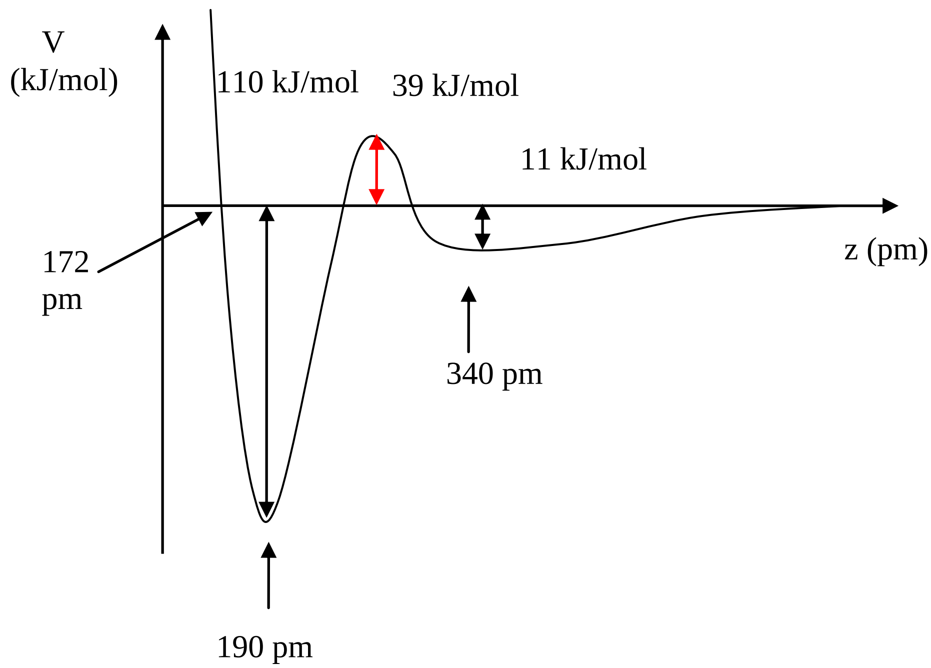
CHEMISTRY 448/548 Winter 2009

Assignment #3 (55 pts)
Due Feb. 6th

SHOW WORKING FOR FULL CREDIT AND ALL WORK MUST BE NEAT AND READABLE OR YOU WILL LOSE POINTS !

Be careful of SF's particularly in spreadsheet o/p

1. (15 pts) Below is sketched an approximate potential energy curve for the dissociative adsorption of a diatomic molecule on a metal.



(a) Does this diagram show (i) physisorption, (ii) activated chemisorption or (iii) non-activated chemisorption? (1 pt)

Ans: (ii) activated chemisorption

(b) What are the bond lengths in the precursor and chemisorbed states? (2 pts)

Ans: precursor = 340 pm, chemisorbed = 190 pm

(c) What is the enthalpy of adsorption into the precursor and chemisorption states. (4 pts)

Ans: precursor = -11 kJ/mol, chemisorbed = -110 kJ/mol

(d) What is the energy of activation for chemisorption? (2 pts).

Ans: ΔH = 39 kJ/mol

(e) What is the enthalpy of desorption as a molecule from the chemisorption state? (2 pts)

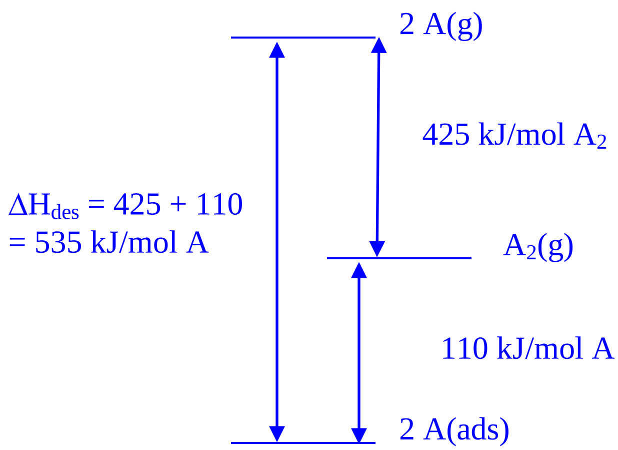
Ans: ΔH = 110 + 39 = 150 kJ/mol

(f) What is the enthalpy of desorption from the precursor state? (1 pts)

Ans: ΔH = 11 kJ/mol

(g) The diatomic gas used has a bond energy of 425 kJ/mol. If the atoms were to desorb without reforming the molecule, what will be the enthalpy of desorption per mole of atoms produced in the gas phase? (3 pts)

Ans:



Per mole of O atoms the ΔH_{des} = 535 /2 = 238 kJ/mol A

2. (20 pts) Some data for the adsorption of carbon monoxide on charcoal at 273 K are given below.

p (torr)	100	200	300	400	500	600	700
V (ml)	10.2	18.6	25.5	31.5	36.9	41.6	46.1

(Assume V has been corrected to 1 atm pressure)

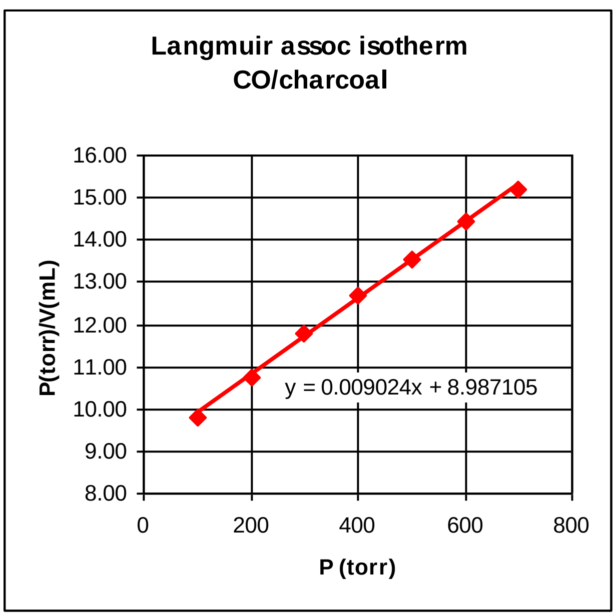
a) Use the associative and dissociative versions of the Langmuir isotherm to find the types of adsorption occurring. Plot on graph paper or spreadsheet/printer. Calculate V_m and b (10 pts)

Solution :

The associative Langmuir isotherm can be written as :

$$\theta = \frac{V}{V_m} = \frac{b\,P}{1 + b\,P} \quad \text{or}$$

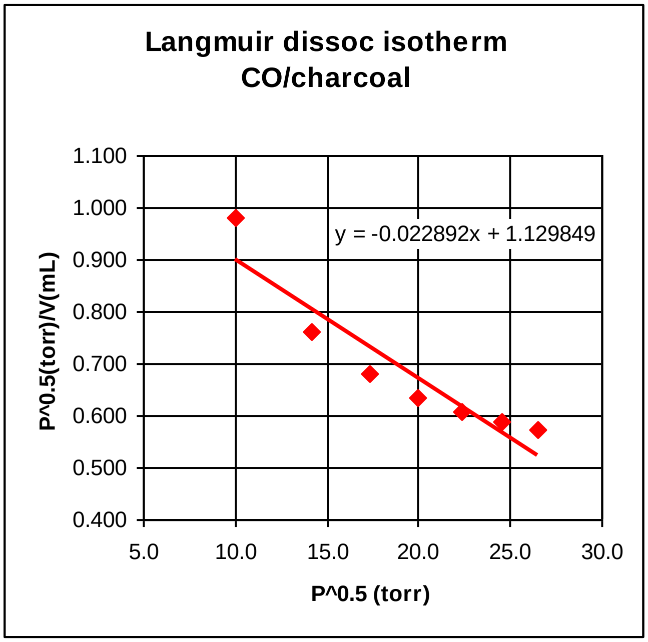
$$\frac{P}{V} = \frac{1}{b\,V_m} + \frac{1}{V_m P}$$



Assoc p(Torr)	V(mL)	P/V
100	10.2	9.80
200	18.6	10.8
300	25.5	11.8
400	31.5	12.7
500	36.9	13.6
600	41.6	14.4
700	46.1	15.2

The dissociative Langmuir isotherm is :

$$\frac{\sqrt{P}}{V} = \frac{1}{b\,V_m} + \frac{1}{V_m \sqrt{P}}$$



Dissoc

p(Torr)	P^0.5	V(mL)	P^0.5/V
100	10.0	10.2	0.980
200	14.1	18.6	0.760
300	17.3	25.5	0.679
400	20.0	31.5	0.635
500	22.4	36.9	0.606
600	24.5	41.6	0.589
700	26.5	46.1	0.574

Clearly the associative isotherm is the correct fit. For the associative data:

Slope = $1 / V_m = 1 / 0.009024$

so $V_m = 110.8$ mL

intercept = $(1 / b\ V_m) = 8.987$

so $b = 1 / (110.8 \times 8.987) = 1.004 \times 10^{-3}$ torr^{-1}

b) given that the total surface area of the charcoal is 13.9 m^2, calculate the area occupied by each adsorbed molecule (5 pts)

Solution :

The surface area of the charcoal is given by

$SA(m^2) = V_m^o\ (L) \times N_A \times a\ (m^2) / 22.4\ L$

where a is the area of 1 molecule

so

$a = SA(m^2) \times 22.4\ (L) / (V_m^o\ (L) \times N_A)$

$= 13.9\ m^2 \times 22.4 / (0.111 \times 6.02 \times 10^{23})$

and $a = 4.67 \times 10^{-21}\ m^2$ or $0.467\ Å^2$

c) what volume of CO would be adsorbed at 273 K when the pressure is 1 atm? (5 pts)

(Use fitted isotherm)

Solution :

Knowing the parameter for the Langmuir eqn we just plug in the values

$$V = \frac{V_m b P}{1 + b P}$$

$= 111$ mL $\times 1.00 \times 10^{-3}$ torr^{-1} $\times$ 760 torr / (1 + 1.00×10^{-3} torr^{-1} $\times$ 760 torr)

or

$V = 47.9$ mL

3. (20 pts) Below are some data for the adsorption of N_2 on 1.00 g of TiO_2 at 75 K.

p (torr)	1.20	14.0	45.8	87.5	127.7	164.4	204.7
V (mm^3)	601	720	822	935	1046	1146	1254

(Assume V corrected to 1 atm and 273 K)

For N_2 at 75 K, take the vapor pressure $p_o = 570$ torr

a) Rearrange the BET isotherm in the form z / {(1-z)V} = ... where z = (p/p_o). Find V_m and c by a suitable plot on graph paper or spreadsheet/printer. (10 pts)

Solution :

The BET isotherm can be written :

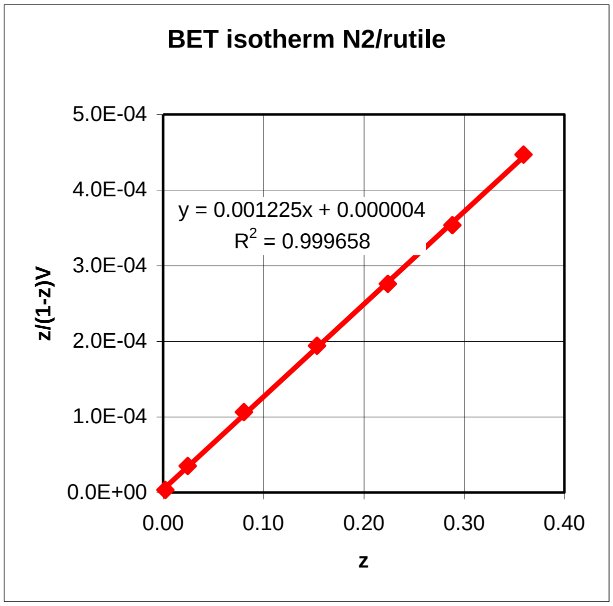
$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P_0}$$

$$\text{Setting } z = \left(\frac{P}{P_0}\right), \quad \frac{P}{V(1-z)} = \frac{1}{V_m c} + \frac{(c-1)z}{V_m c}$$

So plotting the LHS vs. z gives

$$\text{intercept} = \frac{1}{V_m c} \quad \text{and} \quad \text{slope} = \frac{(c-1)}{V_m c} = \frac{1}{V_m} - \frac{1}{V_m c} = \frac{1}{V_m} - \text{intercept}$$

so V_m = 1 / (slope + intercept)



Po=	570		
p(Torr)	**V(mm^3)**	**z = P/P0**	**z/(1-z)V**
1.2	601	2.105E-03	3.510E-06
14	720	2.456E-02	3.497E-05
45.8	822	8.035E-02	1.063E-04
87.5	935	1.535E-01	1.940E-04
127.7	1046	2.240E-01	2.760E-04
164.4	1146	2.884E-01	3.537E-04
204.7	1254	3.591E-01	4.469E-04

Notice the poor SFs in the trend line, so let's do a full regression. The results are:

Regression Statistics	
Multiple R	0.999829
R Square	0.999658
Adjusted R Square	0.99959
Standard Error	3.36E-06
Observations	7

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.65E-07	1.65E-07	14633.14	7.32E-10
Residual	5	5.63E-11	1.13E-11		
Total	6	1.65E-07			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*
Intercept	4.06E-06	2.07E-06	1.95772	0.107601	-1.3E-06
X Variable 1	0.001225	1.01E-05	120.9675	7.32E-10	0.001199

From the plot we find

V_m = 1 / (slope + intercept) = 1 / (4.06 × 10^{-6} + 0.001225) mm^3 = 814 mm^3

and

c = 1 / (intercept × V_m) = 1 / (4.06 × 10^{-6} × 814) = 303 mm^{-3}

b) Assuming that the cross-sectional area of an N_2 molecule in the liquid phase is 0.160 nm^2, estimate the surface area of the sample in m^2/g. (5 pts)

Solution :

The surface area of the catalyst SA is given by

SA = # surface sites × area per adsorbed molecule

$= [V_m^o\ (L) \times N_A / 22.4\ (L)\ ] \times a\ (m^2)$

and

$SA = (0.814 \times 10^{-3}\ L \times 6.02 \times 10^{23} / 22.4\ L) \times 0.160 \times 10^{-18}\ m^2$

$= 3.50\ m^2$