

Reactions

Often interested in thermo-dynamic changes associated w/
a process:



$$\Delta U = U_B(N_B, V_B, T) - U_A(N_A, V_A, T)$$

$$\Delta S$$

"

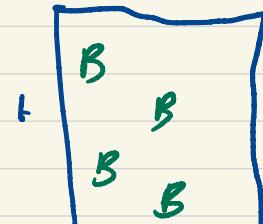
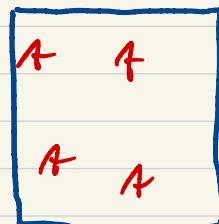
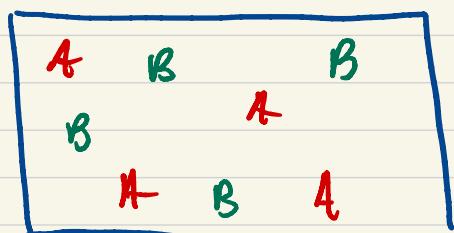
$$\Delta A$$

"

$$\Delta G$$

"

Simple example: ideal gas mixture



$$\downarrow$$
$$P = \frac{(N_A + N_B) k_B T}{V}$$

$$P = \frac{N_A k_B T}{x_A V} =$$

$$\begin{aligned}\Delta U &= U_A + U_B - U_{AB} \\ &= N_A k_B T + N_B k_B T - (N_A + N_B) k_B T \\ &= 0\end{aligned}$$

$$A_A = N_A \left(\bar{A}_A^*(T) + RT \ln \frac{c_A}{c^*} \right)$$

$$c_A = \frac{N_A}{x_A V}$$

$$A_B = N_B \left(\bar{A}_B^*(T) + RT \ln \frac{c_B}{c^*} \right)$$

$$c_B = \frac{N_B}{x_B V}$$

$$A_{AB} = N_A \left(\bar{A}_A^*(T) + RT \ln \frac{c_A}{c^*} \right)$$

$$c_A = \frac{N_A}{V}$$

$$+ N_B \left(\bar{A}_B^*(T) + RT \ln \frac{c_B}{c^*} \right)$$

$$c_B = \frac{N_B}{V}$$

$$\begin{aligned}\Delta A &= A_A + A_B - A_{AB} \\ &= N_A \left\{ RT \ln \left(\frac{N_A}{x_A V} \right) \cdot \left(\frac{V}{N_A} \right) \right\}\end{aligned}$$

$$+ N_B \left\{ RT \ln \left(\frac{N_B}{x_B V} \right) \left(\frac{V}{N_B} \right) \right\}$$

$$= RT \left\{ -N_A \ln x_A - N_B \ln x_B \right\}$$

$$\frac{\Delta A}{N_A + N_B} = -RT \left\{ x_A \ln x_A + x_B \ln x_B \right\}$$



minimum isothermal
work of separation ≥ 0

But $\Delta U = 0$? 

$$\Delta S = \frac{\Delta A - \Delta U}{T} = R \left\{ x_A \ln x_A + x_B \ln x_B \right\} < 0$$

Shows how our simple formulas can be put to work.

Takes work to compress A + B,
energy rejected as heat to envt.

More generally interested in "ways" that rearrange atoms.

Simple example



define cond.

$$\Delta S^\circ(298) = \bar{S}_{\text{trans}}^\circ - \bar{S}_{\text{trans}}^\circ \quad \Delta \text{S}$$

std state?	$+ \bar{S}_{\text{rot}}$	$- \bar{S}_{\text{rot}}$	$\underline{0.6}$
	90.9	90.3	
$\beta_3 \text{LyP} 6^-$	$+ \bar{S}_{\text{vib}}$	$- \bar{S}_{\text{vib}}$	6.6
	15.7	91	

7.2 J/mole K

$$\Delta U^\circ(298) = \bar{U}_{\text{trans}}^\circ - \bar{U}_{\text{trans}}^\circ \quad \Delta U$$

$$+ \frac{3}{2} RT \quad - \frac{3}{2} RT$$

$$+ \bar{U}_{\text{rot}} \quad - \bar{U}_{\text{rot}}$$

$$+ \frac{3}{2} RT \quad - \frac{3}{2} RT \quad 0$$

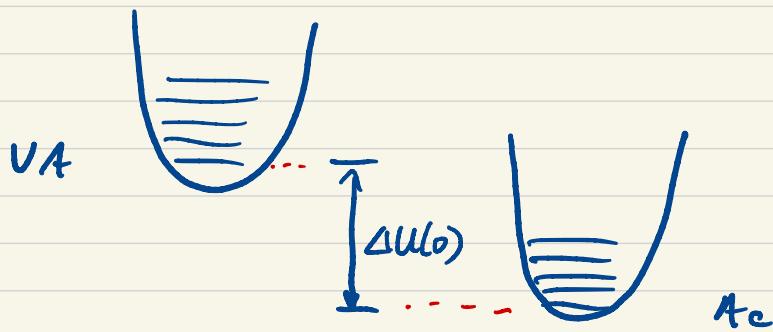
$$+ \bar{U}_{\text{vib}} \quad - \bar{U}_{\text{vib}} \quad 0.8$$

$$2.8 \quad 2.0$$

$$\text{"Bond energy"} + \bar{U}_{\text{elec}} - \bar{U}_{\text{elec}} - 64$$

$$+ \bar{U}_{\text{ZPE}} - \bar{U}_{\text{ZPE}} - 2.0$$

$$\underline{-65 \text{ kJ/mol}}$$



$$\Delta A^\circ(298) = \Delta U^\circ(298) - T \Delta S^\circ(228)$$

$$= -65000 - 298 (7.2)$$

$$= -67 \text{ kJ/mol}$$

H, U appropriate @ const V

Commonly we are interested
is const P .

enthalpy : $H \equiv U + PV$

Gibbs energy : $G \equiv H + PV$

For our ideal gas model

$$PV = RT$$

$$\Delta H = \Delta U$$

$$\Delta G = \Delta A$$

In general, depends on EOS of mat'l.

Key points:

- These thermodynamic diff's are between well defined initial + final states (eg $V_A @ 298\text{ K}, 1\text{ bar}$)

- Those initial + final states **MUST** conserve atom #'s (balance mass + atoms)

effect

- Tells us influence on enthalpy:

$\Delta U, \Delta H \rightarrow$ heat absorbed/rejected in change

$\Delta H > 0$ endothermic

< 0 exothermic

$\Delta A, \Delta G \rightarrow$ work done/doable in change

- At constant T, tells us direction of spontaneous change

$\Delta A, \Delta G < 0$ "spontaneous"

- Does not alone tell us what will happen, or how fast !!

Thermodynamic functions can be computed as we've seen above, or can be measured / tabulated.

It's helpful to define generic rxn



Define $\nu_1, \nu_2 > 0$, $\nu_3, \nu_4 < 0$

Write $\sum \nu_i k_i = 0$

Balanced reaction

Entropy

From 3rd Law, $\bar{S}(T=0) = 0$.

Common to see tabulations of $\bar{S}^\circ(T)$.

For general rxn, write

$$\Delta \bar{S}^\circ(T) = \sum_j \nu_j \bar{S}_j^\circ(T)$$

What if the tabulation
doesn't have the right T?

$$\bar{S}^{\circ}(T') = \bar{S}^{\circ}(T) + \underbrace{(\bar{S}^{\circ}(T') - \bar{S}^{\circ}(T))}_{\text{evaluate from formulas}} \quad -\text{or}-$$

$$\bar{S}^{\circ}(T') = \bar{S}^{\circ}(T) + \int_T^{T'} \left(\frac{\partial \bar{S}^{\circ}}{\partial T} \right) dT$$

const P or V depend
on std state

$$\frac{\partial \bar{S}^{\circ}(T)}{\partial T} = \frac{\bar{C}^{\circ}(T)}{T} \text{ tabulated}$$

Enthalpy First law tells us there
is no unique O of energy.

In QM, we take O to be eg
Energy of $2\text{H}^+ + 2\text{e}^-$, for H_2 .
Not practical often.

Yippee!! We get to define a zero for each element

Conventional to define enthalpy of pure element, in its most stable state, @ 298K + 1 bar, as zero for that element.

$$\bar{H}_{\text{H}_2(\text{g})}^{\circ}(298\text{ K}) \equiv 0$$

$$\bar{H}_{\text{graphite}}^{\circ}(298\text{ K}) \equiv 0$$

Any substance can then be def. in terms of its formation rxn;



$\Delta \bar{H}_f^{\circ}(T)$ tabulated

$$\Delta H^\circ(T) = \sum_j \nu_j \Delta H_{f,j}^\circ(T)$$

For instance, webbook.nist.gov lists

$$\Delta \bar{H}_{f,VA}^\circ = -128 \text{ kJ/mol}$$

$$\nu_{AC} = -171 \text{ kJ/mol}$$



$$\Delta \bar{H}^\circ(298) = -171 + 128$$

$$= -43 \text{ kJ/mol}$$

Right direction, wrong abs magnitude.

Data necessary for ΔS° not available.

Models are great for understanding, filling in gaps, predicting trends.

T-dependence of \bar{H}

$$\bar{H}^\circ(T) = \bar{H}^\circ(T) + (\bar{H}^\circ(T') - \bar{H}^\circ(T))$$

evaluate t. formulas

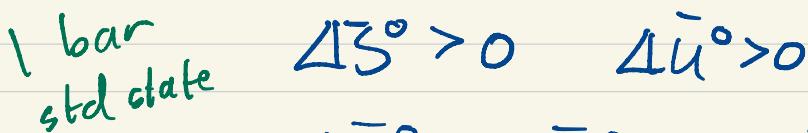
- or -

$$\bar{H}^\circ(T) = \bar{H}^\circ(T_0) + \int_{T_0}^T \left(\frac{\partial \bar{H}^\circ}{\partial T} \right)_{n,p} dT$$

$$= \bar{H}^\circ(T_0) + \int_{T_0}^T \underbrace{\bar{C}_p^\circ(T)}_{\text{tabulated}} dT$$

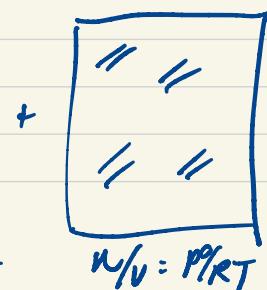
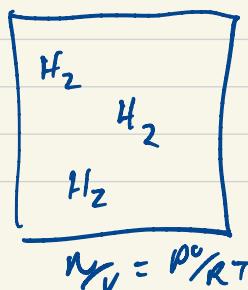
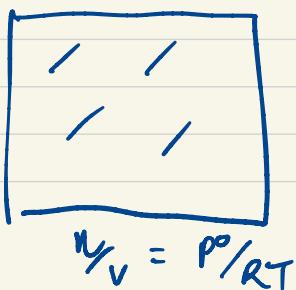
For a reaction, need $\bar{C}_p^\circ(T)$ for reactants & products. Won't typically see for formation rxns.

Refer to $/ \rightarrow // + H_2$ results



$$\Delta \bar{G}^\circ = \Delta \bar{U}^\circ - T \Delta \bar{S}^\circ$$

Shows how $\Delta \bar{A}^\circ$, $\Delta \bar{G}^\circ$ can be computed from all the models.



Note that

1) S_{trans} dominates ΔS

1 molecule \rightarrow 2 molecules

2) $\Delta E(0)$ dominates rxn energy

3) T-dependence dominated

by $\Delta G(T) = \Delta H(T) - T \Delta S$

To first order, $\Delta H + \Delta S$ T-dependence
are small relative to T factor.

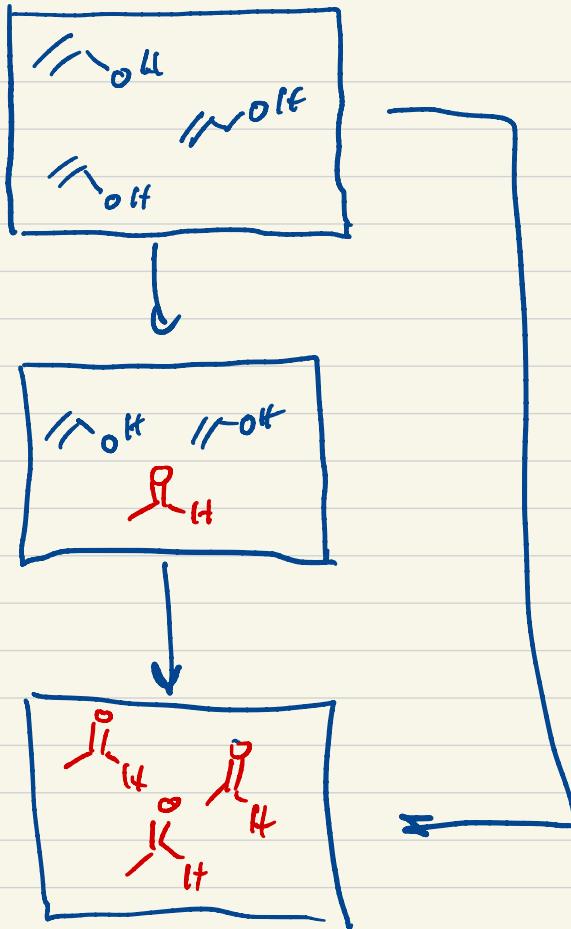
Rigorously $\left(\frac{\partial(G/T)}{\partial T}\right)_{N,P} = -\frac{\Delta H}{T^2}$

Gibbs-Helmholtz equation

} apply to a reaction
assume ΔH ind of T

$$\frac{\Delta G^\circ(T')}{T'} - \frac{\Delta G^\circ(T)}{T} \approx -\Delta H^\circ(T) \left(\frac{1}{T'} - \frac{1}{T} \right)$$

Good approx under many circumstances



1 l box
1 mol VA

std state
change

advancement

$$\xi =$$

Define advancement

$$N_{VA} = N_{VA,0} - \xi$$

$$N_{AC} = \cancel{N_{AC,0}}^0 + \xi \rightarrow 0 \leq \xi \leq N_{VA,0}$$

$$c_{VA} = \frac{N_{VA,0} - \xi}{V}$$

$$c_{AC} = \frac{\xi}{V}$$

ICE chart

$$\begin{array}{ccc}
 I & N_{v_{1,0}} & 0 \\
 C & -\xi & +\xi & \xi = \# / \text{Voll} \\
 E & N_{v_{1,0}} - \xi & \xi
 \end{array}$$

$$G(T, \xi) - G(T, \xi=0)$$

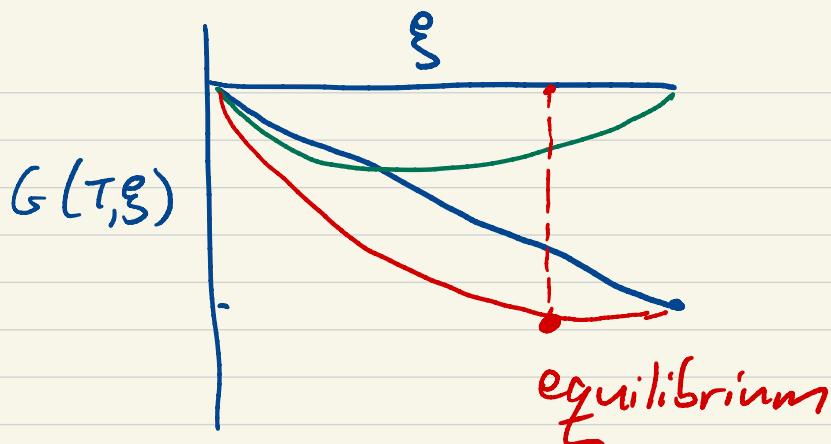
$$= (N_{v_{1,0}} - \xi) (\bar{G}_{v_1}^\circ(T) + k_B T \ln \frac{N_{v_{1,0}} - \xi}{\sqrt{v}})$$

$$+ \xi (\bar{G}_{ac}^\circ(T) + k_B T \ln \xi / v)$$

$$= \xi \Delta \bar{G}^\circ(T) \quad \text{linear in } \xi$$

$$+ k_B T \left\{ \xi \ln \xi + (N_{v_{1,0}} - \xi) \ln (N_{v_{1,0}} - \xi) \right\}$$

mixing
entropy



Convolution of standard reaction
and mixing

One approach to finding ξ_{eq} is
to minimize $G(T, \xi)$.

Alternative is to solve

$$\frac{\partial G(T, \xi)}{\partial \xi} = 0$$

$$\Rightarrow \sum_j v_j \mu_j = 0$$

$$@ \xi_{\text{eq}} \quad \mu_{\text{vt}} - \mu_{\text{ac}} = 0$$

$$\xrightarrow{\text{Z}} \Delta G^\circ(T) + RT \ln \frac{a_{ac}^{eq}}{a_{va}^{eq}} = 0$$

$$\frac{a_{ac}^{eq}}{a_{va}^{eq}} = e^{-\Delta G^\circ(T)/RT}$$

$$\equiv K_{eq}$$

Appropriate concentration units on left
are a function of std state on
the right.

In general

$$K_c(T) = \prod_i \left(\frac{c_i^{eq}}{c^0} \right)^{\nu_i} = \prod_i \underline{q}_i^0 \nu_i e^{-\Delta U^\circ(T)/RT}$$

$$= e^{-\Delta G^\circ(T)/RT}$$

$$\underline{q}^0 \equiv \underline{q}(c^0, T) = \frac{\underline{q}_{trans}}{V} \cdot \underline{q}_{rot} \cdot \underline{q}_{vib} \cdot \left(\frac{V}{N} \right)^0$$

$\#/\text{volume}$

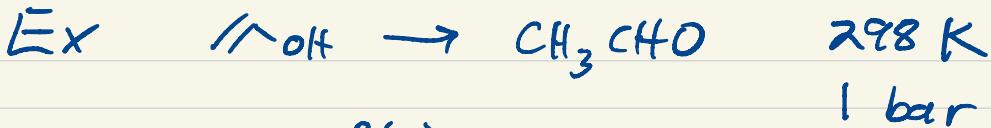
$$K_p(T) = \prod_i \left(\frac{y_i p}{p^0} \right)^{\nu_i} = \prod_i \underline{\mathcal{Q}}_i^{\nu_i} e^{-\Delta U(\alpha)/RT}$$

$$= e^{-\Delta G^\circ(T)/RT}$$

$$\underline{\mathcal{Q}}^0 \equiv \underline{\mathcal{Q}}(p^0, T) = \frac{\underline{\mathcal{Q}}_{\text{trans}} \cdot \underline{\mathcal{Q}}_{\text{rot}} \cdot \underline{\mathcal{Q}}_{\text{vib}}}{V} \cdot \left(\frac{RT}{p^0} \right)$$

$\#/\text{volume}$

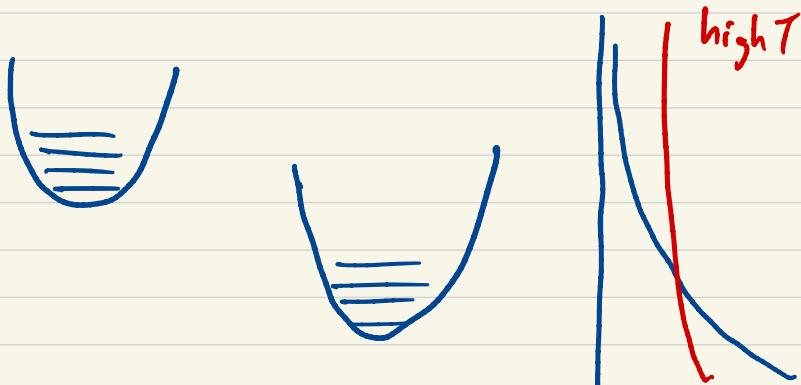
$1/c^0$



$$K_p(T) = \frac{q_{\text{ex}}^{\circ}(T)}{q_{\text{in}}^{\circ}(T)} e^{-\Delta U(0)/RT}$$

$$\frac{q^{\circ}_{\text{ex}}}{q^{\circ}_{\text{in}}} = \frac{q^{\circ}_{\text{trans}}}{q^{\circ}_{\text{trans}}} \cdot \frac{q^{\circ}_{\text{rot}}}{q^{\circ}_{\text{rot}}} \cdot \frac{q^{\circ}_{\text{vib}}}{q^{\circ}_{\text{vib}}} e^{-\frac{66 \text{ kJ/mol}}{RT}}$$

$$\approx 6 \times 10^{11}$$



Products dominate @ equil.

Illustrates Le' Chatlier's principle.

Exothermic reaction, higher T,
higher probability for reactants.

More formally, Gibbs-Helmholtz

$$\left(\frac{\partial \Delta G^\circ / T}{\partial T} \right)_p = \left(\frac{\partial \ln K}{\partial T} \right)_p = - \frac{\Delta \bar{H}^\circ}{R}$$

If $\Delta \bar{H}^\circ(T) \approx$ constant over range of interest

$$\ln \frac{K(T_2)}{K(T_1)} = - \frac{\Delta \bar{H}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

vant Hoff relationship

$$\Delta \bar{H}^\circ < 0 \rightarrow K \downarrow T \uparrow$$

Example



From thermo tables or stat mech

$$K_p = \frac{Q_{H_2}^{\circ}(T) Q_{//}^{\circ}(T)}{Q_{-}^{\circ}(T)} e^{-\Delta U(0)/kT}$$

$$Q_{H_2}^{\circ}(T) = \left(\frac{g_{trans}^{H_2}}{V} \right) \cdot g_{rot} \cdot g_{vib} \cdot \left(\frac{RT}{P^{\circ}} \right)$$

bar · m³/mol · K

1
m³ . P[°] ≡ 1 bar

/ v₀!

$$K_p = e^{-\Delta G^{\circ}(T)/RT} = \frac{P_{C_2H_6} P_{H_2}}{P_{C_2H_4}} \cdot \frac{1}{P^{\circ}}$$

$$P_i = P y_i \quad y_i = \frac{n_i}{N_{\text{tot}}}$$

	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>H₂</u>
I	<u>N₀</u>	0	0
C	-ξ	+ξ	+ξ
G	<u>N₀ - ξ</u>	<u>ξ</u>	<u>ξ</u>

≡ n₀ + ξ
n_{tot}

$$\gamma_{C_2H_6} = \frac{N_0 - \xi}{N_0 + \xi} \quad \gamma_{H_2} = \gamma_{C_2H_4} = \frac{\xi}{N_0 + \xi}$$

$$= \frac{1-x}{1+x} \quad = \frac{x}{1+x}$$

Define $x = \xi/N_0$

$$K_p = \left\{ p \left(\frac{x}{1+x} \right) \right\}^2 / p \left(\frac{1-x}{1+x} \right)$$

$$= p \cdot \frac{x^2}{(1+x)(1-x)}$$

Look at plots of γ_i

Endothermic $T \uparrow$ conversion \uparrow

Moles increase $p \uparrow$ conversion \downarrow

Why? side w/ more molecules
increasingly favored as
 $v \uparrow$

EXTRA

$$\mu_{vA} = E_{vA}(0) - k_B T \ln \frac{\bar{e}_{vA}}{N_{vA}}$$

$$\mu_{Ac} = E_{Ac}(0) - k_B T \ln \frac{\bar{e}_{Ac}}{N_{Ac}}$$

$$\ln \left(\frac{\bar{e}_A}{N_A} \right) = \ln \bar{e}^\circ - \ln \frac{c}{c^\circ}$$

$$\bar{e}^\circ \equiv \bar{e}(c^\circ, T)$$

$$\bar{e}_{trans}^\circ = \frac{1}{\lambda^3 \cdot c^\circ} \quad \#$$

$$\ln \left(\frac{\bar{e}_A}{N_A} \right) = \ln \bar{e}^\circ + \ln \frac{P}{P^\circ}$$

$$\bar{e}^\circ \equiv \bar{e}(P^\circ, T)$$

$$\bar{e}_{trans}^\circ = \frac{1}{\lambda^3} \cdot \frac{RT}{P^\circ} \quad \#$$

→

$$\frac{C_{Ac}^{eq}/c^\circ}{C_{vA}^{eq}/c^\circ} = \frac{\bar{e}_{Ac}^\circ(T, c^\circ)}{\bar{e}_{vA}^\circ(T, c^\circ)} e^{-\Delta U(0)/RT}$$

$\underbrace{\qquad\qquad\qquad}_{K_c(T)}$