

(look back @ Reas Hw)

## Reactions

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



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

$$\Delta S$$

"

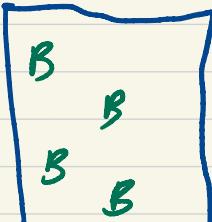
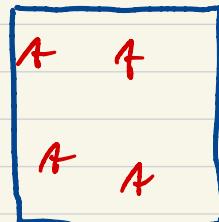
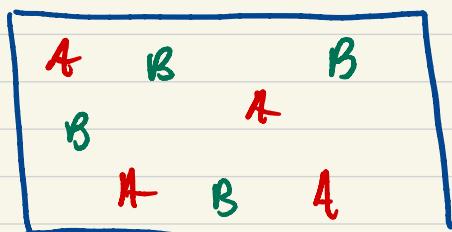
$$\Delta A$$

"

$$\Delta G$$

"

Simple example: ideal gas mixture separation



$$N_A, N_B, V, T$$

$$N_A x_A V T$$

$$N_B x_B V T$$

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

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

$$\begin{aligned}\Delta U &= U_A + U_B - U_{AB} \\ &= \frac{3}{2} \left( N_A k_B T + N_B k_B T - (N_A + N_B) k_B T \right) \\ &= U\end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

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



minimum isothermal  
work of separation  $\geq 0$

But  $\Delta U = 0$ ? 

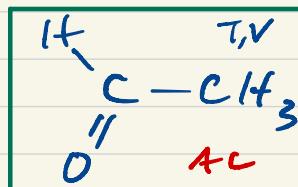
$$\Delta S = \frac{\Delta A - \Delta U}{T} = R \left\{ x_A \ln x_A + x_B \ln x_B \right\} < 0$$

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

Shows how our simple formulas can  
be put to work.

More generally interested in "ways" that rearrange atoms.

### Simple example



define cond.

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

std state?

$$+ \bar{S}_{\text{rot}} - \bar{S}_{\text{rot}} \\ 90.9 \quad 90.3 \quad 0.6$$

$$\beta_3 \text{L}^4 \text{P} | 6-3 | 6^* \quad ?$$

$$+ \bar{S}_{\text{vib}} - \bar{S}_{\text{vib}} \\ 15.7 \quad 91 \quad \underline{6.6}$$

$$7.2 \text{ J/mole K}$$

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

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

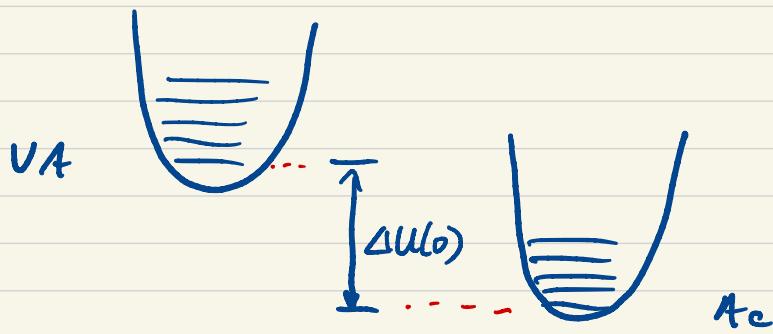
$$+ \bar{U}_{\text{rot}} - \bar{U}_{\text{rot}} \\ \frac{3}{2} RT \quad \frac{3}{2} RT \quad 0$$

$$+ \bar{U}_{\text{vib}} - \bar{U}_{\text{vib}} \\ 2.8 \quad 2.0 \quad 0.8$$

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

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

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



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

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

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

$H, U$  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

$$PV = RT$$

$$\Delta \bar{H}^\circ = \Delta \bar{U}^\circ$$

$$\Delta \bar{G}^\circ = \Delta \bar{A}^\circ = -67 \text{ kJ/mol}$$

In general, depends on EOS of mat'l.

Key points:

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

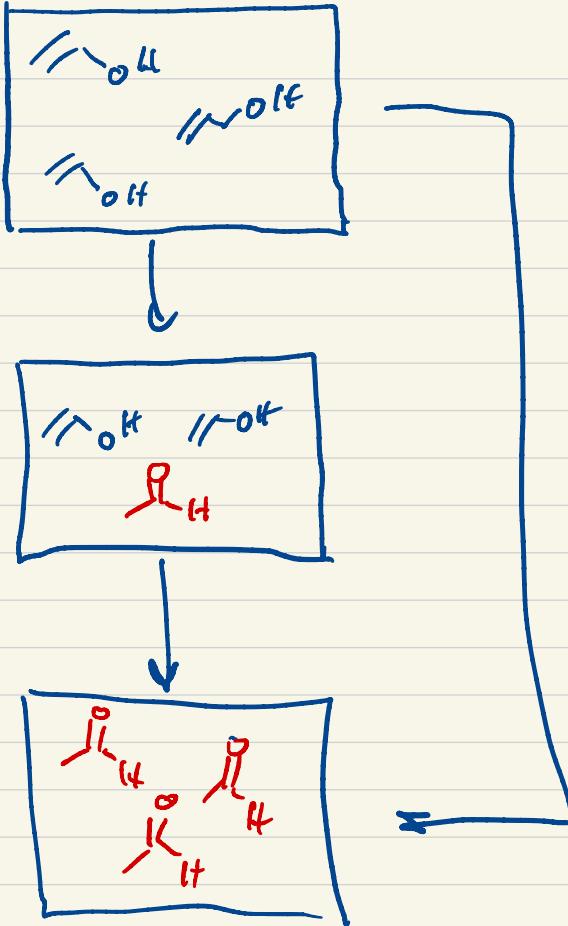
$\Delta A, \Delta G \rightarrow$  work done/doable in change

- 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 !!

# Equilibrium



1 l box  
1 mol VA

constant  
volume

1 M std state

std state  
change

advancement  
 $\xi =$

Define advancement

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

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

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

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

$$\Delta A(T, \xi) - A(T, \xi=0)$$

$$= (N_{VA,0} - \xi) (\bar{A}_{VA}^{\circ}(T) + k_B T \ln \frac{C_{VA}}{C^{\circ}})$$

$$+ \xi (\bar{A}_{AC}^{\circ}(T) + k_B T \ln \frac{C_{AC}}{C^{\circ}})$$

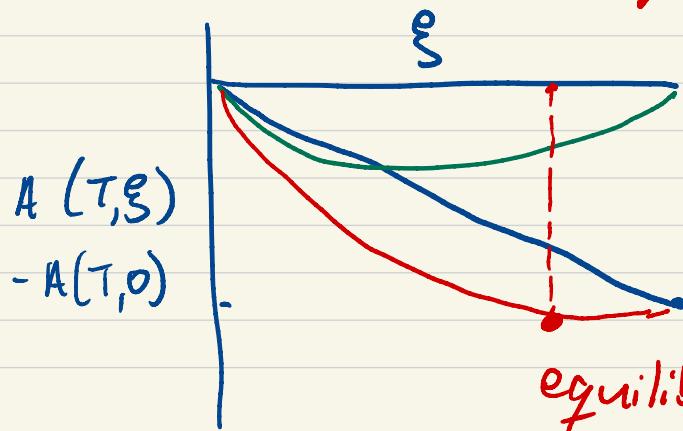
$$- N_{VA,0} \bar{A}_{VA}^{\circ}(T)$$

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

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



mixing entropy



In contact w/  
thermal reservoir,  
chemical equilibrium  
minimizes free  
energy.

Convolution of standard reaction  
and mixing

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

Alternative is to solve

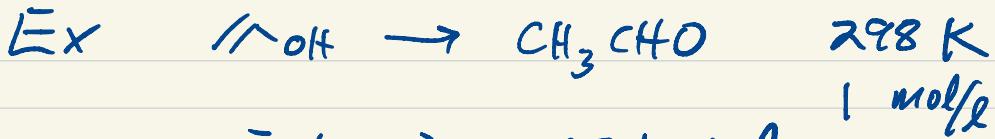
$$\frac{\partial A(T, \xi)}{\partial \xi} = 0 \quad \text{from} \quad dH = -\sum \mu_j dN_j$$

$$\rightsquigarrow \sum_j \nu_j \mu_j = 0$$

$$@ \xi_{eq} \quad \mu_{VA} - \mu_{AC} = 0$$

$$\rightsquigarrow \Delta \bar{A}^\circ(T) + RT \ln \frac{C_{AC}^{eq}}{C_{VA}^{eq}} = 0$$

$$\begin{aligned} \frac{C_{AC}^{eq}}{C_{VA}^{eq}} &= e^{-\Delta \bar{A}^\circ(T)/RT} \\ &\equiv K_{eq}(T) \end{aligned}$$



$$\Delta \bar{\Delta}^\circ(298) = -67 \text{ kJ/mol}$$

$$K_{\text{eq}}(298) = e^{-\Delta \bar{\Delta}^\circ / RT} = 6 \times 10^{-11}$$

ICE chart

I	$C_{v_{1,0}}$	0
C	$-C_{\text{eq}}$	$+C_{\text{eq}}$
E	$C_{v_{1,0}} - C_{\text{eq}}$	$C_{\text{eq}}$

$$\frac{C_{\text{eq}}}{C_{v_{1,0}} - C_{\text{eq}}} = \frac{x}{1-x} = 6 \times 10^{-11}$$

$$x = \frac{C_{\text{eq}}}{C_{v_{1,0}}} \quad \rightarrow x \approx 1$$

reaction goes to  
100% products

What about other temperatures?

Could start over, or...

### Gibbs-Helmholtz relation

$$\left( \frac{\partial \Delta \bar{A}^\circ(T)}{\partial T} \right)_v = \left( \frac{\partial \ln K_c}{\partial T} \right)_v = - \frac{\Delta \bar{U}^\circ}{R}$$

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

If  $\Delta \bar{H}^\circ(T)$  or  $\Delta \bar{U}^\circ(T) \sim \text{constant}$

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

van't Hoff relationship

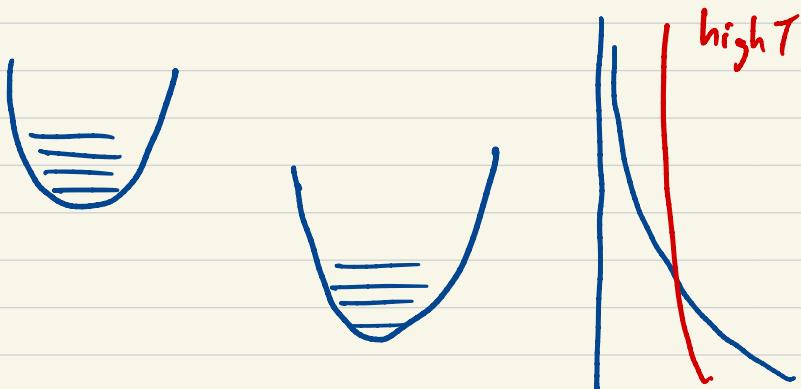
$$\Delta \bar{H}^\circ < 0 \rightsquigarrow K \downarrow T \uparrow$$



$$K(2000\text{ K}) \approx K(298) e^{-\frac{\Delta U^\circ}{R} \left( \frac{1}{2000} - \frac{1}{298} \right)} \\ \approx 120$$

7800 K

$$x_{eq} \approx 0.99$$



Illustrates Le' Chatlier's principle.  
 Exothermic reaction, higher T,  
 higher probability for reactants.

In general  $\gamma_1 A_1 + \gamma_2 A_2 \rightarrow \gamma_3 A_3 + \gamma_4 A_4$

At constant volume / concentration std state:

$$K_c(T) = \prod_i \left( \frac{c_i^{\circ} g}{c^{\circ}} \right)^{\gamma_i} = e^{-\Delta \bar{A}^{\circ}(T)/RT}$$

$$= \prod_i g_i^{\circ}^{\gamma_i} e^{-\Delta \bar{U}(0)/RT}$$

$$g^{\circ} = g(c^{\circ}, T) = \frac{g_{\text{trans}} \cdot g_{\text{rot}} \cdot g_{\text{vib}}}{V} \cdot \left( \frac{V}{N} \right)^{\frac{1}{c^{\circ}}}$$

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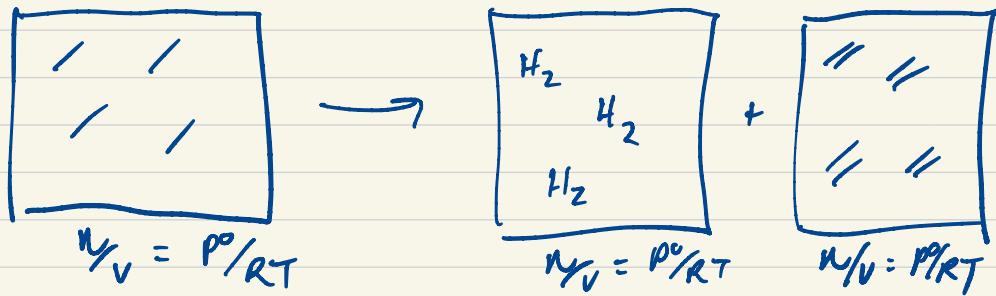
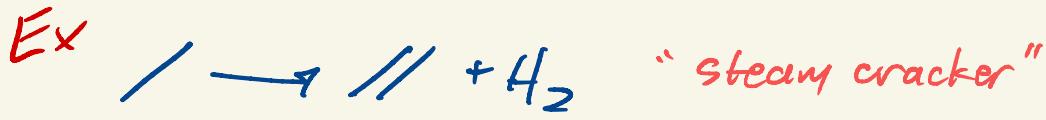
At constant pressure / pressure std state:

$$K_p(T) = \prod_i \left( \frac{y_i p}{p^{\circ}} \right)^{\gamma_i} = e^{-\Delta \bar{G}^{\circ}(T)/RT}$$

$$= \prod_i g_i^{\circ}^{\gamma_i} e^{-\Delta \bar{U}(0)/RT}$$

$$g^{\circ} = g(p^{\circ}, T) = \frac{g_{\text{trans}} \cdot g_{\text{rot}} \cdot g_{\text{vib}}}{V} \cdot \left( \frac{k_B T}{p^{\circ}} \right)^{\frac{1}{c^{\circ}}}$$

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Gas-phase reaction, constant  $P$  makes sense  
1 bar std state

Compute quantities vs T See graphs

$$\Delta\bar{S}^\circ > 0 \quad \Delta\bar{U}^\circ > 0$$

1) Strain dominates  $\Delta\bar{S}^\circ$   
1 molecule  $\rightarrow$  2 molecules

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

3)  $\Delta\bar{G}^\circ(T) = \Delta\bar{H}^\circ(T) - T\Delta\bar{S}^\circ(T)$   
has strongest T dependence

Consequences for equilibrium?

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

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

states  
molecule m<sup>-3</sup>.

1 bar std state

$$k_B T = 1.38 \times 10^{-23} \text{ J Pa} \cdot \text{m}^3$$

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

$$\frac{k_B T}{P^{\circ}} = \frac{1.38 \times 10^{-23} \text{ J Pa m}^3}{10^5 \text{ Pa}}$$

$$= 1.38 \times 10^{-23} \cdot T \text{ m}^3$$

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

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

$$\begin{array}{c}
 \frac{C_2H_6}{N_0} \quad \frac{C_2H_4}{0} \quad \frac{H_2}{0} \\
 I \quad N_0 \quad 0 \quad 0 \\
 C \quad -\xi \quad +\xi \quad +\xi \\
 \hline
 \Sigma \quad N_0 - \xi \quad \xi \quad \xi \quad \equiv N_0 + \xi
 \end{array}$$

$n_{\text{tot}}$

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

$$x = \xi / N_0 = \frac{1-x}{1+x} = \frac{x}{1+x}$$

$$K_p = \left\{ \rho \left( \frac{x}{1+x} \right) \right\}^2 \cancel{\rho \left( \frac{1-x}{1+x} \right) \cdot p^\circ}$$

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

Look at plots of  $y_i$

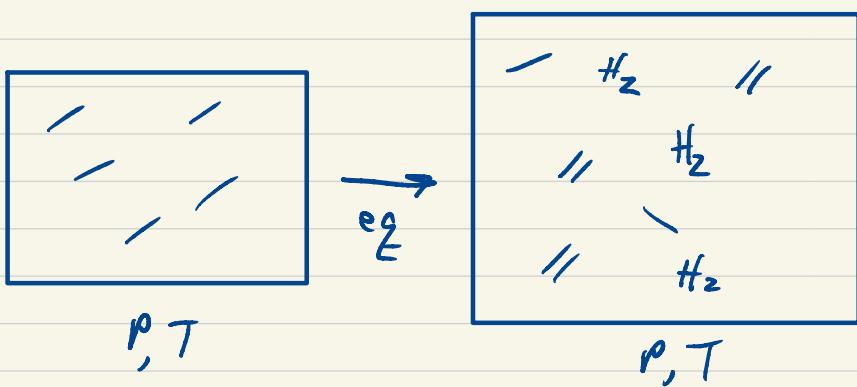
Endothermic  $T \uparrow$  conversion  $\uparrow$

Moles increase

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

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

Lc'Chatlier



## Thermo tabulations

Thermodynamic fns 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

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

Enthalpy First law tells us there is no unique  $\Delta$  of energy.

In QM, we take  $\Delta$  to be eg

Energy of  $2\text{H}^+ + 2e^-$ , for  $\text{H}_2$ .  
Not practical often.

Conventional to define enthalpy of pure element, in its most stable state, @ 298 K & 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

$$\Delta H^\circ(T) = \sum_j n_j \Delta \bar{H}_{f,j}^\circ(T)$$

For instance, webbook.nist.gov lists

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

$$, \text{ac} = -171 \text{ kJ/mol}$$



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

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

Compare to Webmo - 65 kJ/mol

Tabulation doesn't contain  $S^\circ$  data.

Ok to combine model  $S$  + measured  $H$ .

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

## Temperature dependence

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

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

- 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 depends  
on std state

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

T-dependence of  $\bar{H}$

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

evaluate f. formulas

$$\bar{H}^\circ(T) = \bar{H}^\circ(T) + \int_T^{T'} \left( \frac{\partial \bar{H}^\circ}{\partial T} \right)_{n,p} dT$$

$$= \bar{H}^\circ(T) + \int_T^{T'} \bar{c}_p^G(T) dT$$

tabulated

Neither  $S$  nor  $H$  tend to be very strongly T-dependent.

$$\left(\frac{\partial S}{\partial T}\right) = \frac{C_p}{T} \quad \left(\frac{\partial H}{\partial T}\right) = C_p$$

$$\Rightarrow \left(\frac{\partial \Delta S}{\partial T}\right) = \frac{\Delta C_p}{T} \quad \left(\frac{\partial \Delta H}{\partial T}\right) = \Delta C_p$$

$\Delta S$ ,  $\Delta H$  typically have modest T dependence

$$G = H - TS \quad \Delta G = \Delta H - T \Delta S \quad \text{T dependence} \not\equiv$$

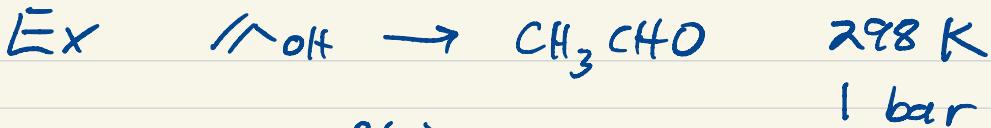
$$\left(\frac{\partial (G/T)}{\partial T}\right)_{n,p} = -\frac{H}{T^2} \quad \begin{matrix} \text{Gibbs-Helmholtz} \\ \text{relation} \end{matrix}$$

{ apply to a reactible  
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





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

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

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

ICE chart

$$\begin{array}{ccc} \text{I} & N_{\text{vap},0} & 0 \\ \text{C} & -\xi & +\xi \end{array}$$

$$\text{E} \quad N_{\text{vap},0} - \xi \quad \xi \quad N_{\text{tot}} = N_{\text{vap},0}$$

$$y_{\text{VA}} = \frac{N_{\text{vap}} - \xi}{N_{\text{vap},0}} \quad y_{\text{AC}} = \frac{\xi}{N_{\text{vap},0}}$$

$$= 1 - x \quad = x$$

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

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

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

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

$\frac{1}{C^\circ}$

$$\frac{\underline{g}_{\text{trans}}}{V} : \frac{1}{m^3}$$

#

$$C^\circ = \frac{1 \text{ mol}}{l} \times \frac{1000 l}{m^3} \times \frac{6.0222 \times 10^{23}}{\text{mol}} = 6.022 \times 10^{26} \frac{1}{m^3}$$

$$\frac{\underline{g}_{\text{trans}}}{V} \cdot \frac{1}{C^\circ} \rightarrow \text{unitless}$$

$$P^\circ = 1 \text{ bar} \quad \frac{k_B T}{10^5 \text{ Pa}} \rightarrow m^3$$

1 H std state

$$1 \frac{\text{mol}}{l} \times \frac{1000 l}{m^3} \times \frac{6.0222 \times 10^{23}}{\text{mol}} = 6.022 \times 10^{26} \frac{1}{m^3}$$

$$= C^\circ$$