

The Equilibrium Constant for Ideal-Gas Mixtures

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Thermo II Presentation 2

Sections 15.2-15.3

Overview

- Review of Gibbs Function
- What is the Gas Constant
- Examples of how/when to use it.
- Example problems.
- **NO QUESTIONS!!**

Review of Gibbs

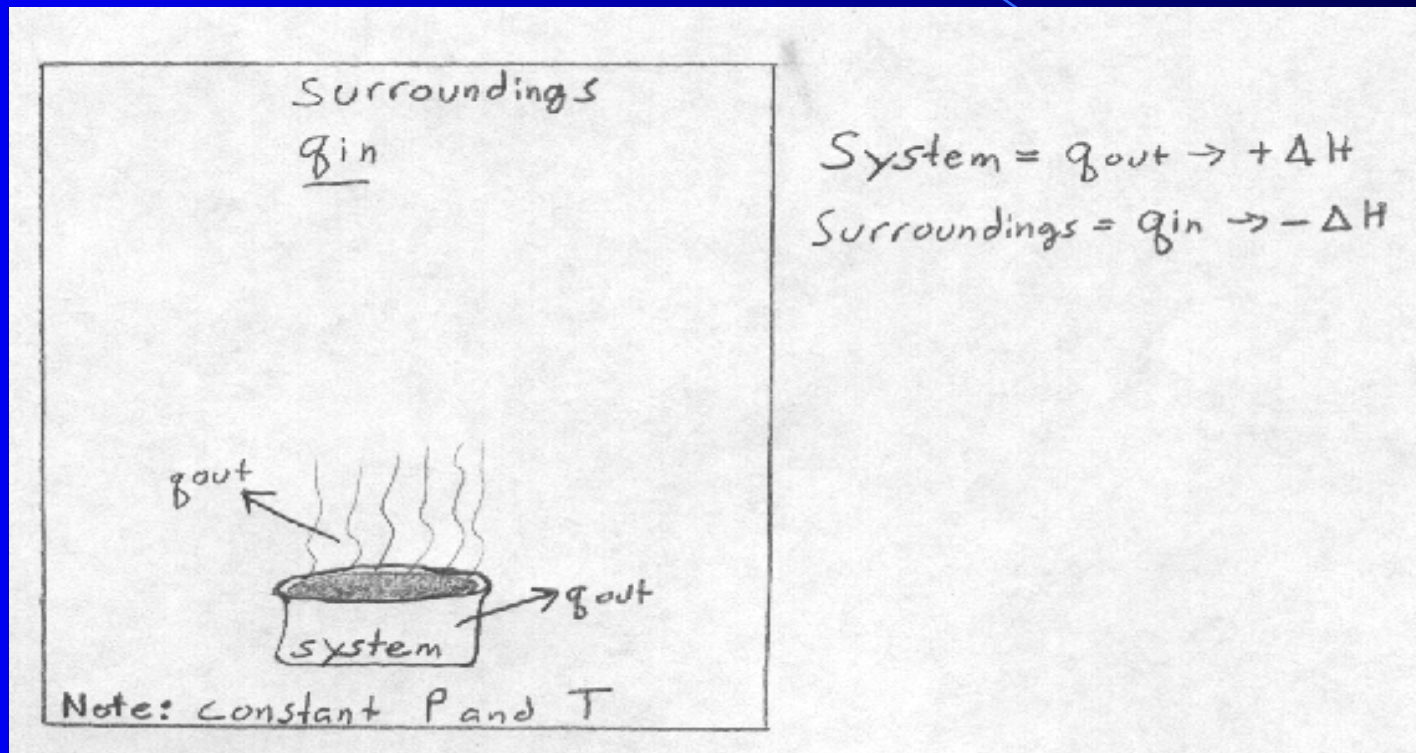
If the Gibbs function is used to monitor a reaction it will tell you the energy change of the reaction between the system and the surroundings.

$$\Delta G = \Delta H(\text{system}) + T\Delta S(\text{surroundings})$$

ΔH = Enthalpy, “Thermal Energy Transfer” i.e. “Heat Transfer”, q

ΔS = Entropy, “Heat Transfer” over abs. Temp., q/T .

Take for instance a pot of boiling water. It is giving off heat, “+q” and the area around it is absorbing that heat, “-q”.



When the heat transfer, q , between the system and the surroundings Equal zero than equilibrium for the reaction has been reached.

What is the Gas Constant ...K_P

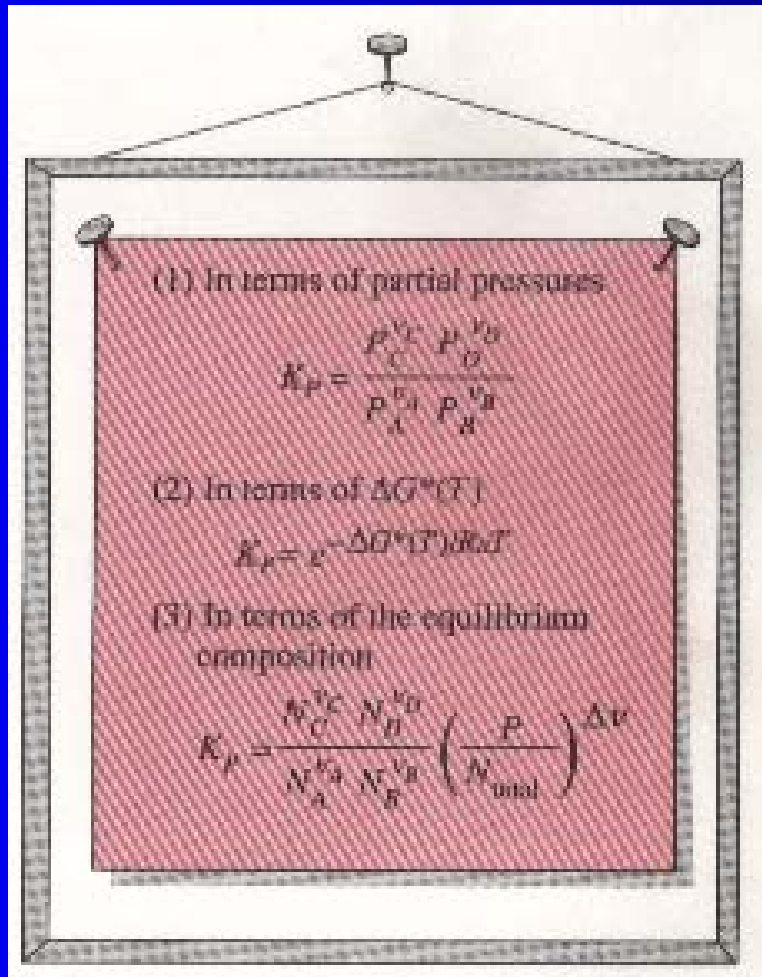
- K_p is a constant that can be used to determine equilibrium composition of the reacting ideal-gas mixtures.
- K_p is determined from the Gibbs function, assuming
The change in enthalpy is zero.

$$\Delta G = 0 - T\Delta S$$

$$\Delta S = -R_u * T * \ln(P_2/P_1) \quad K_p = P_2/P_1$$

$$K_p = e^{(-\Delta G^*/T)/(R_u*T)}$$

More about Kp



(1) In terms of partial pressures

$$K_p = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

(2) In terms of $\Delta G^\circ(T)$

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

(3) In terms of the equilibrium composition

$$K_p = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{\text{total}}} \right)^{\Delta \nu}$$

1. From Partial Pressures of products and reactants raised to their stoichiometric coef.
2. From Gibbs on previous slide.
3. From equilib. Composition. where N is the molar amounts and P is the total pressure.

How and When to use K_p

The K_p of a reaction depends on temperature only.

- K_p depends on $\Delta G^*(T)$...independent of pressure.
- So these three reactions have the same K_p ,
T is the same.



How and When to use K_p

- The K_p of the reverse reaction is $1/K_p$.

- $K_p = 0.1147 \times 10^{11}$ for



- $K_p = 8.717 \times 10^{-11}$ for



How and When to use K_p

- The larger the K_p , the more complete the reaction.
- Look at $K_p = (P_c^{v_c} P_d^{v_d}) / (P_a^{v_a} P_b^{v_b})$
Partial pressures of C & D \gg A & B
- $K_p > 1000$ or $\ln(K_p) > 7 \rightarrow$ complete reaction
- $K_p < 1000$ or $\ln(K_p) < 7 \rightarrow$ no reaction

Note: reaction with small K_p can be neglected, aint gonna happen

How and When to use K_p

- The mixture pressure affects the equilibrium composition.
- TRICKY....but as said before K_p does not change.
- What does change with the mixture pressure is the ratio of number of moles of reactants to the number of moles of product

How and When to use K_p

- The presence of inert gases affect the equilibrium composition.
- TRICKY....but as said before K_p does not change.
- Again...it is the ratio that changes.
An increase in the number of moles of inert gases gives a greater number or moles of products compared to number of moles of reactants.
- The reverse is also true...less inert gives less products.

How and When to use Kp

- When the stoichiometric coefficients are doubled, the value of Kp is squared.
- Proven by:

$$K_p = (P_{\text{H}_2\text{O}}^1) / (P_{\text{H}_2}^1 P_{\text{O}_2}^{0.5})$$

IS NOT EQUAL TO

$$K_p = (P_{\text{H}_2\text{O}}^2) / (P_{\text{H}_2}^2 P_{\text{O}_2}^1)$$

How and When to use K_p

- Free electrons in the equilibrium composition can be treated as an ideal gas.

- For $T \gg 2500\text{K}$

Gas molecules start to dissociate into unattached atoms and even lose electrons and ionize.

- Ions and electrons can be treated like inert gasses

And incorporated into:

$$K_p = (P/N_{\text{tot.}})^{\Delta v} [(N_c^{v_c} N_d^{v_d}) / (N_a^{v_a} N_b^{v_b})]$$

How and When to use K_p

- Equilibrium calculations provide information on the equilibrium Composition of a reaction, not on the reaction rate.

- The reaction:



- From Rule 3, K_p is large so....complete reaction.
- But it does not say how fast it reacts...
VERY SLOW.

EXAMPLE!!!!!!!

Example 15-3,

A mixture of 2 kmol of CO and 3 kmol of O₂ is heated to 2600K at a pressure of 304 kPa.

Determine the equilibrium composition, assuming
The mixture consists of CO₂, CO, and O₂

Questions???

