FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA
Departamento de Química

Problems of Physical Chemistry 2

Heterogeneous Catalysis

1 - The hydrogenation of ethylene catalysed by metal surfaces follows different kinetic laws in nickel and copper

on Nickel $$v = \frac{a.P_{H_2}.P_{C_2H_4}}{1 + bP_{C_2H_4}}$$

on Copper $$v = \frac{a.P_{H_2}.P_{C_2H_4}}{(1 + bP_{C_2H_4})^2}$$

Explain the difference in detail by proposing a reaction mechanism for each case.

R: Ni – Rideal, H_2 not adsorbed; Cu – bimolecular, with H_2 weakly adsorbed

2 - Explain the following facts:

a) The decomposition reaction of ammonia (NH_3) on a tungsten surface (W), when the initial pressure of NH_3 is reasonable, gradually changes from an initial order 0 to order 1, when most of the reagent has disappeared.

b) The speed of the same reaction on a platinum surface is given by $v = \frac{a.P_{NH_3}}{P_{H_2}}$

(*NOTE: H_2 is a reaction product*)

R: a) unimolecular; b) unimolecular with H_2 strongly adsorbed

3 – The reaction $2NO \rightarrow N_2 + O_2$ catalysed by Pt obeys the following speed law

$$dp_{NO}/dt = -k\, p_{NO}/p_{O_2}$$

Interpret this law based on the Langmuir adsorption isotherm.

R: O_2 strongly adsorbed inhibitor

4 - Calculate the order and rate constant of the ammonia decomposition reaction on a tungsten surface based on the following results:

Initial pressure/Torr	65	105	150	185
$t_{1/2}$/s	290	460	670	820

Deduce the mechanism of heterogeneous catalysis followed in this reaction.

R: Unimolecular, high p(NH_3), zero order

5 - The kinetics of the reaction between CO and O_2 catalysed by platinum or quartz follows a kinetic such that the rate is directly proportional to $p_{O2}^{1/2}$ and inversely proportional to p_{CO}. Propose a mechanism for this reaction.

R: Bimolecular, CO strongly adsorbed

6 - The decomposition of nitrous oxide on noble metals and oxides of calcium and aluminium gives:

$$2\,N_2O \xrightarrow{cat} 2\,N_2 + O_2$$

p_{N2O} (bar)	$t_{½}$ (s)
0.1	3460
0.5	3450
0.7	3460
1.0	3458
1.4	3450
3.4	8625
6.4	16235
13.4	34000

The half-reaction times were obtained for different initial partial pressures of nitrous oxide at 925℃.

Based on the experimental data presented, propose a heterogeneous catalysis mechanism for this reaction.

R: unimolecular

7 - Suppose the ozone dissociation with adsorption in an icy cloud $O_3 \rightarrow 3O_{ads}$ and later the O_{ads} reaction with B(g) according to a Rideal mechanism. Assuming that O adsorbs following a Langmuir isotherm, explain the reaction rate of O_{ads} with B(g) as a function of O_3 pressure and B pressure.

R: $v = kp_B \frac{\sqrt[3]{bp_{O3}}}{1+\sqrt[3]{bp_{O3}}}$

8 - The following reaction is considered 1st order in relation to the reagent H_2O and 1st order in relation to the reagent H_2CO

$$H_2O\,(g) + H_2CO\,(g) \rightarrow 2\,H_2\,(g) + CO_2\,(g)$$

When the reaction proceeds on platinum, the rate is given by:

$$v = k' \frac{p_{H_2O} p_{H_2CO}}{p_{H_2}^2}$$

When the reaction proceeds on nickel, the velocity is given by:

$$v = k'' \frac{p_{H_2O} p_{H_2CO}}{p_{H_2}}$$

When the reaction proceeds on rhodium, the velocity is given by:

$$v = k''' \frac{p_{H_2O}}{p_{H_2CO}}$$

Explain in detail the reason for these observations, deducing the expressions and advancing a mechanism.

R: On Pt the 2 gases are adsorbed with strong H_2 inhibition; on Ni one gas is adsorbed and the other is not, with strong H_2 inhibition; on Rh the 2 gases are adsorbed, H_2CO strongly adsorbed

9 - The reaction of CO with O_2 on platinum is given by $v = \frac{ap_{O_2}^{1/2}}{p_{CO}}$

$$CO(g) + ½O_2\,(g) \rightarrow CO_2\,(g)$$

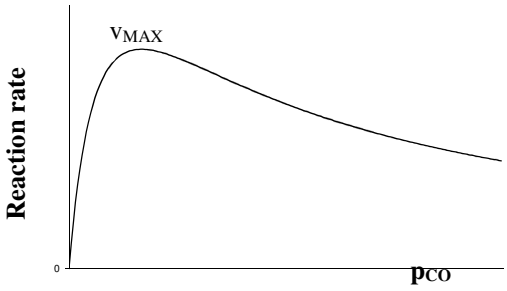
where **a** is a constant. Provide a detailed explanation for this law, deducing the expressions and advancing a mechanism.

R: bimolecular, CO strongly adsorbed, O_2 adsorbed with dissociation

10 – The reaction between NO and CO

$$NO_{(g)} + CO_{(g)} \rightarrow 1/2\ N_{2\,(g)} + CO_{2\,(g)}$$

performed on rhodium *(100)* presents a variation of the reaction rate with the CO pressure as shows in the figure below.



Explain the progress of the curve by proposing a mechanism.

R: Bimolecular

11 - The decomposition of N_2O on Mn_3O_4

$$N_2O \xrightarrow{Mn_3O_4} N_2 + \frac{1}{2}O_2$$

is given by

$$v = \frac{ap_{N_2O}}{1 + bp_{N_2O} + cp_{O_2}^{1/2}}$$

where a, b e c are constants. Propose an explanation for this law.

R: unimolecular, O_2 as inhibitor adsorbed with dissociation

12 - It was observed that this reaction on an iron catalyst

$$NH_3\ (g) + D_2(g) \rightarrow NH_2D(g) + HD\ (g)$$

where D represents deuterium, is given by

$$v = \frac{k' p_{D2}^{1/2} p_{NH3}}{(1 + k'' p_{NH3})^2}$$

12.1. Recall what the Deuterium is and represent its electronic configuration.

12.2. Propose a mechanism of heterogeneous catalysis and give meaning to k 'and k".

R: bimolecular, D_2 weakly adsorbed with dissociation

13 - In the reaction between H_2 and CO_2 on platinum

$$2H_2(g) + CO_2(g) \rightarrow CH_4(g) + O_2(g)$$

it is observed that at low H_2 partial pressures, the $t_{1/2}$ of the reaction does not depend on p_{H2}. For higher H_2 partial pressures, it is observed that the rate decreases as p_{H2} increases.

Propose a heterogeneous catalysis mechanism for this reaction.

R: bimolecular, H_2 strongly adsorbed, CO_2 weakly adsorbed

14 - Explain in detail the following phrases, deducing the expression and proposing a mechanism:

14.1. The decomposition of NO into N_2 and O_2 catalysed by Pt obeys the rate law

$$\frac{dp_{NO}}{dt} = -k\frac{p_{NO}}{p_{O_2}}$$

14.2. The kinetics of the reaction between NO and CO on Rh (100) to give N_2 and CO_2 is given by

$$\frac{dp_{CO_2}}{dt} = k\frac{p_{NO}p_{CO}}{p_{CO_2}}$$

R: 1. Unimolecular, NO adsorbed and N_2 not adsorbed and O_2 strongly adsorbed without dissociation; 2. One of the reagents adsorbed and CO_2 as an inhibitor strongly adsorbed.

15 - Derive the heterogeneous catalysis mechanism leading to the following rate equation for the reaction between ozone and ethylene on a metal surface:

$$v = \frac{a.P_{O_3}^{1/3}.P_{C_2H_4}}{1+bP_{O_3}^{1/3}}$$

Assign meanings to ***"a"*** and ***"b"***.

R: O_3 adsorbed with dissociation, C_2H_4 not adsorbed

16 - The oxidation reaction of CO by O_2 on a platinum surface to give CO_2 can be described according to two mechanisms:

$$v = \frac{k b_{CO} b_{O2}^{1/2} p_{CO} p_{O2}^{1/2}}{(1 + b_{O2}^{1/2} p_{O2}^{1/2} + b_{CO} p_{CO})^2}$$

Langmuir-Hinshelwood

or

$$v = \frac{k b_{O2}^{1/2} p_{CO} p_{O2}^{1/2}}{1 + b_{O2}^{1/2} p_{O2}^{1/2} + b_{CO} p_{CO}}$$

Langmuir-Rideal

Explain in detail these equations and represent for each of them the variation of the rate with the pressure of CO, for a given fixed pressure of O_2.

R: L-H O_2 adsorbed with dissociation and CO adsorbed; L-R O_2 adsorbed with dissociation and CO not adsorbed

17 - The reaction of NO with CO made on rhodium (100) shows a variation of the rate with the pressure of CO as shown in the table below.

P_{CO} / bar	**v / M s^{-1}**
0	0
1	0.57
5	2.434
10	4.402
20	2.201
50	1.684

Explain the values of the table by proposing a mechanism for the reaction.

R: bimolecular