

CBE 40455

8/30/17

## CHEMICAL REACTION EQUILIBRIUM

THERMODYNAMICS TELLS  
WHAT IS POSSIBLE

- ARE PRODUCTS OR  
REACTANTS FAVORED?

... HOW FAR TO  
COMPLETION?

- WHAT IF  $T \uparrow$

... RATE INCREASES  
BUT EXTENT MAY  
DROP

- WHAT IF  $P \uparrow$

# TODAY

- ① REVIEW / CONTEXT
- ② REACTION EQUILIBRIUM
- ③ ADIABATIC HEAT RISE

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# What could be better than...

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- ❖ A large muffin...
- ❖ Why not even bigger?  
Can we decide if this is possible?
- ❖ Of course, use the “cooking number”



# REACTION TIME SCALES FOR DIFFERING ACTIVATION ENERGY

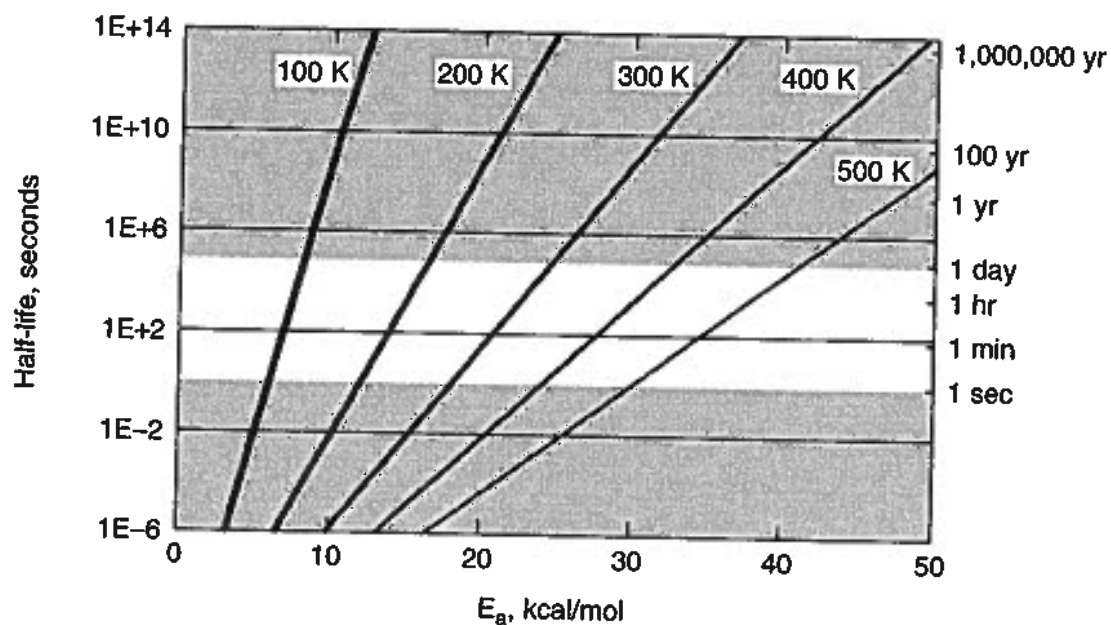


Figure 2.8 A plot of  $\tau_{1/2}$  versus  $E_a$  at 100, 200, 300, 400, and 500 K.

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# First some of (my) culture

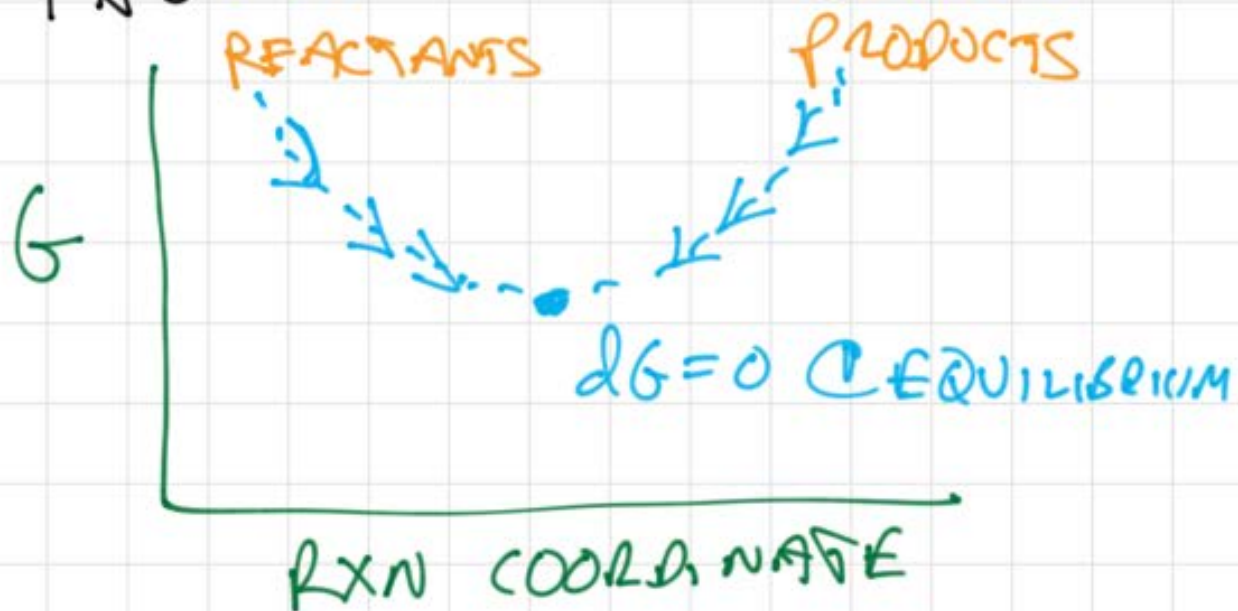
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- ❖ That was Tony Bennett with Count Basie and his Orchestra
  - ❖ (also of *Blazing Saddles* fame!)





FOR TYPICAL CHEMICAL  
 REACTOR CONFIGURATIONS  
 WE KEEP  $T, P$  CONSTANT  
 AS REACTION PROCEEDS  
 THUS



$$dG = -SdT + VdP + \sum_j \mu_j dN_j = 0$$

CHEMICAL  
 POTENTIAL

$$dG = \sum_j \mu_j dN_j = 0, N_j = N_{j0} + \nu_j \xi$$

$$dG = \sum_j \mu_j \nu_j d\xi$$

$$\frac{dG}{d\xi} = 0 = \sum_j \mu_j \nu_j \quad \text{① EQUILIBRIUM}$$

NOW WE NEED AN EXPRESSION  
FOR CHEMICAL POTENTIAL  
THAT ALLOWS CALCULATION...

STANDARD  
STATE

$$\mu_j = \mu_j^\circ(T) + RT \ln a_j$$

298 K  
1 ATM

$$\mu_j^\circ = G_j^\circ(T)$$

↑  
ACTIVITY,  
DEPENDS ON  
COMPOSITION  
(CONCENTRATION)  
AND CHEMICAL  
INTERACTION  
EFFECTS

FOR "IDEAL" CASE

$$a_j(M_j, P, T)$$

GASES:  $a_j = \frac{P_j}{P^0}$

SOLUTIONS:  $a_j = \frac{C_j}{C^0}$

PARTIAL PRESSURES

$P^0 = 1 \text{ ATM}$   
STANDARD STATE

$C^0 = 1 \text{ M}$   
STANDARD STATE

AT EQUILIBRIUM

$$\sum_j \nu_j V_j = 0$$

$$\sum_j \nu_j (M_j^0(T) + RT \ln a_j) = 0$$

LET'S DO SOME REARRANGEMENTS  
TO MAKE ULTIMATE CALCULATION  
OF FINAL STATE EASIER

$$\sum_j \nu_j M_j^0(T) = -RT \sum_j \ln a_j^{\nu_j}$$

WE KNOW ALL  
OF THIS



BECAUSE

$$\mu_j^{\circ}(T) = G_j^{\circ}(T)$$

SWITCH  
SUM TO  
PRODUCT

WE WRITE:

$$\Delta G_R^{\circ}(T) \equiv \sum_j \nu_j G_j^{\circ}(T) = -RT \ln \prod_j q_j^{\nu_j}$$

DEFINE:  $K_{EQ} \equiv \prod_j q_j^{\nu_j}$

THUS

$$\Delta G_R^{\circ}(T) = -RT \ln K_{EQ}$$

.....  
KEY RESULT

$$K_{EQ} = \prod_j q_j^{\nu_j} = e^{-\frac{\Delta G_R^{\circ}}{RT}}$$

$$K_{EQ} = F(T)$$

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# WHERE DO WE GET $\Delta G_r^\circ$ ?

VALUES FOR  $\Delta G_{\text{FORMATION}}$  ,  $\Delta H_{\text{FORMATION}}$

(FROM ELEMENTS)  
ARE TABULATED:

## Standard Gibbs free energy of formation

From Wikipedia, the free encyclopedia

This article **relies largely or entirely on a single source**. Relevant discussion may be found on the [talk page](#). Please help improve this article by introducing citations to additional sources. (December 2011)

The **standard Gibbs free energy of formation** of a compound is the change of **Gibbs free energy** that accompanies the formation of 1 mole of a substance in its **standard state** from its constituent elements in their standard states (the most stable form of the element at 1 bar of pressure and the specified temperature, usually 298.15 K or 25 °C).

The table below lists the Standard Gibbs function of formation for several elements and chemical compounds and is taken from [Lange's Handbook of Chemistry](#). Note that all values are in kJ/mol. Far more extensive tables can be found in the [CRC Handbook of Chemistry and Physics](#) and the [NIST JANAF tables](#).<sup>[1]</sup> The [NIST Chemistry WebBook](#) (see link below) is an online resource that contains standard standard enthalpy of formation for various compounds along with the standard absolute entropy for these compounds from which the Standard Gibbs Free Energy of Formation can be calculated.

Hydrobromic acid			
Calcium	Solid	Ca	0
Calcium carbide	Solid	CaC <sub>2</sub>	-64.9
Calcium Carbonate (Calcite)	Solid	CaCO <sub>3</sub>	-1129.1
Calcium Chloride	Solid	CaCl <sub>2</sub>	-748.8
Calcium Chloride	Aqueous	CaCl <sub>2</sub>	-816.05
Calcium Hydride	Solid	CaH <sub>2</sub>	-142.5
Calcium hydroxide	Solid	Ca(OH) <sub>2</sub>	-897.5
Calcium Oxide	Solid	CaO	-603.3
Calcium Sulfate	Solid	CaSO <sub>4</sub>	-1309.1
Calcium Sulfide	Solid	CaS	-477.4

Calcium			
Calcium	Solid	Ca	0
Calcium	Gas	Ca	178.2
Calcium(II) ion	Gas	Ca <sup>2+</sup>	1925.90
Calcium carbide	Solid	CaC <sub>2</sub>	-59.8
Calcium carbonate (Calcite)	Solid	CaCO <sub>3</sub>	-1206.9
Calcium chloride	Solid	CaCl <sub>2</sub>	-795.8
Calcium chloride	Aqueous	CaCl <sub>2</sub>	-877.3
Calcium phosphate	Solid	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	-4132
Calcium fluoride	Solid	CaF <sub>2</sub>	-1219.6
Calcium hydride	Solid	CaH <sub>2</sub>	-186.2
Calcium hydroxide	Solid	Ca(OH) <sub>2</sub>	-986.09
Calcium hydroxide	Aqueous	Ca(OH) <sub>2</sub>	-1002.82

## Standard enthalpy of formation

From Wikipedia, the free encyclopedia

The **standard enthalpy of formation** or **standard heat of formation** of a compound is the change of **enthalpy** during the formation of 1 mole of the substance from its constituent elements, with all substances in their **standard states**, and at a pressure of 1 bar (100 kPa). There is no standard temperature. Its symbol is  $\Delta_f H^\circ$ . The superscript **Plimsoil** on this symbol indicates that the process has occurred under standard conditions at the specified temperature (usually 25 °C or 298.15 K). Standard states are as follows:

1. For a gas: the hypothetical state it would have assuming it obeyed the ideal gas equation at a pressure of 1 atm
2. For a **solute** present in an **ideal solution**: a concentration of exactly one mole per liter (1 M) at a pressure of 1 atm
3. For a pure substance or a **solvent** in a condensed state (a liquid or a solid): the standard state is the pure liquid or solid under a pressure of 1 atm
4. For an element: the form in which the element is most stable under 1 atm of pressure. One exception is phosphorus, for which the most stable form at 1 atm is **black phosphorus**, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation.<sup>[1]</sup>

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

handling of this energy is a major concern in reaction engineering. This topic is an application of the First Law of Thermodynamics, which says that mechanical and thermal energy is conserved in any process. When we describe a chemical reaction, we designate its rate, but

**TABLE 2-2**  
**Standard State Enthalpy and Free Energy Changes for Some Important Reactions**  
**Discussed in This Book**

Reaction	$\Delta H_R^o, 298$	$\Delta G_R^o, 298$
$\text{NO} \rightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2$	-90.37	-86.69
$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	-180.75	-173.4
$\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$	+180.75	+173.4
$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	-114.14	-70.785
$\text{trans-2-C}_4 \rightleftharpoons \text{cis-2-C}_4 =,$ $1-\text{C}_4 \rightleftharpoons \text{trans-2-C}_4 =$		
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-802.32	-800.78
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	+206.15	+142.12
$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	-35.677	-86.475
$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	+136.95	+101.01
$\text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	-209.75	-255.17
$\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$	-929.45	-919.69
$\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$	-218.47	-199.75
$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$	-28.987	-7.8529
$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	-90.642	-24.317
$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	-282.99	-257.12
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-41.163	-28.522
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-241.83	-228.59
$\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$	-45.857	-16.33
$\text{NH}_3 + \frac{5}{4}\text{O}_2 \rightarrow \text{NO} + \frac{3}{2}\text{H}_2\text{O}$	-226.51	-239.87
$\text{NH}_3 + \frac{3}{4}\text{O}_2 \rightarrow \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2\text{O}$	-316.88	-326.56

Note: All values are in kJ/mole of the first species listed.



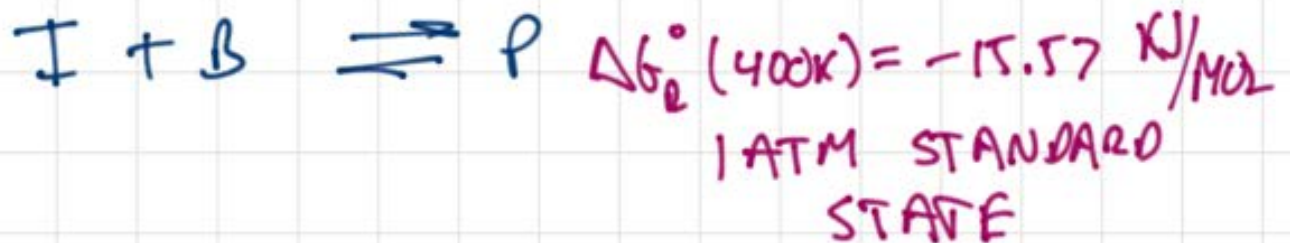


$$\Delta G_r^\circ(298) = \sum \nu_i \Delta G_{f,i}^\circ(298)$$

AND/OR

$$\Delta H_r^\circ(298) = \sum \nu_i \Delta H_{f,i}^\circ(298)$$

LET'S DO AN EXAMPLE:



WHAT IS EQUILIBRIUM CONVERSION?

$$T = 400 \text{ K}, P = 2.5 \text{ ATM}$$



START WITH  $N_{I0} = N_{B0}$

$N_I$  WILL ALWAYS =  $N_B$

$$K_{EQ} = e^{-\Delta G/RT} = 108 = \frac{\pi_i q_i^{y_i}}$$

$$= \frac{a_P}{a_I a_B} = \frac{P/P^0}{\left(\frac{P_I}{P^0}\right) \left(\frac{P_B}{P^0}\right)}$$

$$P_j = y_j P$$

$$\therefore K_{EQ} = 108 = \frac{y_P}{y_I y_B} \frac{P/P^0}{\left(\frac{P}{P^0}\right) \left(\frac{P}{P^0}\right)}$$

$$= \frac{y_P}{y_I y_B} \left(\frac{P}{P^0}\right)^{-1}$$

NOW USE KNOWLEDGE OF  
STARTING EQUIMOLAR  
REACTANTS . . .

$$N_j = N_{j0} - \frac{V_j}{V_A} N_{A0} X$$

"A" LIMITING REACTANT

IN OUR CASE, I & B ARE SAME

USE "I"

$$N_I = N_{I0} (1-x)$$

$$N_B = N_{I0} (1-x)$$

$$N_P = \cancel{N_{P0}} - \left(\frac{-1}{-1}\right) N_{I0} X = N_{I0} X$$

$$N_T = \sum N_j = N_{I0} (2-x)$$

$$\therefore y_I = y_B = \frac{N_I}{N_T} = \frac{(1-x)}{(2-x)}$$

$$y_P = \frac{N_P}{N_T} = \frac{x}{(2-x)}$$

FINALLY:

$$K = 108 = \frac{x}{2-x} \left( \frac{2.5 \text{ ATM}}{1 \text{ ATM}} \right)^{-1} \left( \frac{(1-x)/(2-x)}{1} \right)^2$$

SOLVE FOR X

$$x = .939$$

~ 94% CONVERSION @ 400K  
2.5 ATM

WHAT IF  $P \uparrow$



LECHATLIER'S PRINCIPLE . . .  
SHIFT TO PRODUCTS..

$$@ 8 \text{ ATM } X = .96$$

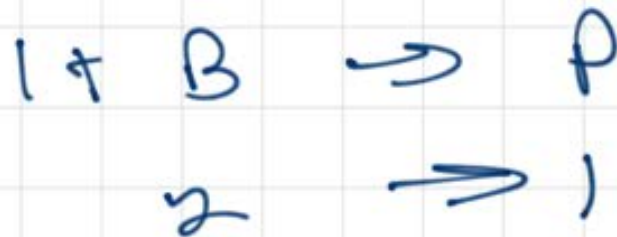
$$\left\{ \frac{y_P}{y_A y_B} = K \left( \frac{P}{P_0} \right) \right\}$$



SUPPOSE WE RUN AT  
CONSTANT VOLUME

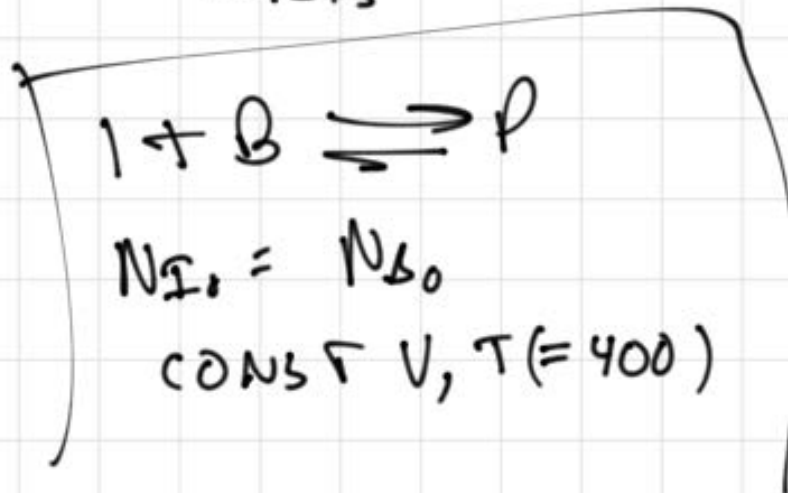
• BATCH, CLOSED VESSEL

HOW DOES X CHANGE



PRESSURE WILL BE DRIPPING  
X WILL BE LESS

$K_{EQ}$  :  $K_p$  vs  $K_c$   
          ↑                  ↑ CONCENTRATION  
          PRESSURE      BASIS  
          BASIS



$$K_{FO} = K_P = 108 = \frac{(P_P/P^0)}{(P_A/P^0)(P_B/P^0)}$$

TO CONVERT:

$$C_j = P_j/RT$$

$$K_P = \frac{C_P (RT/P^0)}{(C_A (RT/P^0))(C_B (RT/P^0))} = \frac{C_P}{C_A C_B} \left(\frac{P^0}{RT}\right)$$

$$\therefore \frac{C_P}{C_A C_B} = K_P \left(\frac{P^0}{RT}\right)^{\Delta \nu}$$

$$K_c \equiv K_P \left(\frac{P^0}{C^0 RT}\right)^{\Delta \nu} = \prod_j \left(\frac{C_j}{C^0}\right)^{\nu_j}$$

$C^0 \equiv$  STANDARD CONCENTRATION  
(1 M)

$$K_c(400) = 108 \left( \frac{1 \text{ atm}}{\left( \frac{.08206 \text{ L-atm}}{\text{mol-K}} \right) (400 \text{ K})} \right)^{-1}$$

$$K_c = 3545$$

$$C_j = C_{j0} - \frac{V_j}{V_A} C_{A0} X$$

$$C_I = C_{I0} (1-X) = C_{B0}$$

$$C_P = \cancel{C_{P0}} + C_{I0} X$$

$$K_c = \frac{C_P / C^0}{(C_I / C_0)(C_B / C_0)} = \frac{C_{I0} X C^0}{C_{I0}^2 (1-X)^2}$$

$$= \frac{X C^0}{C_{I0} (1-X)^2} = 3545$$

$$C_{I0} = \frac{P_{I0}}{RT} = \frac{1.25 \text{ atm}}{\left( .08206 \frac{\text{L-atm}}{\text{mol-K}} \right) (400 \text{ K})}$$

$$C_{I_0} = .0381 \text{ M}$$

SOLVE FOR X

$$X = .918 \quad (2.939)$$

IF  
 $P = \text{CONST}$



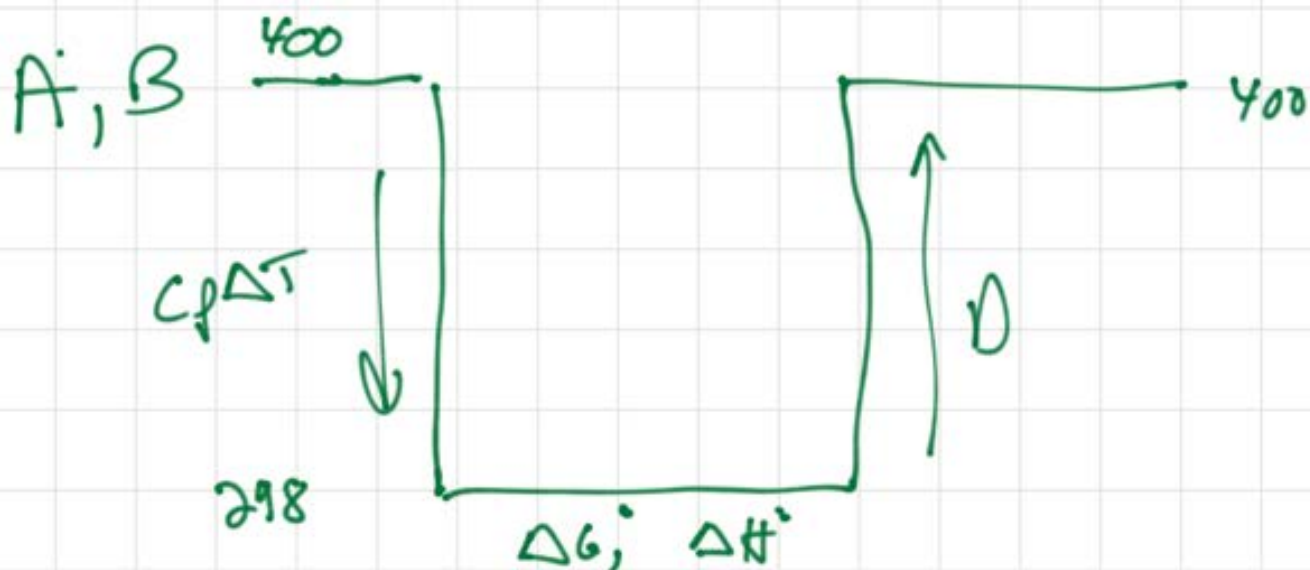
# TEMPERATURE EFFECTS

IF YOU NEED AN ENTHALPY OF FORMATION @  $T \neq 298$

YOU "FORM COMPOUND" @ 298

BUT YOU MAY HAVE COOLED REACTANTS, THEN HEATED PRODUCTS TO MATCH RXN CONDITIONS

- THIS HEATING/COOLING IS OFTEN NEGLIGIBLE



$$H(T) \rightarrow H(T')$$

$$\left( \frac{\partial H_i^0}{\partial T} \right)_p = C_{p,i}^0$$

$$\left( \frac{\partial \Delta H_{rxn}}{\partial T} \right)_p = \sum \nu_i C_{p,i}^0$$

$$\Delta H_r^0(T) = \Delta H_r^0(298) + \int_{298}^T \sum \nu_i C_{p,i}^0 dT$$

$C_{p,i}^0 \sim \text{CONST}$

THEN:

$$\Delta H_r^0(T) = \Delta H_r^0(298) + (T-298) \sum \nu_i C_{p,i}^0$$

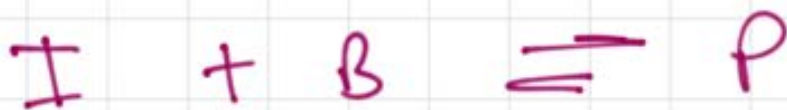
SCHMIDT DEFESTITHS

WE COULD CONSIDER 3 CASES..

①  $\Delta H_{\text{RXN}}^{\circ}(T) = \Delta H_{\text{RXN}}^{\circ}(298) \neq F(T)$

②  $C_{p,i}^{\circ}(298) = C_{p,i}^{\circ}(T)$

③  $C_{p,j}^{\circ} = F(T)$  WITH SOME WORK... YOU COULD GET THIS..



$\Delta H_f^{\circ}(298)$     -134.2    -63    -220.1 KJ/MOLE  
 = -85.3 KJ/MOLE (EXOTHERMIC)

$C_{p,j}^{\circ}(298)$     96.95    85.56    185.5 J/MOL-K  
 $\sum \nu_j C_{p,j}^{\circ} =$  2.99 J/MOLE-K

$C_{p,j}^{\circ}(400)$     124.43    108.45    242.7 J/MOL-K  
 $\sum \nu_j C_{p,j}(400) =$  9.79 J/MOL-K



THE 3 DIFFERENT  $\Delta H$ 'S ARE

①  $-85.3 \text{ kJ/mole}$

②  $= -85.3 + (400 - 298)(2.99) = -84.99 \text{ kJ/mole}$

③  $\hat{=} -85.3 + (400 - 298)\left(\frac{9.79 + 2.99}{2}\right) = -84.67 \text{ kJ/mole}$

"FIND SOMETHING MORE PRODUCTIVE  
TO DO !!"  
..

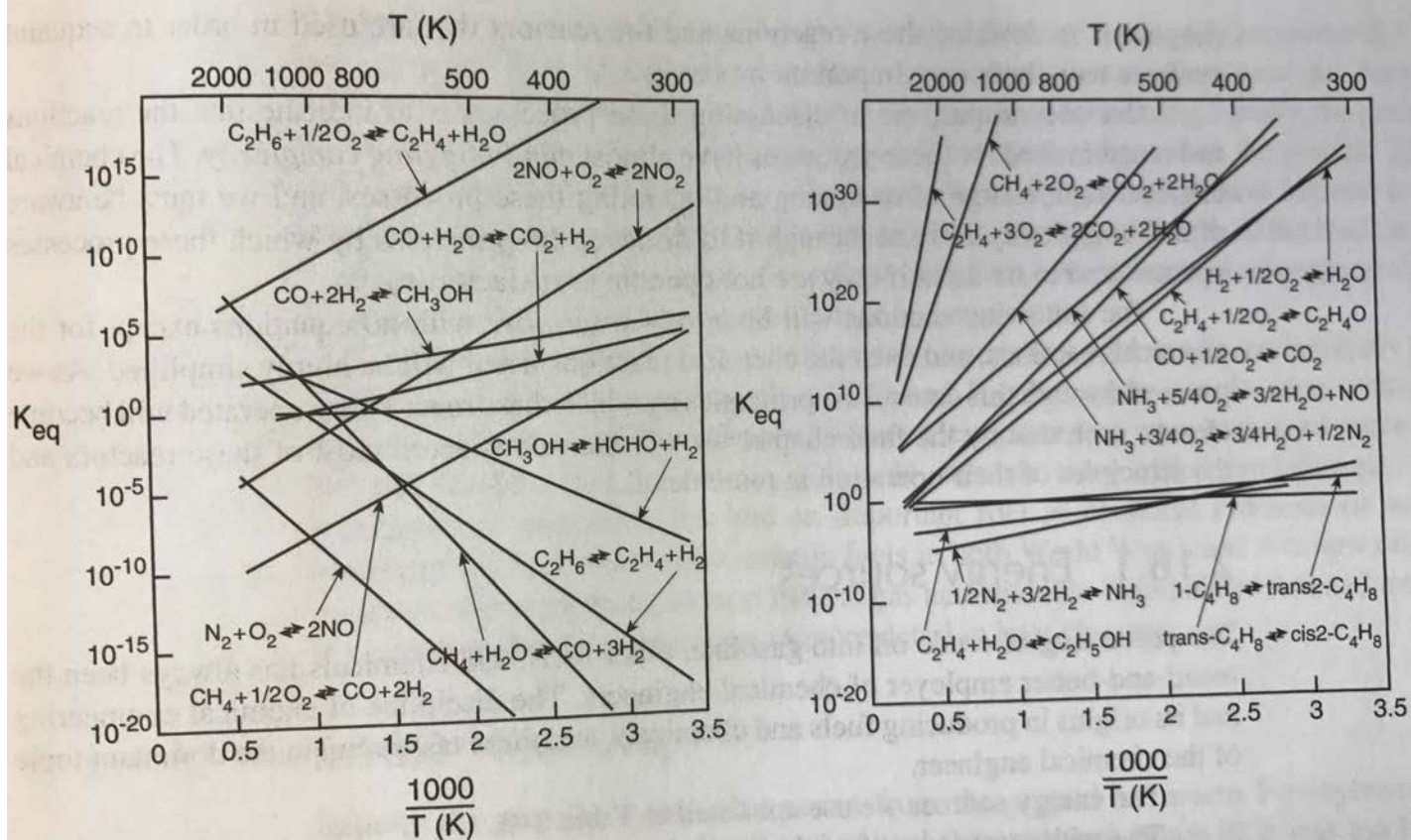
$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2}$$

REALLY BIG  
EFFECT OF  
T !!

VAN'T HOFF EQ.  
SEE BELOW

$$\frac{\partial(G/T)}{\partial T} = -\frac{\Delta H}{T^2}$$



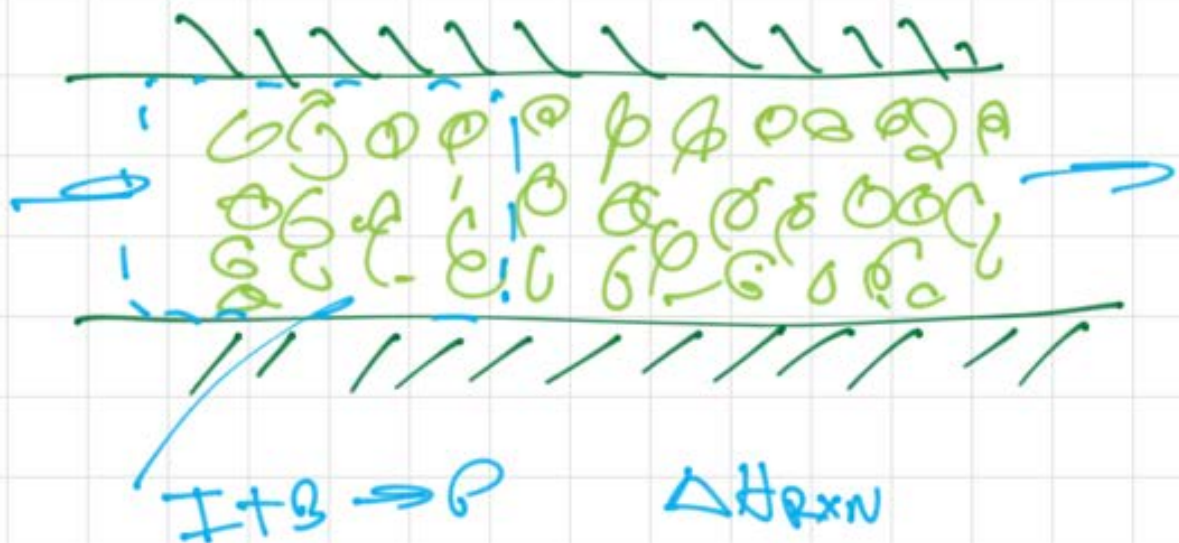


**Figure 2-11** Plots of equilibrium constant  $K_T$  versus temperature for several chemical reactions we will consider in this text. All reactions give nearly straight lines when plotted as  $\log K_T$  versus  $1/T$ . Exothermic reactions have large  $K_T$  at low  $T$ , while endothermic reactions have large  $K_T$  at high  $T$ .

# ADIABATIC TEMPERATURE RISE (EXOTHERMIC RXN)

PACKED BED, GAS PHASE  
REACTOR,

HOW BIG CAN TUBES BE?



YOU HAVE ONLY  $C_p$  OF GASES  
TO SOAK UP HEAT!!

SIMPLISTICALLY . . . .

$$\Delta H_{rxn} X = \bar{C}_p \Delta T$$

$$\Delta T \approx \frac{\Delta H_{rxn}}{C_p}$$

FULL  
CONVERSION

FOR  $I + B \rightarrow P$

$$\Delta T_{\text{ADIBATIC}} \approx \frac{85 \text{ KJ/MOLE E}}{(243 \text{ J/MOLE E})}$$

$$\Delta T = 350 \text{ K}$$