UNIVERSITY OF TORONTO
FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATION, DECEMBER 12, 2001

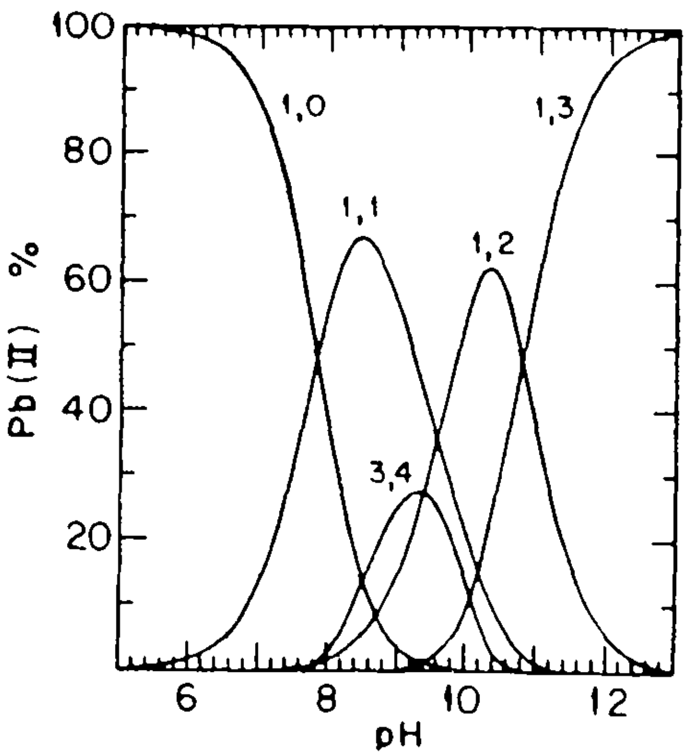
JTC 413F and CHE465F : Aqueous Process Engineering
Examiner: V.G. Papangelakis

Notes:

- Open book – non programmable calculator type of exam
- Answer all questions
- All questions and sub-questions bare an equal mark. Mark is shown in brackets.

1. [20] The Figure below presents speciation data for Pb(II) species in aqueous solution, where the symbol (x,y) refer to the species $Pb_x(OH)_y^{(2x-y)+}$. Use this information to determine the equilibrium constants for the following reactions:

$$Pb^{2+} + OH^- = Pb(OH)^+$$
$$Pb^{2+} + 2OH^- = Pb(OH)_2(aq)$$
$$Pb^{2+} + 3OH^- = Pb(OH)_3^-$$



2. [20] Thermodynamic data for the silver-nitrite aqueous system are provided below

$Ag^+ + NO_2^- = AgNO_2$ $\log\beta_1 = 2.32$

$Ag^+ + 2NO_2^- = Ag(NO_2)_2^-$ $\log\beta_2 = 2.51$

$Ag^+ + NO_2^- = AgNO_{2\,(s)}$ $\log K_{SP} = -4.13$

On the basis of the above data, show that the solubility S of $AgNO_{2\,(s)}$ as a function o free nitrite ion concentration is given by:

$S = A/[NO_2^-] + B + C[NO_2^-]$

What quantities do the parameters A, B, and C represent? Calculate their values and sketch the function: logS vs $[NO_2^-]$.

3. [40] In a process to recover metal from copper scrap, chlorine gas was used to dissolve copper in aqueous solution in its divalent state. The copper feed material was in the form of small particles having the same size (diameter) of 100 μm. In one set of dissolution tests where the concentration of dissolved chlorine gas was held constant at 1×10^{-3} mol/L and the temperature at 25°C, the following data were obtained.:

Time (min)	3	6	9	12	15
Conversion (x)	0.066	0.13	0.19	0.25	0.3

a) Verify that the dissolution reaction follows the shrinking core model for surface reaction control.
b) Calculate the apparent rate constant
c) Calculate the time to completely dissolve the particles.
d) Calculate the copper reaction rate constant (intrinsic)
e) Calculate the reaction rate
f) Calculate the chlorine rate of generation

The same experiment is repeated, this time with particles having half of the above size

g) Calculate the time to completely dissolve these particles and compare with that of question c).
h) Calculate the ratio of the surface areas of the two particle sizes tested. How does it relate to the times for their complete dissolution?
i) Calculate the reaction rate for this particle size. How does it relate to that in question e)?
j) Conclude how does the reaction rate change when the surface area changes.

Two more experiments are performed where the copper particles of the 100 μm size are dissolved at 50°C and 75°C in a dissolved chlorine concentration of 2×10^{-3} mol/L. The resulting apparent rate constants were calculated as 7.14×10^{-2} and 0.27 min^{-1} respectively. Calculate the activation energy and comment whether it is consistent with a surface reaction rate-limiting step.
GIVEN: Copper density=8.96 g/mL, Copper molar mass=63.55 g/mol

4. [20] A mixed oxide sludge contains mostly Ga_2O_3 and GeO_2. It is desired to prepare pure solid products of the respective Ga and Ge oxides. Propose three alternative aqueous-based methods that may be used to accomplish this. At least one of the methods should involve initial co-dissolution (i.e., simultaneous) of both metals. For each method consult the relevant Eh-pH diagrams below and:

a) Identify the relevant reaction paths
b) Provide the balanced chemical equations corresponding to the reaction paths
c) Prepare a fully labelled flow diagram of the process.

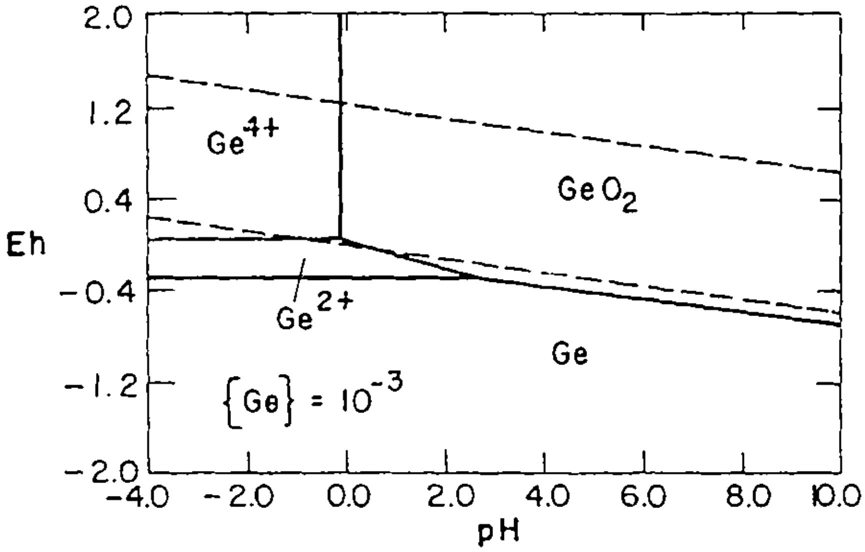


Figure 3a: Eh-pH diagram for the Ge-H_2O system, {Ge} = 10^{-3}.

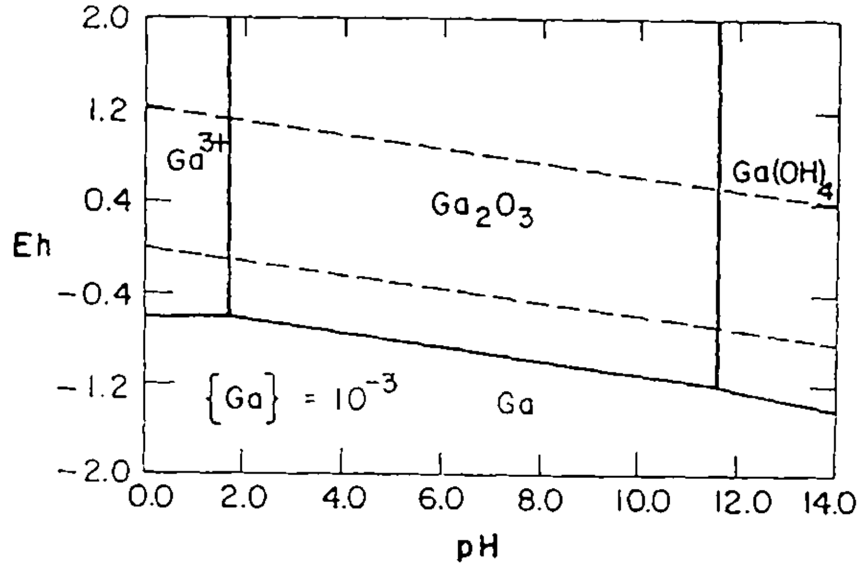


Figure 3a: Eh-pH diagram for the Ga-H_2O system, {Ga} = 10^{-3}.