

## Reaction Kinetics II: Heterogeneous Systems

- P109. A monolayer of  $N_2$  molecules (effective area  $0.165 \text{ nm}^2$ ) is adsorbed on the surface of  $1.00 \text{ g}$  of an  $Fe/Al_2O_3$  catalyst at  $77 \text{ K}$ , the boiling point of liquid nitrogen. Upon warming, the nitrogen occupies  $2.86 \text{ cm}^3$  at  $0.0 \text{ }^\circ\text{C}$  and  $760 \text{ Torr}$ . What is the surface area of the catalyst? ( $12.68 \text{ m}^2/\text{g}$ )
- P110. A certain solid sample adsorbs  $0.44 \text{ mg}$  of  $CO$  when the pressure of the gas is  $26.0 \text{ kPa}$  and the temperature is  $300 \text{ K}$ . The mass of gas adsorbed when the pressure is  $3.0 \text{ kPa}$  and the temperature is  $300 \text{ K}$  is  $0.19 \text{ mg}$ . The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures. ( $\Theta_{26.0 \text{ kPa}} = 0.828$ ,  $\Theta_{3.0 \text{ kPa}} = 0.358$ )
- P111. For how long on average would an  $H$  atom remain on a surface at  $298 \text{ K}$  if its desorption activation energy were  
 a.  $15 \text{ kJ mol}^{-1}$ , and ( $4.259 \cdot 10^{-11} \text{ s}$ )  
 b.  $150 \text{ kJ mol}^{-1}$ ? ( $1.966 \cdot 10^{13} \text{ s}$ )  
 Take  $\tau_0 = 0.10 \text{ ps}$ . For how long on average would the same atoms remain at  $1000 \text{ K}$ ? ( $6.075 \cdot 10^{-13} \text{ s}$  and  $6.846 \cdot 10^{-6} \text{ s}$ )
- P112.  $HI$  is very strongly adsorbed on gold but only slightly on platinum. Assume the adsorption follows the Langmuir isotherm. Predict the order of the  $HI$  decomposition reaction on each of the two metal surfaces. (Au: zeroth-order, Pt: first-order)

- P113. The following data were obtained for the extent of adsorption,  $s$ , of acetone on charcoal from an aqueous solution of concentration  $c$  at  $18 \text{ }^\circ\text{C}$ :

$c / (\text{mmol dm}^{-3})$	15.0	23.0	42.0	84.0	165	390	800
$s / (\text{mmol acetone/g charcoal})$	0.60	0.75	1.05	1.50	2.15	3.50	5.10

Which isotherm fits these data best, Langmuir, Freundlich or Temkin? (Freundlich)

- P114. In some catalytic reactions the products may adsorb more strongly than the reagent gas. This is the case *e.g.* in the catalytic decomposition of ammonia on  $Pt$  at  $1000 \text{ }^\circ\text{C}$ .
- a. As a first step in examining the kinetics of the process, show that the rate of ammonia decomposition should follow  $\frac{d p(\text{NH}_3)}{dt} = -k_c \frac{p(\text{NH}_3)}{p(\text{H}_2)}$  in the limit of very strong adsorption of  $H_2$ . ( $k_c = kK_{\text{NH}_3}/K_{\text{H}_2}$ )
- b. Show that plotting the  $(1/t) \cdot \ln(p/p_0)$  values as a function of  $(p-p_0)/t$  (where  $p = p(\text{NH}_3)$ ) gives a straight line.
- c. Check the rate law based on the data below and find  $k_c$ . ( $k_c = 0.0258 \text{ Torr/s}$ )

$t / \text{s}$	0	30	60	100	160	200	250
$p(\text{NH}_3) / \text{Torr}$	100	88	84	80	77	74	72