

## Reactions

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



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

$$\Delta S$$

"

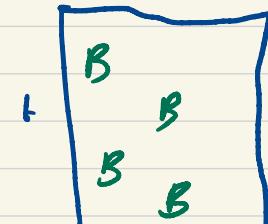
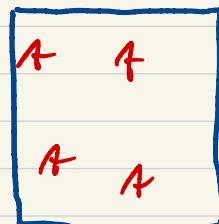
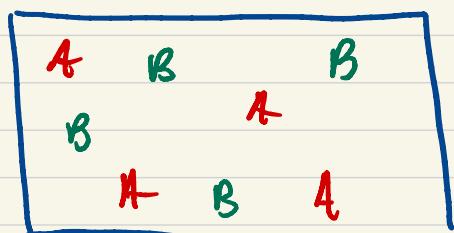
$$\Delta A$$

"

$$\Delta G$$

"

Simple example: ideal gas mixture



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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



minimum isothermal  
work of separation  $\geq 0$

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

$7.2 \text{ J/mole K}$

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

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

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

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

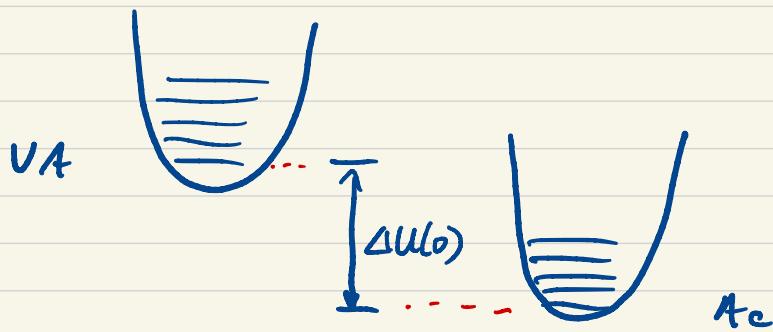
$$+ \bar{U}_{\text{vib}} \quad - \bar{U}_{\text{vib}} \quad 0.8$$

$$2.8 \quad 2.0$$

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

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

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



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

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

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

$H, U$  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  $\text{H}_2$ .  
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  $\Delta S^\circ$  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

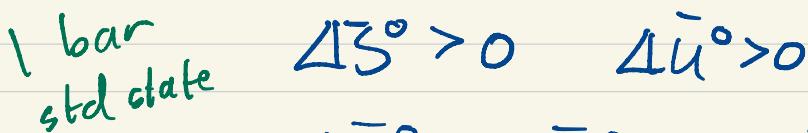
- or -

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

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

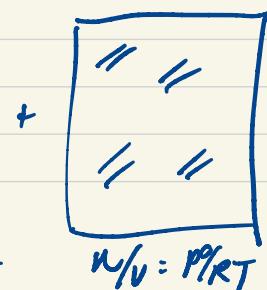
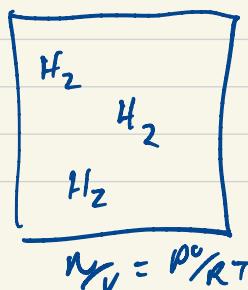
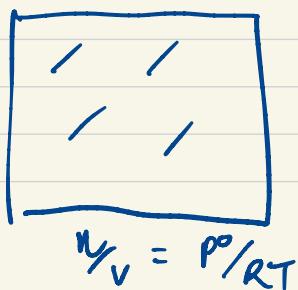
For a reaction, need  $\bar{C}_p^\circ(T)$  for reactants & products. Won't typically see for formation rxns.

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)  $S_{\text{trans}}$  dominates  $\Delta S$

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.

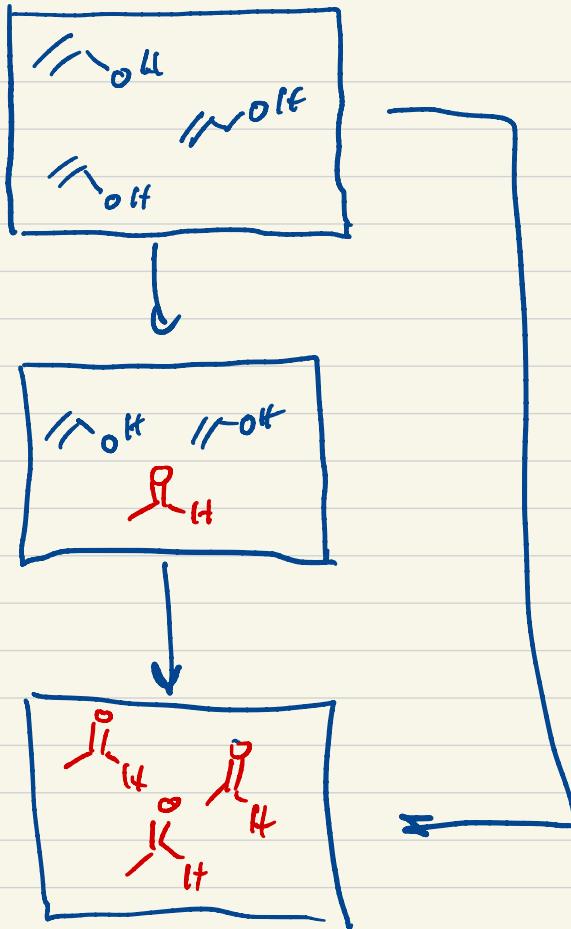
Rigorously  $\left(\frac{\partial(G/T)}{\partial T}\right)_{N,P} = -\frac{\Delta H}{T^2}$

Gibbs-Helmholtz equation

} apply to a reaction  
assume  $\Delta H$  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

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

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

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

# ICE chart

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

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

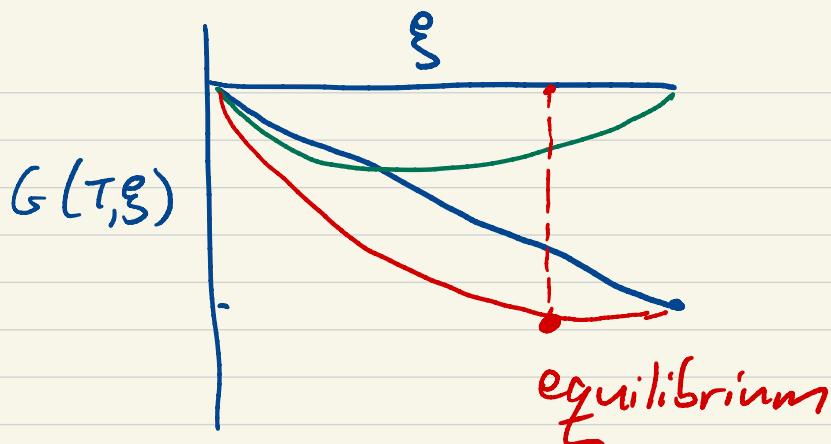
$$= (N_{v_{1,0}} - \xi) (\bar{G}_{v_1}^{\circ}(T) + k_B T \ln \frac{N_{v_{1,0}} - \xi}{\sqrt{v}})$$

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

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

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

mixing  
entropy



Convolution of standard reaction  
and mixing

One approach to finding  $\xi_{\text{eq}}$  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

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

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

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

$\#/\text{volume}$

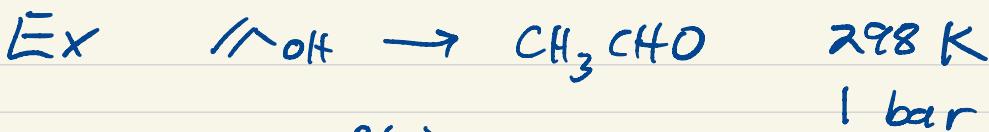
$$K_p(T) = \prod_i \left( \frac{y_i p}{p^0} \right)^{\nu_i} = \prod_i \underline{\mathcal{Q}}_i^{\nu_i} e^{-\Delta U(\alpha)/RT}$$

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

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

$\#/\text{volume}$

$1/c^0$



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

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

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

ICE chart

$$\text{I} \quad N_{\text{vA},0} \quad 0$$

$$\text{C} \quad -\xi \quad +\xi$$

$$\text{E} \quad N_{\text{vA},0} - \xi \quad \xi \quad N_{\text{TOT}} = N_{\text{vA},0}$$

$$y_{\text{vA}} = \frac{N_{\text{vA},0} - \xi}{N_{\text{vA},0}}$$

$$= 1 - x$$

$$y_{\text{AC}} = \frac{\xi}{N_{\text{vA},0}}$$

$$= x$$

$$K_p = \frac{P_{\text{AC}}}{P_{\text{vA}}} = \frac{P \cdot x}{P \cdot (1-x)} = 6 \times 10^{11}$$

$$x_{eq} \approx 1$$

Exothermic reaction, what happens as  $T \uparrow$ ??

Could resolve from beginning.

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

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

van't Hoff relationship

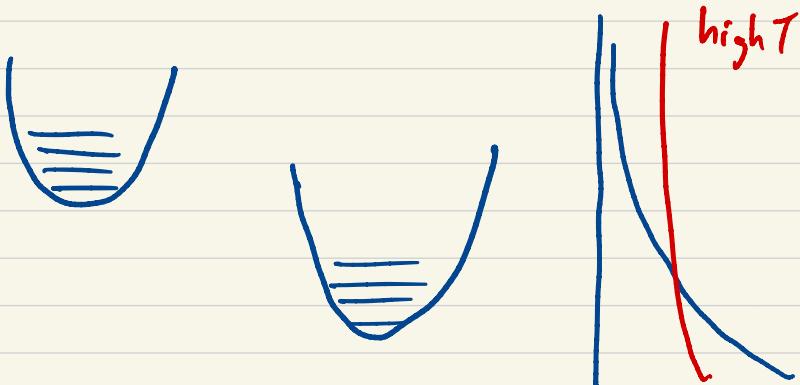
$$\Delta \bar{H}^\circ < 0 \rightarrow K \downarrow T \uparrow$$



$$K(2000\text{ K}) \approx K(298) e^{-\frac{\Delta H^\circ}{R} \left( \frac{1}{2000} - \frac{1}{298} \right)}$$

$\approx 120$        $7800\text{ K}$

$$x_{\text{eq}} \approx 0.99$$



Products dominate @ equil.

Illustrates Le'Chatlier's principle.

Exothermic reaction, higher T,  
higher probability for reactants.

Example



From thermo tables or stat mech

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

$$Q_{H_2}^{\circ}(T) = \left( \frac{g_{trans}^{H_2}}{V} \right) \cdot g_{rot} \cdot g_{vib} \cdot \left( \frac{RT}{P_0} \right)$$

states  
molecule m<sup>3</sup>

Units always confusing (to me!)

1 bar std state

$$RT = 8.314 T \text{ Pa m}^3/\text{mol}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$\frac{RT}{P_0} = \frac{8.314 T \text{ Pa m}^3/\text{mol}}{10^5 \text{ Pa}}$$

$$= 8.314 T \left( \frac{\text{m}^3}{\text{mol}} \right)$$

$$\frac{\text{states}}{\text{molecule } m^3} \cdot \frac{m^3}{\text{mole}} = \frac{\text{states}}{\text{mole}}$$

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

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

$$\begin{array}{cccc}
 & \underline{C_2H_6} & \underline{C_2H_4} & \underline{H_2} \\
 I & N_0 & 0 & 0 \\
 C & -\xi & +\xi & +\xi \\
 \hline
 \Sigma & N_0 - \xi & \xi & \xi \quad \equiv N_0 + \xi \\
 & & & n_{\text{tot}}
 \end{array}$$

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

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

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  $\gamma_i$

Endothermic  $T \uparrow$  conversion  $\uparrow$

Moles increase

$$P \uparrow \quad \frac{K_p}{P} \downarrow \quad \text{conversion} \downarrow$$

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



## EXTRA

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

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

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

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

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

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

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

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

→

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

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

$$c^{\circ} = \left(\frac{n}{V}\right)^{\circ} = \left(\frac{P^{\circ}}{RT}\right) = \frac{10000 \text{ Pa}}{RT \text{ Pa} \cdot \text{m}^3/\text{mol}}$$

$$P^{\circ} \equiv 1 \text{ bar} \equiv 10000 \text{ Pa}$$

$$\frac{\text{states}}{\text{m}^3} \cdot \frac{\text{m}^3}{\text{mol}} = \frac{\text{states}}{\text{mol}}$$

$$\frac{\text{mol}}{\text{m}^3}$$