Consider a flask with chemicals in it. They react, the flask heats up. Heat flows in. It can be related to changes in state functions. These changes can be used to predict, whether other reactions—which we want to know about, but don’t want to experiment on yet—are possible.

Collection of thermodynamic data are useful for this reason. How are thermodynamic tables set up? This is the subject of the next lectures.

Calorimetry
The quantitative measurement of heat.

\[
\begin{align*}
\text{adiabatic wall} & \quad \text{reaction vessel} \\
\text{H}_2\text{O} & \\
\text{system} & = \text{water} + \text{reaction vessel} \quad q = 0 \text{ since adiabatic} \\
\text{reaction vessel} & = \text{real } V, \ X, \text{ and } W = 0. \text{ And} \\
\Delta U & = q = 0 \\
\text{New } q & = \text{water} + \text{reaction}. \text{ Thus } q_{\text{water}} = -q_{\text{reaction}} \\
\text{Could test water electrically to get } & \text{ temperature rise } \Delta T. \text{ And } (\text{Calculate } \text{heat content} \text{ of water}) \\
q_{\text{water}} & = \text{Voltage} \times \text{Current} \times \text{time} \times \text{known constant}
\end{align*}
\]
\[ C_V(\text{cal}) = \frac{\text{gallon}}{\Delta T} \quad \text{for calorimeter.} \]

Then let reaction happen. Knowing \( C_V(\text{cal}) \) and \( \Delta T \).

Then let

\[ \Delta f(\text{react}) = C_V(\text{cal}) \Delta T, \text{ for reaction} \quad \Delta V = 0 \Rightarrow \Delta H_{\text{rxn}} = \text{constant} \]

Very practical: Actual device very conducted to obtain close ideality.

- Standard states and reference states

- We measure \( \Delta f \) (\( J = H, U, \text{etc} \)) values. Not \( J \) value in thermo. So need values of \( J \) in a reference state. Then

\[ J = J - J_{\text{ref}} + J_{\text{ref}} = \Delta J + J_{\text{ref}} \]

To define \( J_{\text{ref}} \), let’s first define a standard state.

Solid or liquid \( J^0 \leq 1 \text{ atm, pressure} \quad \text{and} \quad T \leq \text{absolute temp.} \)

\( \text{Gas} \quad J^0 \leq 1 \text{ atm, and ideal gas} \)

In chemical transformation, don’t change element into another element (e.g., no fusion, fission, decay) \( O_{16} \rightarrow O_{18} \)

Thus, elements are always the same. So assign the standard

\( J \) value.
Enthalpy - \( \Delta H^\circ = H_2(g) + \frac{1}{2} O_2(g) = H_2O(l) \) at 298° C.

\( \Delta H^\circ = 298.15 \) kJ/mol, LV used J/mole.

Each atom in the stable (6T, 1P) form.

\( H(gas) = 0 \) graphite, diamond, since graphite is stable.

Then \( \Delta H(T,p) = \Delta H + 0 \) and \( \Delta H(T,p) = \int_{298}^{T} \Delta H(T,p) \) atm.

From experimental values of \( \Delta H(T,p) \) get \( \Delta H(T,p) \) at 1 atm.

From experimentally values of \( \Delta H(T,p) \) get \( \Delta H(T,p) \) at 1 atm.

For compounds, what is the enthalpy? We define an enthalpy of formation (Heat of formation), as \( \Delta H_f^\circ \) in the elements.

\( \Delta H_f^\circ (\text{compound}) = \sum \Delta H_f^\circ (\text{elements that make up compound}) \) in their standard states.

Since \( \Delta H_f^\circ (\text{elements}) = 0 \) at T=298,

\( \Delta H_f^\circ (\text{compound}) = H_f^\circ (\text{compound}) \)

How do we measure \( \Delta H_f^\circ \) for a compound? Put it in a calorimeter and measure \( \Delta H \) at constant pressure.

For formation from the elements in their stable form(s) that are stable.

Ex: \( H_2(g) + \frac{1}{2} O_2(g) = H_2O(l) \)

\( \Delta H_f^\circ = -241.8 \) kJ at 298° C.
Now, the slow reaction goes if a pinch of catalyst is added. 
But, what if you want, say,

\[ \text{CA} + 2 \text{H}_2(g) \rightarrow \text{CH}_4(g) \]

This won't go at \( T = 25^\circ C \), say and \( p = 1 \text{ atm} \).

But add up reaction Yet will go - and have been measured
in a calorimeter, ALL COMBUSTION REACTIONS THEY "GO".

\[ \begin{align*}
(1) & & \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + \text{CO}_2(g) & \Delta H^\circ_{12} = -890 \text{ kJ} \\
(2) & & \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) & \Delta H^\circ_{2} = -393.5 \text{ kJ} \\
(3) & & \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) & \Delta H^\circ_{3} = -285.8 \text{ kJ} 
\end{align*} \]

What we want

\[ \Delta H^\circ_{\text{C}_2\text{H}_4} = \Delta H^\circ_{\text{CH}_4} - 2\Delta H^\circ_{\text{H}_2} - \Delta H^\circ_{\text{C}} \]

\[ \begin{align*}
\Delta H^\circ_{1} &= 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{CH}_4} - 2\Delta H^\circ_{\text{O}_2} \\
\Delta H^\circ_{2} &= \Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{C}} - \Delta H^\circ_{\text{O}_2} \\
\Delta H^\circ_{3} &= \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_2} - \frac{1}{2}\Delta H^\circ_{\text{O}_2} \\
\Delta H^\circ_{\text{CH}_4} &= -\Delta H^\circ_{1} - \Delta H^\circ_{2} - \Delta H^\circ_{3} + \left(\Delta H^\circ_{\text{H}_2\text{O}} - 2\Delta H^\circ_{\text{H}_2\text{O}}\right) + \left(\Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{CO}_2}\right) + \left(2\Delta H^\circ_{\text{O}_2} - \Delta H^\circ_{\text{O}_2}\right)
\end{align*} \]
2. \[ \Delta H_f^0 \text{CH}_4 = -\Delta H_f^0 \text{H}_2 + \Delta H_f^0 \text{H}_2O + 2 \Delta H_f^0 \text{H}_2 \]

\[ = 211.8 - 94.8 - 2(64.3) = -17.6 \text{ kJ/mol} \]

Thus, the \( \Delta H_f^0 \) for a reaction is not equal to zero at normal T and p=1 atm. Can be obtained from reaction that does.

This is known as Hess' Law - very important.

\[ \Delta H_f^0 = 2 \Delta H_f^0 \text{H}_2O + \Delta H_f^0 \text{CO}_2 - \Delta H_f^0 \text{CH}_4 - 2 \Delta H_f^0 \text{H}_2 \]

we can tabulate just heats of formation of various compounds - which one do we get heats of other reactions in. Read 1 above. And then add them to get \( \Delta H_f^0 \) for reaction that does.

What have we done in the above? The above is \[ \]

\[ (-1) [ \text{CH}_4 + 2\text{O}_2 = 2\text{H}_2\text{O} + \text{CO}_2 ] \]

\[ (+1) [ \text{C} + \text{O}_2 = \text{CO}_2 ] \]

\[ +2 [ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} ] \]

\[ \text{CH}_4 = \text{C} + 2\text{H}_2 \]
Thus, the
\[ \Delta H^\circ = -\Delta H_1 + \Delta H_2 + 2\Delta H_3 \]
in agreement with our long calculation.

Exothermic - reaction has \( \Delta H < 0 \)

Endothermic - \( \Delta H > 0 \)

Since \( \Delta H = q_p \) for \( p \) constant, then
\( q_p < 0 \) heat given off by system \( (\text{the reactant}) \)
heat absorbed by surroundings \( (\text{the product}) \) at \( T \to T + \Delta T \)
uptake \( \Delta T \) power. Thus \( q_p \) reaction heats surroundings.

General notation for reactions:
\[ \text{reactants} \quad \rightarrow \quad \text{products} \]
\[ aA + bB = cC + dD \quad \text{(as have more often)} \quad \text{(of course)} \]

Then write this as
\[ 0 = -aA - bB + cC + dD \equiv \nu_A A + \nu_B B + \nu_C C + \nu_D D \]
The \( \nu \)'s are called stoichiometric coefficients
\( \nu < 0 \) reactant, \( \nu > 0 \) product, \( \nu = 0 \) non-participate.

Then, for this reaction
\[ \Delta H^\circ = \nu_A \Delta H_{A}^\circ + \nu_B \Delta H_{B}^\circ \]
\[ = \nu_A \Delta H_{A}^\circ + \nu_B \Delta H_{B}^\circ \]
And then for any reaction can often be set desired.
Temperature Dependence of Reaction Heat

Want to convert \( \Delta H^\circ_{\text{rxn}} \rightarrow \Delta H^\circ_{T} \) where \( \Delta H^\circ \) is
for given reaction at \( T \). Then

\[
\frac{d\Delta H^\circ}{dT} \bigg|_p = \frac{d\Delta H^\circ}{dT} \quad \text{at } p = 1 \text{ atm.}
\]

And

\[
\frac{\partial}{\partial t} \sum_i dH^\circ_i = \sum_i \frac{\partial}{\partial t} \sum_i C_p^\circ_i = \Delta C_p^\circ
\]

Then

\[
\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1} = \int_{T_1}^{T_2} \Delta C_p^\circ(T) \, dT
\]

\[
[\Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}}] = \int_{T_1}^{T_2} C_p^\circ(\text{products}) \, dT - \int_{T_1}^{T_2} C_p^\circ(\text{reactants}) \, dT
\]

Typical heat capacity vs. \( T \) curves.

![Graph showing heat capacity vs. temperature for CH₄(g) and H₂O(l)]

Simple curves, Take

\[
C_p^\circ = a + bT + cT^{-2}
\]

Usually not a big difference between \( \Delta H^\circ \)'s for

\( T \) is not too far away
Example

\[ \text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2 \]

From Levine data,

\[ \Delta H_{298}^\circ = -67.635 \text{ kcal/mol} \]

\[ \Delta H_{1000}^\circ = -67.541 \text{ kcal/mol} \]

Very small difference. I could be larger. But still.

See example 5.5

[Handwritten notes:]

- [Handwritten notes:]

Caps are
For a reversible process we found

$\Delta S = \int dq / T$

At constant $p = \text{let me say}$

$\Delta S^o = \int_{T_1}^{T_2} dS^o / T$

Choose a reference state for entropy at $T = 0$

$s^o(T) = s^o_0 + \int_{s^o_0}^{s^o} dT$

Need to know $s^o_0$.

For elements in stable form at $T = 0$, $s^o_0 = 0$.

Experiementally found that for chemical reactions and let's think specifically about formation (from the elements) such that

$\lim_{T \to 0} \frac{\partial \Delta G^o}{\partial T} \to 0$

$dG = -SdT + VdP$

$\lim_{T \to 0} \frac{\partial \Delta G^o}{\partial T} = -\Delta S_f^o$

$\lim_{T \to 0} \Delta S_f^o \to 0$

For formation reaction of a compound from its elements, we have

$\Delta S_f^o = \text{Solute} - \text{Solvent}$
But $S^o_{\text{element}} = 0$. Thus $S^o_{\text{compound}} = 0$. (As $x$ is not $S^o$).

So $S^o = 0$. element + compound.

Third law - For any isothermal process involving only pure substances, each in internal energy $\Delta S = 0$.

Pure substances, internal energy $\Rightarrow$ no randomness (crystalline material - no free energy, gas).

Except NO $\Rightarrow T > 0$. NO NO NO on on on on $\Rightarrow$ no $\Delta S > 0$.

But can calculate the residual entropy. Heat with calculation, at 1, mol cal., + exp. agree. $S = k T \ln \Omega. \Omega = 2^n S = k T$.

From $H^o$ and $S^o$, all the other functions follow.

$U^o = H^o - pV^o$ where $V^o$ is mol volume at $T, p$.

$A^o = U^o - T S^o \Rightarrow A^o = U^o$ - mixture. Easy to measure.

$G^o = H^o - TS^o \Rightarrow G^o = H^o$.

$H = U + pV$

$G = A + pV$

$G = U + pV - TS = H - T$

For substances that undergo phase change, sgp. solid = liquid.

$S^o = \int \frac{C_p}{\Delta T} dT + \int \frac{T G^o(\text{g})}{\Delta T} dT$

need law $T \cdot C_p$ in Kelvin. Then provides hard to measure $U^o$.
Now one can calculate $\Delta S^\circ_{T}$, $J = S, U, H, G, A$, as we did for $\Delta H^\circ$ is from the $\Delta F^\circ$ value.

Also note, changes. For example $\Delta H^\circ$ means PROD-REAQ

$$\Delta S^\circ_{T} = \Delta S^\circ_T = \int_{T_1}^{T_2} \frac{\Delta C_p^\circ}{T} \,dT$$

at constant $p = 1 \text{atm}$

To calculate $\Delta G^\circ$ need either c-table or $\Delta G^\circ$ a

get it from $\Delta H^\circ$ and $\Delta S^\circ$.

Consider the example

$$C_8H_{18}(g) + 12.5O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

$\Delta H^\circ_{298} = 8 \Delta H^\circ_{CO_2} + 9 \Delta H^\circ_{H_2O} - 12.5 \Delta H^\circ_{O_2}$

$\Delta S^\circ_{298}$ FORMATION

Get $\Delta H^\circ_{298} = -1219 \text{ kcal/mol}$

$\Delta S^\circ_{298} = 100 \text{ cal/K mol}$.

$\Delta G^\circ_{298} = [(-1219 - (288)(1))] \text{ kcal/mol} = -1249 \text{ kcal/mol}$.

This is maximum amount of useful work (work in cell $+ pV$

work of process) obtainable.
But \[ \text{mol} \text{ C}_8\text{H}_{18} = 8 \times 1 + 18 \times 1 = 114 \text{ g mol} \sim 100 \text{ cm}^3 = 0.14 \text{ liter} \]

44 mol of C to H ratio = 1 yellow.

Thus, \[ \Delta G^\circ \_\text{octane/glycer} = 44 \times (1250 \text{ kcal/mol}) \times 0.5 \text{ cal} \]

\[ \Delta G^\circ = 2.2 \times 10^8 \text{ Joules} \]

Burn it in one second to get \[ 2 \times 10^8 \text{ Joules/sec} = 10^8 \text{ watts} = 100 \text{ megawatts} \]. Roughly the nuclear power plant wattage.

Of course, can't get all of \[ \Delta G \] combustion in an engine process; so infinite time to get all of \[ \Delta G \]. BUT still, that's why cars run on gasoline.
Other tricky part is use of tables $\frac{\Delta H_i}{\Delta H} \cdot \frac{\Delta G_i}{\Delta G}$

Write $\Delta G$ for some reaction. Can get $\Delta G$ from $\Delta H + \Delta S$

where $\Delta H = \sum \Delta H_{(prod)} - \sum \Delta H_{(react)}$ etc.

But $\Delta G$ or $G_{(prod)} - G_{(react)}$ limited fine.

But, its $\Delta G_i$ that limited, not $G_i$... 

Nevertheless $\Delta G^o_T = \sum_i \Delta G_i^o(T)$

because $G$ is still function of $T$

\[
\text{reactant} \overset{\text{ri}}{\rightarrow} \text{product} \\
\begin{array}{c}
\text{element in} \\
\text{solid, liquid, or} \\
T
\end{array}
\]

\[-\Delta G_i (\text{react}) + \Delta G_i (\text{prod}) = \Delta G_T \quad \text{(1:2)}\]

If want $G$ of some compound. It is $\Delta G_i$ of hide

But it is $G = \Delta H_T - TS$

$H$ pure $H_{( Auburn)} = 0$ at $298^\circ$
So far we have only discussed closed systems, i.e. 
\[ dU = dq + \delta W \]
\[ dS \geq \delta q / T \]
no matter exchange. If matter exchanged, the last term is ambiguous because matter carries energy with it.

Also 
\[ dU = T dS - pdV \]
not applicable to closed system with irreversible constant charge. If work 
\[ dU = 0, \quad dV = 0 \Rightarrow dS = 0. \]
But 
\[ dS \leq 0 \] for chemical reaction or diffusional mixing.

[Doesn't make sense] Also, if P is fixed, but if double fixed and work is done, this cannot happen because we implicitly assume that two are fixed. State of system. This is only true for bodies of fixed composition. Thus must introduce molar number.

Consider one phase with k different substances with mole number \( n_1, \ldots, n_k \):

\[ U = U(V, n_1, \ldots, n_k) \]

Really should be \( U(T, p, v, n_1, \ldots, n_k) \).

\[ dU = \left( \frac{\partial U}{\partial V} \right)_n dV + \left( \frac{\partial U}{\partial n_i} \right)_V dn_i \quad (i = 1, \ldots, k) \]

[Explain notation.]

Since \( \frac{\partial U}{\partial n_i} \) is all \( n_i \) constant,

\[ \frac{\partial U}{\partial n_i} = -p \]

Define \( \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_V, \] for chemistry.
\[ \mu_i = \frac{U(n_i \text{d}n_i)_{\text{g}} - U(n_i)_{\text{g}}}{\text{d}n_i} \]

how to keep \( V \) fixed? For \( V \), just readjust \( p \). For \( s \), a certain amount \( s \) and it, then take it out by contrast with heat bath, hence 

\[ \Delta T = \text{decrease of heat flow} \]
\[ \Delta p = \text{dissipation of entropy} \]
\[ \mu_i = \text{draw} \quad \text{from one place to another} \quad \text{(we will show)} \]

Another form of \( \mu_i \):

\[ dG = \frac{\delta G}{\delta n_i} \left( \frac{\partial}{\partial t} \right)_p, \eta \]
\[ + \frac{1}{2} \sum_{i,j} \frac{\delta G}{\partial n_i} \left( \frac{\partial}{\partial n_j} \right)_p, \eta \]

Again, for \( p, \eta \) fixed:

\[ \frac{\delta G}{\delta n_i} = -S \left( \frac{\partial G}{\partial n_i} \right) = V \]

\[ dG = -S (\text{d}p_i + \sum \mu_i \text{d}n_i) \]

Finally, \( \Delta G \) change gives amount of work done by \( V \)

\[ \mu_i = \frac{\partial G}{\partial n_i} \]
for dU added at fixed T, p. For example, electrochemical cell.

Substance increases cell ability to do electrical work.

\[ \mu_i = x_i \mu_i \ln \left( \frac{\nu_i}{\nu_i^0} \right) \]

Add d(pV - TS) to both sides of \( dU = Tds - pdV + \mu_i \, d\nu_i \). \( \mu_i \) is:

\[ d(U + pV - TS) = Tds - pdV + d(pV - TS) + \mu_i \, d\nu_i \]

\[ dG = -SdT + Vdp + \mu_i \, d\nu_i \]

\[ \mu_i = \frac{\partial G}{\partial \nu_i} \] at \( T, V, \nu_i \).

New: Gibbsian
\[ \frac{dU}{dA} = -SdT - pdV + \mu_i \, d\nu_i \]
\[ dH = Tds + Vdp + \mu_i \, d\nu_i \]

\[ \mu_i = \frac{\partial G}{\partial \nu_i} = \frac{dU}{dA} \frac{1}{\nu_i} \]


dU = Tds - pdV + \sum \mu_i \, d\nu_i \]

3. if \( \mu_i \) cont. vary process \( \mu_i(\nu_i) = 0 \)

if \( \mu_i \) diminishes """" d\nu_i < 0

1. \( \mu_i \) is intensive -Rates of extensive quanta.

2. Can do work w/o PV change, i.e. lift weight, etc., without doing dU.
At equilibrium, \( dG = \Delta \text{Work} \) (\( T, p \) fixed),

Thus, since \( G \) minimum at eqn, \( dG = 0 \) and

\[ \text{Work} = \frac{1}{2} \mu \text{d}n_i = 0 \]

Thus \( \sum \mu_i \text{d}n_i = 0 \) at eqn, fixed \( T, p, \) constant.

Some work is done for \( dU = dH - dA \) eqn. of the law of quanta.

Thus, in general \( \sum \mu_i \text{d}n_i = 0 \) closed system.

Again, at eqn = zero net process.

\[ dG = -SdT + Vdp \implies \sum \mu_i \text{d}n_i = 0 \]

Consider chem. reaction explicitly now; at equilibrium

\[ \sum n_i \Delta v_i = 0 \]

Define extent of reaction \( \xi = (n_i) \) via (unit)

\[ n_i = n_i^0 + \xi n_i \]

The in reaction, \( \xi \) is same for all \( n_i \) changes.

\[ 2C + O_2 = 2CO \]

\[ \xi = 2 \quad n_i^0 - 1 \quad n_{C,0} = 2 \]

\[ n_i = n_i^0 - 2 \xi \quad n_{O,0} - n_{O,0} - 2 \xi \quad n_{C} = n_{C,0} + 2 \xi \]

When \( 2 \) molecules of \( C \) react with \( 1 \) \( O_2 \), form \( 2 \) molecules of \( CO \)

\[ n_i \Delta v_i = \gamma_i \bar{d} \xi \]

(Plenty of molecules in \( d \xi \), so can treat it as continuous, diff.)
The equation to consider is \( \sum \mu_i \Delta n_i = 0 \). Thus,

\[
\sum \mu_i \Delta n_i = \left( \sum \mu_i \Delta n_i \right)_0 = 0 \Rightarrow
\]

\[
\frac{d\mu_i}{dH} = 0 \quad \text{(closed system)}
\]

i.e., just replace species \( A_i \) by their respective \( \mu_i \) to get condition of reaction again.

For cont. \( T \),

\[
dG = \sum \mu_i \Delta n_i
\]

or

\[
dG = \left( \sum \mu_i \Delta n_i \right) d\delta = \left( \sum \mu_i \Delta n_i \right) e - Q
\]

Since \( G \) min. at eqn., \( dG = 0 \). Affinity \( A + B \rightarrow C \)

De Dode

\[
A + B \rightarrow C
\]

Equ.: \( A, B \rightarrow C \).

Now let's explore correlation between \( G \) and eqn. content of a reaction. And how to quantifying within eqn. content:

\[
\frac{\Delta G}{\Delta \delta} = \frac{dG}{d\delta} > 0
\]
Reaction Equilibrium in Ideal Gas Mixture.

For a one component gas, we have from

\[ dG = -SdT + VdP + \mu d\mu \]
\[ \Rightarrow G = G(T, P, \mu) \]
\[ dG = -SdT + VdP, \quad T \text{ fixed, } P \text{ fixed} \]

If we consider a fixed temperature then integrate is

\[ V = nRT/P \quad \text{ideal gas} \]
\[ dG = \frac{nRTdP}{P} \]
\[ G(p_2) = G(p_1) + nRT \ln \left(\frac{p_2}{p_1}\right) \]

If we do this for one more

\[ G(p_3) = G(p_2) + RT \ln \left(\frac{p_3}{p_2}\right) \]

Then noting that \( G \) is extensive, so \( G = n \bar{G} \)

\[ \frac{dG}{dn} \bar{\mu} = \bar{G} \]

\[ \bar{\mu}(p_3) = \bar{\mu}(p_2) + RT \ln \left(\frac{p_3}{p_2}\right) \quad \text{ideal gas, } T \text{ fixed} \]

Now fix \( p_2 = 1 \text{ atm} \). Then define

\[ \bar{\mu}(\bar{P} = 1 \text{ atm}, T) \]

\[ \bar{\mu}^0(T) = \bar{\mu}(p = 1 \text{ atm}, T) \]
Thus \( \mu_i(T) = \mu^0_i + RT \ln (\rho_i/\rho) \) for an ideal gas mixture, the pressure of a given component or \( p_i \) and is the same pressure all gas would have if it were alone. Since ideal gas molecules don't know others' presence, we have

\[ \mu(T) = \mu^0 + RT \ln (p) \]

For reaction equilibrium, we have for the example:

\[ dG = \mu_A d\bar{n}_A + \mu_B d\bar{n}_B \]

Now, \( \mu_A < \mu_B \)

\[ \frac{dG}{d\bar{n}_A} = \mu_B - \mu_A \]

When \( \mu_A > \mu_B \) reaction proceeds from \( A \) to \( B \) and

\[ \mu_A < \mu_B \]

Thus, at equilib. \( \frac{dG}{d\bar{n}_A} = 0 \) and

\[ \mu_B = \mu_A \]

Now, ideal gas condition of MAT GPEL for any

\[ (T = T_B \text{ for thermal}) \]

Then

\[ -(\mu^0_B - \mu^0_A) = RT \ln (p_B/p_A) \]
\[
\Delta G^\circ_T = \mu_B - \mu_A = -RT \ln \left( \frac{P_B}{P_A} \right) e^2
\]

Define \[ K_p^\circ(T) = \frac{P_B}{P_A} e^2 \]

Thus, \[ \Delta G^\circ_T = -RT \ln K_p^\circ \]

Because \[ e \] is needed, we measure \[ K_p^\circ \] experimentally.

\[ K_p^\circ = \frac{P_B^o}{P_A^o} \]

Thus, plotting \[ \frac{P_B}{P_A} e^2 = e^{-\Delta G^\circ_T / RT} \]

Therefore, \[ \Delta G^\circ_T \] as \[ \Delta G \to -\infty \] partial pressure of \[ B \] in mixture increases exponentially.

Equilibrium lies toward \[ B \].

[NOT intended plot; this is equimolar versus \[ \Delta G^\circ_T \]. The standard state chosen is \[ \text{diff.} \]

In general, \[ aA + bB + \cdots \to cC + dD + \cdots \]

\[ \Delta G^\circ_T = -RT \ln K_p^\circ \]

where

\[ K_p^\circ = \frac{P_C^o e^c P_D^o e^d}{P_A^o P_B^o} \]

OTHER UNITS:
Let us be general for a moment and consider any process at fixed T, P. Then, we found that \( \Delta G \leq 0 \) was a condition to determine the direction of change.

But \( \Delta G = \Delta H - T\Delta S \) (T, P) fixed. Then

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>(-T\Delta S)</th>
<th>Spont.</th>
<th>( \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>-</td>
<td>+</td>
<td>no</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>-</td>
<td>yes</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>+</td>
<td>maybe</td>
<td>&lt; 0 ( \text{if } T \Delta S &gt; 0 )</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>-</td>
<td>maybe</td>
<td>&lt; 0 ( \text{if } T \Delta S &lt; 0 )</td>
</tr>
</tbody>
</table>

For chemical reactions, \( \Delta H \) negative (exothermic reaction) is favored by formation of strong chemical bonds. \( \Delta S \) positive is favored by increase in order available. Example:

\[ \text{N}_2 \rightarrow 2\text{N} \]

\( \Delta H < 0 \) endothermic — must put in energy (cold bead) to break \( \text{N}_2 \) bond. But form 2 molecules from 1, as \( \Delta S > 0 \). The equilibrium is compromise between these two competing tendencies. However, when \( \Delta H < 0 \), \( \Delta S > 0 \), and \( T > 0 \), the system in equilibrium is favored formation of \( \text{N}_2 \) atoms. The \( T \) rise is equivalent to an increase of energy content of the system and the energy content will be most "randomized" if, in addition to just heating the system, the reaction is displaced to the side of taking up
This energy toward N atoms. Thus $T$ increase causes conformation to change in the endothermic direction (Le Chateliers Principle).

To see this quantitatively, let's return to ideal gas equilibrium and see how it changes with $T$. From the Gibbs-Helmholtz equation [you prove in problems]$

\left[ \frac{\partial (\Delta G^*/T)}{\partial T} \right]_P = -\frac{\Delta H^o}{T^2}

\text{And: } \Delta G^o = -RT \ln K^o

\frac{\partial \ln K^o}{\partial T} \bigg|_P = \frac{\Delta H^o}{RT^2} = \frac{d \ln K^o}{dT} \text{ van't Hoff eq.}

Note that the ideal gas entropy is independent of pressure. $\Delta H = \Delta U + \Delta (pV) = \Delta U + n \Delta (RT)$ and this goes into R.H.S.

Since $\Delta H^o$ is ordinary derivative can integrate it.

Also $\frac{d \Delta H^o}{dT} = \Delta C_P = \Delta a + (\Delta b)T + (\Delta c)T^2$

$\Delta H(T) - \Delta H_0 = \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3$

Thus $\frac{d \ln K^o}{dT} = \frac{\Delta H_0}{RT^2} + \frac{\Delta a}{RT} + \frac{\Delta b}{2} T + \frac{\Delta c}{3} T^2$
\[
\ln K^0 = \frac{C - \Delta H_0 + \Delta S_0}{T} + \frac{\Delta S_0}{2}
\]

C is the enthalpy constant.

If you know \(\Delta H_0\), then get \(\Delta H_0\) from first integration, get \(C\) from final answer from one value of \(K^0\).

Returning to van't Hoff:

\[\text{If } \Delta H^0 \neq 0 \Rightarrow \frac{d \ln K^0}{dT} > 0 \text{ so } \frac{dT}{dT} > 0 \Rightarrow \frac{d \ln K^0}{dT} > 0.\]

Verifying our example \(N_2 \rightarrow 2N\).

le Chatelier in general (important since max yield etc.)

\[
\frac{d\theta}{d\theta} = \left(\frac{1}{T} \frac{dS}{dV}\right)
\]

And hence:

\[
A = \frac{-\Delta H^0}{kT} \quad Q = \frac{\text{reaction quotient}}{P_{\text{sys}}}
\]

If \(P_{\text{sys}}\) pressure \(Q\) are not equilibrium pressure.
Only when $A=0$ are the f's equal and is:

$$Q_{eq} = \prod_i p_i^{y_i} \quad A=0$$

$$\frac{A}{RT} = -\left(\ln Q - \ln Q_0\right) = \ln \frac{Q_{eq}}{Q_0}$$

$$\frac{A}{RT} = \ln \frac{Q_{eq}}{Q_0} \quad Q_{eq} = K_p^0$$

Le Chatelier's principle is contained above.

To $Q_{eq} > Q$ the $A > 0$ and reaction goes to the right:

$$\frac{dG}{d\theta} = -A$$

$$dG < 0 \quad A > 0 \quad \text{and react $\rightarrow$ prod. reaction goes to the right.}$$

All the cases are written this way.

Note that since $Q_e = [Q_p^0]^{-A/1}$

where $Q_x = \prod_i q_i^{x_i} \quad x_i$ are mole fractions.

Then and $A/1 = \sum x_i \Rightarrow$ we have

$$A = RT \ln \left(\frac{Q_{eq}}{Q_x}\right)$$

Exp. 1.647 to understand $A$.
Phase Equilibrium

Several phases in thermal and mechanical equilibrium. Index phases with subscript $\alpha$, $\beta$... Thus

$$\mu_i^\alpha = \text{chem. pot. of species } i \text{ in phase } \alpha.$$ 

Consider the Gibbs free energy at fixed $T$ and $p$. We have

$$dG = \sum_\alpha \sum_i \mu_i^\alpha \, di^\alpha \leq 0 \quad (T, p \text{ fixed})$$

Let amount $dn_i^\beta$ flow from phase $\beta \to S$, then

$$-dn_i^\beta \equiv d\bar{n}_i^\beta$$

with $d\bar{n}_i^\beta > 0$

Keep all $n_i^\alpha$ fixed $j \neq i \neq \beta, S$. Then

$$dG = \mu_i^\alpha \, dn_i^\beta + \mu_i^\beta \, dn_i^\beta \leq 0$$

$$= (\mu_i^\beta - \mu_i^\alpha) \, dn_i^\beta \leq 0$$

Since $dn_i^\beta > 0$

$$\mu_i^\delta - \mu_i^\beta \leq 0 \Rightarrow \mu_i^\delta \leq \mu_i^\beta$$

And, at equilibrium: $\mu_i^\delta = \mu_i^\beta$

Conclude: Any substance tends to pass from region of high chemical potential to region of lower chemical potential.

- hence move chem. pot.

Conclude: The addition of material equi between phases.
is that each species will have an equal value of the
spot in all phases between which the substance can
freely pass.

For semi-permeable membranes between phases, not true.
- Important for osmosis (Mitchell semi-organic hypothesis)

Since $p_j$ is arbitrary, holds for all the phases.

Exception: If substance initially absent from phase $S$, then $\mu_j > \mu_S$; we can transfer stuff in $\mu_j = \frac{2\sigma_{jS}}{r_{jS}}$.

If $\mu_j > \mu_S$, stuff flows from $\beta \rightarrow S$.

If $\mu_S > \mu_j$, clearly no flow - no change, stay in original.
Thus, when component $j$ absent from $S$,

$$\mu_S > \mu_j$$

phase again $j$ absent from $S$.

The phase rule

Equilibrium of a pure substance. Consider two phases $\alpha, \beta$. Then

\[
\begin{align*}
T_\alpha &= T_\beta \\
\rho_\alpha &= \rho_\beta \\
\mu_\alpha(\rho_\alpha) &= \mu_\beta(\rho_\beta)
\end{align*}
\]
In each phase \( T \), \( P \), \( \mu \) fix all other intensive properties. In particular, \( \mu \).

Of the 4 variables, \( T \), \( P \), \( \mu \), \( \rho \), when fix state completely, only one independent: One Degree of Freedom. So if we fix \( T \), other phase has same temperature, then phase pressure will be the same and be fixed by the eq. of state.

Consider Figure 1

\[ \mu \quad P \]

along this line, 3 equations are satisfied.

Consider now 3 phases in equilibrium. Then

\[ T_1 = T_2 = T_3 \quad \rho_1 \rho_2 \rho_3 = P_1 P_2 P_3 \quad \mu_1 \mu_2 \mu_3 = \mu \]

Of the 3 \( T \), \( P \), \( \rho \) pairs = 6, 6 relations to NO DEGREES or FREEDOM.

Third surface, given intensive at a point.
Phase diagram (one component), $S(T) = \int_{0}^{T} \frac{G}{T} dT + \sum_{\alpha} f_{\alpha} S_{\alpha}$

From $\frac{\partial G}{\partial T} = -S$, $\frac{\partial G}{\partial p} = V$ for a given phase, we know that as $T \uparrow G \uparrow$ and $p \uparrow G \downarrow$ (Supers)

At solid-liquid transition, $G_{S} = G_{L}$ but $S_{S} < S_{L}$, so $G$ continuous but slope has abrupt change.

Linear 2 intersection are for phase coexistence

3 phase meet at triple point

As $p$ increases, molar volume of gas decreases faster than molar volume of liquid. So, reach a point where $\frac{\partial G}{\partial p}|_{T} = \frac{\partial G}{\partial p}|_{V}$, when...
\[ V(l) = V(g) \]. Thus, "close" in surface displacement this and all points of hyper plane (for \( c \) fixed \( T \)).

The point - \( pVT \) where this occurs is the critical point - \( p_cT_c \). You can't tell difference between gas and liquid.

From projection onto plane of \( p-T \) get conventional representation.

\[ T \rightarrow \]

For \( CO_2 \) at \( p = 1 \text{ atm} \), \( T = -78^\circ \text{C} \), solid + gas coexist.

Thus, solid \( CO_2 \) sublimes when it is warmed up to \(-78^\circ \text{C} \).

(\text{Dry ice})

At \( p = 10 \text{ atm} \), \( T = -56.6^\circ \text{C} \), solid \( CO_2 \) will melt to liquid \( CO_2 \).

Above \( p_cT_c \), we start from point \( a \). One runs off fluid phase exits. If we reduce \( T \) to \( p \), we have a fluid that is gas. How do we know? Reduce \( p \) to \( 8 \). The gas + liquid again with gas. Can reduce \( p \) further until all \( N \) liquid phase disappears. Drop further, all gas.

[CRITICAL APPENDIX / CURVES OF OPERATIONS / LOW RANK / FACTOR ORDER]
The phase rule

Degree of Freedom: Number of independent variables required to specify system state.

Consider C species and P phases. Equilibria given by PT\{X\}. No chem. rev. All species in each phase.

Each phase composition given by C-1 relations: \( \sum_{i=1}^{C} X_i = 1 \) (also T, P)

Number of variables = \( P(C+1) \)

At equi:

\[
\begin{align*}
\text{C relations} & \quad (P-1) \text{ eq.} & \quad T_1 = T_2 = \ldots \\
\text{(P-1) eq. & (P-1) eq.} & \quad \mu_1 = \mu_2 = \ldots \\
\text{and eq.} & \quad (P-1) \text{ eq.} & \quad \mu_c = \mu_{P-1} = \ldots \\
\end{align*}
\]

number of eqs. between variables = \( P-1)(C+2) \)

Thus \( f = \text{deg. of freedom} = \text{number of variables} - \text{number of eqs.} \)

\[
f = P(C+1) - (P-1)(C+2) = C+2-P
\]

\[
f = C+2-P \quad \text{Gibbs' phase rule.}
\]
If a given component is absent from a certain phase, then we reduce by one the number of concentration variables required to fix the state. But, also one of the relations is gone.

\[ \mu^0_g > \mu^0 \Rightarrow \mu^0 \]

Thus no change.

Now, assume component. If r independent reactions, then reduce f by r. (not per specie if in equi. in one phase, then equi. in all)

If other constraints put on electrostrictility of some solution, such that:

\[ f = c + p + 2 \]

Deciding cird can be trickly!

An example:

Acetic acid in water: 5 species: \( \text{H}_2\text{O}, \text{HAc}, \text{H}^+, \text{OH}^-, \text{Ac}^- \)

Two dissociation reactions:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \\
\text{HAc} & \rightarrow \text{H}^+ + \text{Ac}^-
\end{align*}
\]

Electrostrictility \( x(\text{H}^+) = x(\text{OH}^-) + x(\text{Ac}^-) \quad x = \text{mole fraction} \)
c = 5, n = 2, a = 1, c + 2d = 5 - 2 - 1 = 2

f = 4p = 3, here.

So $T_P, \chi(HAC)$ specify the system.

If we would consider 6 species: $H_2O, HAC, H^+, OH^-, A^-_2, O^-_2$
then add other reactions:

$$H_2O \rightarrow 2H^+ + O^-_2$$

So c = 6, n = 3, a = 1, $\chi(\chi^a) = \chi(\chi^a) + \chi(\chi^a) + \chi(\chi^a)$
$c + 2d = 6 - 1 - 1 = 2$ again

$$\frac{\Delta H_0 = H^+_2O - O^-_2 + H^+}{\frac{\Delta H_0 = H^+_2O - O^-_2 + H^+}{\frac{\Delta H_0 = H^+_2O - O^-_2 + H^+}{\frac{\Delta H_0 = H^+_2O - O^-_2 + H^+}{\Delta H_0 = H^+_2O - O^-_2 + H^+}}}$$

One component system. What's stable $\delta P/\delta T$ of the two phase equilibria in a PT diagram? Clausius-Clapeyron equation.

Return to picture of line of intersection of the $\alpha$ and $\beta$ phases. If $\mu^0$ and $\mu^0$ are particular values, then $\mu^0 = \mu^0$

At a closely point, we have

$$\mu^0 + \delta \mu^0 = \mu^0 + \delta \mu^0$$

(since still at eqm. And since $\mu^0 = \mu^0$)

$$d\mu^0 = d\mu^0$$

$$\frac{d\mu^0}{d\mu^0} = \frac{d\mu^0}{d\mu^0}$$

$$\frac{d\mu^0}{dT} + d\mu^0$$

$$\frac{d\mu^0}{dP}$$
and $d\mu = \frac{\partial \mu}{\partial \rho} d\rho + \frac{\partial \mu}{\partial T} dT$

But since $P = \rho$, $T = T'$, $dP = d\rho$, and $dT = dT'$, so

$$d\mu = \frac{\partial \mu}{\partial \rho} d\rho + \frac{\partial \mu}{\partial T} dT$$

For a pure substance $\mu = \bar{G} = \bar{G}_0$, $\rho = \bar{\rho}, \mu = \bar{\mu}$,

noting $\bar{S} = -\frac{\partial \bar{G}}{\partial T}$, $\bar{V} = \frac{\partial \bar{G}}{\partial \rho}$,

$$\bar{S} dT + \bar{V} d\rho = -\bar{P} dT + \bar{V} d\rho$$

Furthermore, $\bar{S} = \frac{\Delta H}{T}$ where $\Delta H$ is the latent heat.

8 The latin text. Thus

$$\frac{dP}{dT} = \frac{\Delta H}{T}$$

Clausius - Clapeyron Eq.

$$\frac{dP}{dT} = \frac{\Delta H}{T A V}$$

Note that for a single phase - as $\nu_2 = \nu_1$ - $\frac{d\mu}{dT} = \frac{\Delta H}{T A V}$, and

(Notice that for $H_2O$, say, we can still consider $\Delta H$ as $\Delta U$, as $\Delta S = 0$.

Thus $f = 1$. And $\Delta T$, will, for $1 \Delta \rho$. Thus ordinary $d\rho$)
For gas & solid:
1. \( V_g \gg V_s \), ideal
2. \( V_g = \frac{RT}{P} \)
3. \( \Delta H \) const.

\[ \ln \frac{P_2}{P_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \]

Exercise: increase pressure with temperature.
(Don't heat things in sealed containers)
Phase Rule Example.

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]

Start with all \( \text{CaCO}_3(s) \).

\[ C = 3 \quad \alpha = 1 \quad \text{ie. } \mu_{\text{\text{CaCO}_3}} = \mu_{\text{\text{CaO}}} + \mu_{\text{\text{CO}_2}} \]

Are there other restrictions among intensive variables?

Since we start with all \( \text{CaCO}_3(s) \) we do produce a known amount of product so possible mole fraction restrictions.

But read more info for this problem. How many phases?

If \( \text{CaCO}_3(s) + \text{CO}(s) \) are two solid phases, then

\[
\begin{align*}
\chi_{\text{\text{CaCO}_3(s)}} &= 1 \quad \text{in phase } \text{CaCO}_3(s) \\
\chi_{\text{\text{CO}(s)}} &= 1 \quad \text{in phase } \text{CO}(s)
\end{align*}
\]

Since these mole fractions are fixed, not variable, we have no further restriction than

\[ C_i = c_2 - c_1 = 3 - 1 - 0 = 2 \]

And

\[ f = c_1 + 2 - p = 2 + 2 - 3 = 1 \]

On the other hand, suppose \( \text{CaCO}_3(s) + \text{CO}(s) \) forms a solid solution. Then, since each \( \text{CO}(s) \) is formed from a \( \text{CaCO}_3(s) \),

\[ \chi_{\text{\text{CaCO}_3(s)}} + \chi_{\text{\text{CO}(s)}} = 1 \]

Since they are in the same phase, this is a new restriction.

Then

\[ C_i = c_2 - c_1 = 3 - 1 - 1 = 1 \]

And

\[ f = c_1 + 2 - p = 2 + 2 - 2 = 1 \] again.