The background features a large, stylized blue and grey buffalo mascot. The buffalo is facing forward with its mouth open, showing its teeth. Below the buffalo's head, the word "BUFFALO" is written in a large, bold, white, italicized font with a grey outline. The text is centered horizontally.

# **A First Course on Kinetics and Reaction Engineering**

**Class 10 on Unit 10**

# Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
  - ▶ A. Rate Expressions
    - 4. Reaction Rates and Temperature Effects
    - 5. Empirical and Theoretical Rate Expressions
    - 6. Reaction Mechanisms
    - 7. The Steady State Approximation
    - 8. Rate Determining Step
    - 9. Homogeneous and Enzymatic Catalysis
    - 10. Heterogeneous Catalysis
  - ▶ B. Kinetics Experiments
  - ▶ C. Analysis of Kinetics Data
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors



# Heterogeneous Catalysis

- In heterogeneous catalytic reactions, reaction is often assumed to take place at specific locations on the surface called active sites
- When reactions take place on a surface, surface concentrations, not volume concentrations, are used in the rate expressions for elementary steps
  - ▶ Rate and equilibrium expressions for surface reactions often use fractional coverages in place of surface concentrations
  - ▶  $C_{i_{surf}} = C_{sites} \theta_i$
  - ▶ The total surface concentration of sites,  $C_{sites}$ , is incorporated into the pre-exponential factor of the rate coefficient
- Active sites are usually assumed to be conserved
  - ▶  $\theta_{vacant} + \sum_{\substack{i = \text{all} \\ \text{adsorbed} \\ \text{species}}} \theta_i = 1$
- Simplifications may be possible if one species is the most abundant surface intermediate (masi):  $\theta_{masi} \gg \theta_{i(\neq masi)}$
- Langmuir-Hinshelwood kinetics are a common type of rate expression for heterogeneous catalytic reactions results when
  - ▶ A surface reaction step is assumed to be rate-determining
  - ▶ All of the adsorption/desorption steps are quasi-equilibrated



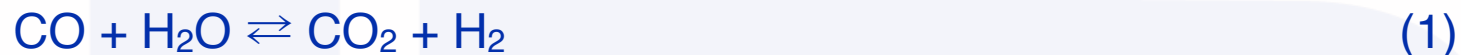
Questions?



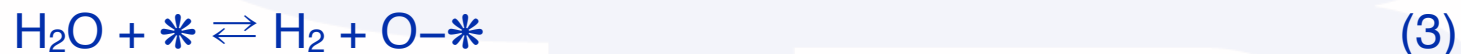
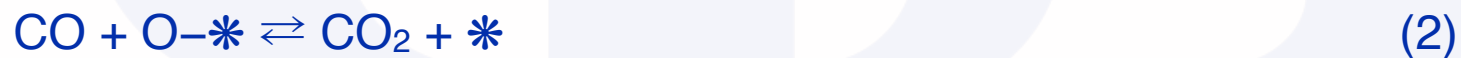
# Activity 10.1

The water-gas shift reaction, equation (1), might take place according to the mechanism given in equations (2) and (3). If step (3) is irreversible, find an expression for the rate of water-gas shift in terms of the partial pressures of the stable species (and rate and equilibrium constants).

Overall, macroscopically observed reaction:



Postulated mechanism:



We will solve this problem as a relay race. When told to start, one group member should go to the board and write one equation needed to solve the problem, then sit down. The next member should then go to the board and either correct an existing equation or write an additional one. The first group to list all necessary equations correctly and indicate how to solve them wins!



# Solution

- No step has been identified as rate-determining
  - ▶ Set the rate of the macroscopically observed reaction with respect to one of its reagents equal to the sum of the rates of generation of that reagent in each of the mechanistic steps

- ▶ For H<sub>2</sub> this gives

$$r_{H_2,1} = k_{3,f} P_{H_2O} \theta_v - k_{3,r} P_{H_2} \theta_o$$

- Identify the reactive intermediates and apply the Bodenstein steady state approximation to each of them

- ▶ Reactive intermediates appear in the mechanistic steps, not in the macroscopically observed reaction
- ▶ Here there are two: O-\* and \*
- ▶ Set their net rate of generation equal to zero

- For \* this gives

$$0 = \left( k_{2,f} P_{CO} \theta_o - k_{2,r} P_{CO_2} \theta_v \right) - \left( k_{3,f} P_{H_2O} \theta_v - k_{3,r} P_{H_2} \theta_o \right)$$

- For O-\* it gives the exact same equation; need another equation

- Assume conservation of active sites

$$1 = \theta_o + \theta_v$$

- Solve to obtain expressions for the surface coverages

$$\theta_v = \frac{k_{2,f} P_{CO} + k_{3,r} P_{H_2}}{k_{2,f} P_{CO} + k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O} + k_{3,r} P_{H_2}} \quad \theta_o = \frac{k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O}}{k_{2,f} P_{CO} + k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O} + k_{3,r} P_{H_2}}$$

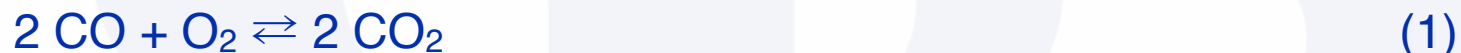
- Substitute into the rate expression:  $r_{H_2,1} = \frac{k_{2,f} k_{3,f} P_{CO} P_{H_2O} - k_{2,r} k_{3,r} P_{CO_2} P_{H_2}}{k_{2,f} P_{CO} + k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O} + k_{3,r} P_{H_2}}$



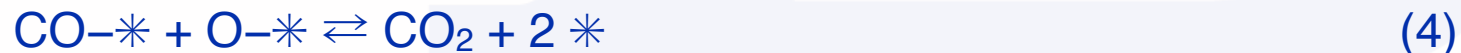
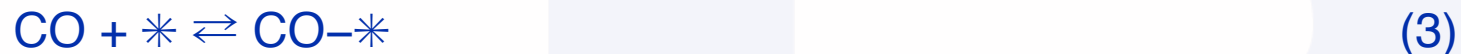
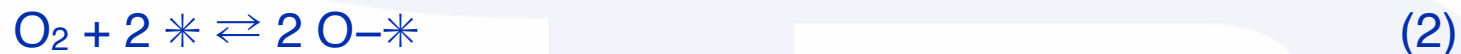
## Activity 10.2

The oxidation of carbon monoxide is given in equation (1) below. Suppose that the mechanism is given by equations (2) through (4) and that step (4) is rate-limiting. Derive a rate expression in terms of only the partial pressures of the reagents and constants. How does the result change if  $O-*$  is the most abundant surface intermediate? Comment upon the resulting rate expression.

Overall, macroscopically observed reaction:



Postulated mechanism:



# Generating the Rate Expression

- Step (4) is rate-determining

- ▶  $r_1 = r_{4,f} = k_{4,f} \theta_o \theta_{CO}$

- ▶ Not useful in this form; the fractional coverage of CO<sub>2</sub> is difficult to measure

- Steps (2) and (3) are quasi-equilibrated

$$K_2 = \frac{\theta_o^2}{P_{O_2} \theta_v^2}$$

$$K_3 = \frac{\theta_{CO}}{P_{CO} \theta_v}$$

- Sites are conserved

$$\theta_v + \theta_o + \theta_{CO} = 1$$

- Solve to obtain expressions for the surface coverages

$$\theta_v = \frac{1}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad \theta_o = \frac{\sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad \theta_{CO} = \frac{K_3 P_{CO}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}}$$

- Substitute into the rate expression

$$r_1 = k_{4,f} \theta_o \theta_{CO} = k_{4,f} \frac{K_3 P_{CO} \sqrt{K_2 P_{O_2}}}{\left(1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}\right)^2}$$





# Simplify for O-\* as MASI

$$r_1 = k_{4,f} \frac{K_3 P_{CO} \sqrt{K_2 P_{O_2}}}{\left(1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}\right)^2}$$

$$\theta_O \gg \theta_v$$

$$\frac{\sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \gg \frac{1}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}}$$

$$\sqrt{K_2 P_{O_2}} \gg 1$$

$$\theta_O \gg \theta_{CO}$$

$$\frac{\sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \gg \frac{K_3 P_{CO}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}}$$

$$\sqrt{K_2 P_{O_2}} \gg K_3 P_{CO}$$

$$r_1 = k_{4,f} \frac{K_3 P_{CO} \sqrt{K_2 P_{O_2}}}{\left(1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}\right)^2} \approx k_{4,f} \frac{K_3 P_{CO} \sqrt{K_2 P_{O_2}}}{\left(\sqrt{K_2 P_{O_2}}\right)^2} = \frac{k_{4,f} K_3}{\sqrt{K_2}} \frac{P_{CO}}{\sqrt{P_{O_2}}}$$

- Normally as the concentration of a reactant increases, the rate increases



- Here as the concentration of O<sub>2</sub> increases, the rate decreases
  - ▶ The reaction is reactant-inhibited



# Activity 10.3

## Three Minute Paper

- Units 6 through 10 have presented different ways of generating a rate expression for a non-elementary reaction if the mechanism is known or can be postulated
- Write an “instruction manual” that incorporates all the approaches presented in these units and describes a general approach to solving these types of problems
- You have three minutes



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