}}$$

Under these conditions, the substance would be present at equilibrium as

(a) a gas  (b) a liquid  
(c) a solid  (d) solid plus gas  

(6) 8. The solid-liquid equilibrium of water is unusual in the sense that increasing pressure lowers the melting point rather than raising it (which is the case for most substances). The reason for this unusual behavior is that

(a) The molar volume of liquid water is less than that of the solid (ice).
(b) The molar volume of liquid water is greater than that of the solid.
(c) The enthalpy of fusion of $\text{H}_2\text{O}$ is negative (for most substances its positive).
(d) The chemical potential of the solid form is always greater than that of liquid water.

(End of Quiz 3)
(6) 1. One gram of solute (molecular weight = 100 gm/mole) is added to 10 moles of solvent. The vapor pressure of solvent drops from 100 torr to 95 torr. The activity coefficient, $f$, of solvent is

(a) .001  
(b) .050  
(c) .951  
(d) .999

(8) 2. Methane dissolves in benzene with a Henry's law constant of $4.27 \times 10^5$ Torr. If the partial pressure of methane over benzene is 0.3 atm (1 atm ~ 760 Torr), the mole fraction of methane dissolved in benzene will be

(a) $(0.3)/(4.27 \times 10^5)$  
(b) $(0.3)(760)/(4.27 \times 10^5)$  
(c) 0.3  
(d) $4.27 \times 10^5$

(6) 3. At $20^\circ$C, the vapor pressures of pure n-propanol and pure isopropanol are 14.6 Torr and 39.0 Torr, respectively. Assuming a solution of the two alcohols is ideal, estimate the partial vapor pressure of n-propanol (in torr at $20^\circ$C) of a solution obtained by combining 200 gm of n-propanol with 100 gm of isopropanol. (The molecular weights are the same for both.)

(a) 9.7  
(b) 14.6  
(c) 25.9  
(d) 29.2

(6) 4. What is the total vapor pressure of the solution in the previous problem?

(a) 14.6  
(b) 22.7  
(c) 30.9  
(d) 39.0

(6) 5. What is the mole fraction of isopropanol in the vapor phase above the solution in problem 3?

(a) .333  
(b) .500  
(c) .572  
(d) .667
(8) 6. 1.346 gm of the protein β-lactoglobulin dissolved in 100 ml of water at 25 °C produces an osmotic pressure of 0.010 atm. The molecular weight of the protein (in kg/mole) is

(a) 1.346  (b) 2.76
(c) 32.91  (d) 3,340.

(6) 7. One gram of naphthalene (MW = 128.2 gm/mole) lowers the melting point of 100 gm of camphor by 2.94 K. What is K_f (freezing point depression constant) for camphor (in K kg/mole)?

(a) .294  (b) 2.94
(c) 3.77  (d) 37.7

(6) 8. Suppose 1 gram of phenanthrene (MW = 178.2) was added to 100 gm of camphor. The melting point of camphor would be lowered by (in K)

(a) 2.94  (b) (2.94)(178.2)/128.2
(c) (2.94)(128.2)/178.2  (d) Cannot say unless we are given the enthalpy of fusion of phenanthrene.

(End of Quiz 4)

Chem 4110/6110
Physical Chemistry
Quiz # 5

Name: __________________________________________________________________

(Quiz is closed book, but one 8.5 by 11 inch sheet of notes can be used.)

(5) 1) How many components are present in the following system?
   \[ \text{CO(g) + 3H}_2\text{(g) } \rightarrow \text{CH}_4\text{(g) + H}_2\text{O(g)} \]

(a) 2  (b) 3  (c) 4  (d) 5

(5) 2) Consider a mixture of \text{H}_2\text{O, CCl}_4, \text{ and I}_2 which is held at 20 °C and 1 atm pressure. If we have two liquid phases present, (\text{CCl}_4, + \text{I}_2, and \text{H}_2\text{O} + \text{I}_2), and add a small amount of \text{I}_2(s), what will happen? (Hint: Consider the phase rule!)

(a) \text{I}_2(s) will form a new phase  (b) \text{CCl}_4 \text{ and H}_2\text{O will form a new liquid phase}
(c) \text{CCl}_4, + \text{I}_2 phase disappears  (d) \text{I}_2(s) dissolves into both liquid phases
(6)  2) Two liquids, A and B, form an ideal liquid mixture. The vapor pressures of the pure liquids are 50 Torr (A) and 250 Torr (B) at 20 °C. If we had a mixture with a liquid composition of 75 % (mole percent) A and 25 % B, what would be the total vapor pressure, $P_{\text{tot}}$, in Torr?

(a) 87.5   (b) 150   (c) 200   (d) 237.5

(8)  3) What would be the mole percent composition of B in the gas phase?

(a) 25   (b) $(25)(50)/P_{\text{tot}}$   (c) $(25)(250)/P_{\text{tot}}$   (d) $(25)(P_{\text{tot}})/250$

15)  4) In the space provided below, construct the P versus composition phase diagram of the ideal liquid system considered in the previous two problems. The diagram should be accurate and liquid, vapor, and biphasic regions must be identified.

![Phase Diagram](image)

Shown at right is the T versus composition phase diagram of the Tl$_2$O - TIBO$_2$ system.

(5)  6) Suppose we started with Tl$_3$BO$_3$ at 600 K and proceeded to heat it up. The solid would melt at (in K)

(a) 650   (b) 682   (c) 740   (d) 767
(5) 7) Suppose we had a mixture with 10% (by weight) B₂O₃ at 600 K. The composition would be

(a) Tl₂O + liq  (b) Tl₂O + Tl₃BO₃  (c) Tl₃BO₃ + TlBO₂  (d) TlBO₂ + liq

(8) 8) Indicate with a “o” on the graph the eutectic point and a “x” the monotectic point (4 pts each).

(12) 9) Consider a sample with 2% (by weight) B₂O₃ at 600 K and proceeded to heat it up to a final temperature of 900 K. Describe, in detail, exactly the various forms present at all temperatures in the range 600 to 900 K.
10) The limiting molar ionic conductivities of Ba\(^{2+}\) and SO\(_4^{2-}\) are 127.2 and 160 S cm\(^2\)/mole, respectively, in water at 25 °C. A saturated solution of BaSO\(_4\) has a conductivity of 2.87 x 10\(^{-6}\) S/cm. Assuming no other ions contribute to the conductivity, the solubility of BaSO\(_4\) in moles/liter is

(a) 2.87 x 10\(^{-6}\)  (b) 1.00 x 10\(^{-5}\)  
(c) .001  (d) .038

11) The ionic strength of a .01 moles/liter MgCl\(_2\) solution is (in moles/liter)

(a) .01  (b) .02  (c) .03  (d) .05

12) A solution contains .01 moles/liter MgCl\(_2\) and is also saturated with BaSO\(_4\). According to the Debye-Huckel limiting law, the activity coefficient, \(\gamma_\pm\) of Ba\(^{2+}\) and SO\(_4^{2-}\) will be

(a) .443  (b) .625  (c) .816  (d) .889

13) The presence of MgCl\(_2\)

(a) increases  (b) decreases
the solubility of BaSO\(_4\) in water.

(End of Quiz 5)

Chem 4110/6110
Physical Chemistry
Quiz # 6

Name: ________________________________

(Quiz is closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. At 25 °C, the half life for the decomposition of cyclopropane, C\(_3\)H\(_6\), is 2.05 x 10\(^5\) sec and is independent of the initial concentration of C\(_3\)H\(_6\). The order of the reaction with respect to C\(_3\)H\(_6\) concentration is

(a) zero  (b) first
(c) second  (d) cannot tell given the above information

2. The time required for 87.5 % of the C\(_3\)H\(_6\) (previous problem) to decompose would be (in 10\(^5\) sec)
(a) 4.1 (b) 6.15
(c) 8.2 (d) 16.4

The following three questions concern the reaction between A and B and the initial rates at various initial concentrations of A and B.

<table>
<thead>
<tr>
<th>[A] (moles/L)</th>
<th>[B] (moles/L)</th>
<th>Initial Rate (moles/L sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 x 10^{-4}</td>
<td>3.1 x 10^{-5}</td>
<td>5.2 x 10^{-4}</td>
</tr>
<tr>
<td>4.6 x 10^{-4}</td>
<td>6.2 x 10^{-5}</td>
<td>4.2 x 10^{-3}</td>
</tr>
<tr>
<td>9.2 x 10^{-4}</td>
<td>6.2 x 10^{-5}</td>
<td>1.7 x 10^{-2}</td>
</tr>
</tbody>
</table>

(6) 3. The order of the reaction with respect to A is
(a) fourth (b) third (c) second (d) first

(6) 4. The order of the reaction with respect to B is
(a) fourth (b) third (c) second (d) first

(6) 5. The rate constant is
(a) $5.2 \times 10^{-4}$ mole/L sec (b) 16.8 sec^{-1}
(c) $3.17 \times 10^{+8}$ L/mole^{2} sec (d) $3.17 \times 10^{+8}$ mole/L sec
The following two questions concern the mechanism for the decomposition of ozone, O$_3$, into oxygen, O$_2$:

\[ O_3 \rightarrow O_2 + O \]
\[ O_3 + O \rightarrow 2 \text{O}_2 \]

(8) 6. Applying the steady state approximation to [O], the steady state concentration of [O] is

(8) 7. On the basis of the proposed mechanism $d[O_3]/dt =$

(a) $-k_1 [O_3]$
(b) $-k_1 [O_3] + k_2 [O_3][O]$
(c) $-k_2 [O_3][O]$
(d) $k_1 [O_2][O] - k_1 [O_3] - k_2 [O_3][O]$

(6) 8. The substrate for the enzyme superoxide dismutase is the anion O$_2^-$. At an ionic strength of $10^1$ mole/liter, the reaction rate is only 13% of its value at an ionic strength from $10^2$ mole/liter. Modeling superoxide dismutase as a simple ion, its "effective charge" on the basis of the observed salt dependence is

(a) +4  (b) +2
(c) 0    (d) -4