

FINAL EXAM GEO2-1202 Physical Chemistry

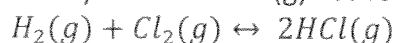
Thursday 8 November 2012 11 – 13

General remarks:

- This exam contains *five* questions.
- Please answer *concisely*, but present *intermediate calculations*.
- Report the *units* of the numbers, particularly for your final answer
- Answers in English or in Dutch are allowed.
- At the end of the examination hand in *all* your answer sheets.
- Write down your *name or student number* on all answer sheets.

1.

The synthesis of HCl(g) has following stoichiometry:



	H ₂ (g)	Cl ₂ (g)	HCl
$\Delta_f \bar{H}^0$ [kJ mol ⁻¹]	0	0	-92.3
$\Delta_f \bar{G}^0$ [kJ mol ⁻¹]	0	0	-95.3

- (a) Calculate the equilibrium constant K_p for the synthesis of HCl at 298 K.
- (b) Calculate the equilibrium constant K_p for the synthesis of HCl at 450 K.
- (c) Discuss qualitatively the effect of pressure on the yield of the reaction (how much HCl can be produced from H₂ and Cl₂ when equilibrium is reached).
- (d) Discuss qualitatively the effect of adding a catalyst on the yield of the reaction.
- (e) In a reaction vessel of 50 L, 2 moles of ~~H₂~~ and 2 moles of Cl₂ are added. Calculate the number of moles of HCl in equilibrium at 450K. ~~H₂~~

2.

- (a) Calculate the equivalent conductance of acetic acid (CH₃COOH) at infinite dilution from the information given in the table 8.2 (see next page).

The equivalent conductance was measured at various concentrations of CH₃COOH:

Concentration (mol L ⁻¹)	Equivalent Conductance (Ω ⁻¹ equiv ⁻¹ cm ²)
0.010	21.36
0.020	15.23
0.030	12.48
0.040	10.83
0.050	9.70
0.060	8.87

- (b) Calculate the dissociation constant K_a of acetic acid.

Table 8.2
Equivalent Ionic Conductance and Ionic Mobility of Some Common ions at
298 K

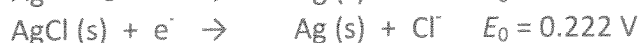
Ion	λ_0^{eq} $\Omega^{-1} \cdot \text{equiv}^{-1} \cdot \text{cm}^2$	Ionic Mobility ^b $10^{-4} \text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$	Ionic Radius/ \AA
H ⁺	349.81	36.3	
Li ⁺	38.68	4.01	0.60
Na ⁺	50.10	5.19	0.95
K ⁺	73.50	7.62	1.33
Rb ⁺	77.81	7.92	1.48
Cs ⁺	77.26	7.96	1.69
NH ₄ ⁺	73.5	7.62	
Mg ²⁺	53.05	5.50	0.65
Ca ²⁺	59.50	6.17	0.99
Ba ²⁺	63.63	6.59	1.35
Cu ²⁺	53.6	5.56	0.72
OH ⁻	198.3	20.50	
F ⁻	55.4	5.74	1.36
Cl ⁻	76.35	7.91	1.81
Br ⁻	78.14	8.10	1.95
I ⁻	76.88	7.95	2.16
NO ₃ ⁻	71.46	7.41	
HCO ₃ ⁻	44.50	4.61	
CH ₃ COO ⁻	40.90	4.24	
SO ₄ ²⁻	80.02	8.29	

^a From Robinson R. A.; Stokes, R. H. *Electrolyte Solutions*, Academic Press, New York, 1959. Used by permission. Note that for ions carrying multiple charges, the molar conductance is given by the product of the magnitude of the charge and the equivalent ionic conductance. Thus, the molar ionic conductance of Mg²⁺ is 2×53.05 or $106.1 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

^b From Adamson, A. W. *A Textbook of Physical Chemistry*, Academic Press, New York, 1973. Used by permission.

3.

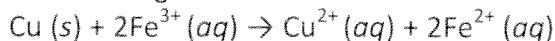
(a) Calculate the solubility product for silver(I) chloride (AgCl) given the standard reduction potentials of the half reactions:



(b) Calculate $[\text{Ag}^+]$ in a 0.015 M MgCl₂ solution. Assume that the Debye-Hückel limiting law is appropriate to calculate the activity coefficients.

4.

Consider a galvanic cell that uses the reaction:



with $[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M}$, $[\text{Cu}^{2+}] = 0.25 \text{ M}$, and $[\text{Fe}^{2+}] = 0.20 \text{ M}$

(a) Calculate the emf of this cell at 25 °C.

The solutions of the half cells are diluted by a factor of two.

(b) Calculate the emf of this cell at 25 °C.

5.

The progress of a reaction with a single reactant in the aqueous phase was monitored by measuring the concentrations at various times:

Time (s)	Concentration (mol L ⁻¹)
0	2.0
10	1.3
20	0.9633

(a) Determine the reaction order.

(b) Calculate the rate constant.

(c) Calculate the concentration of the reactant at two half-lives.

Values of Some Fundamental Constants

Constant	Value
Avogadro's constant (N_A)	$6.0221367 \times 10^{23} \text{ mol}^{-1}$
Bohr radius (a_0)	$5.29177249 \times 10^{-11} \text{ m}$
Boltzmann constant (k_B)	$1.380658 \times 10^{-23} \text{ J K}^{-1}$
Electron charge (e)	$1.602177 \times 10^{-19} \text{ C}$
Electron mass (m_e)	$9.1093897 \times 10^{-31} \text{ kg}$
Faraday constant (F)	$96485.309 \text{ C mol}^{-1}$
Gas constant (R)	$8.314510 \text{ J K}^{-1} \text{ mol}^{-1}$
Neutron mass (m_N)	$1.674928 \times 10^{-27} \text{ kg}$
Permittivity of vacuum (ϵ_0)	$8.845 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
Planck constant (h)	$6.626075 \times 10^{-34} \text{ J s}$
Proton mass (m_P)	$1.672623 \times 10^{-27} \text{ kg}$
Rydberg constant (R_H)	$109737.31534 \text{ cm}^{-1}$
Speed of light in vacuum (c)	$299792458 \text{ m s}^{-1}$

Useful Conversion Factors

$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0.1 \text{ nm}$
$1 \text{ atm} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$
$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 100 \text{ kPa} = 0.986923 \text{ atm}$
$1 \text{ cal} = 4.184 \text{ J}$
$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 96.4853 \text{ kJ mol}^{-1}$
$1 \text{ R} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$
$1 \text{ L atm} = 101.34 \text{ J}$

Key Equations

$G = H - TS$	{Definition of Gibbs energy}	(6.1)
$dG_{\text{sys}} \leq 0$	{At constant T and P }	(6.2)
$\Delta G = \Delta H - T\Delta S$	{At constant T and P }	(6.3)
$A = U - TS$	{Definition of Helmholtz energy}	(6.4)
$dA_{\text{sys}} \leq 0$	{At constant T and V }	(6.5)
$\Delta A = \Delta U - T\Delta S$	{At constant T and V }	(6.6)
$\Delta A = w_{\text{rev}}$	{Relating ΔA to maximum work}	(6.8)
$dU = TdS - PdV$	{Combining first and second laws of thermodynamics}	(6.9)
$dG = VdP - SdT$	{Dependence of G on T and P }	(6.10)
$\Delta G = w_{\text{el,max}}$	{Relating ΔG to electrical work}	(6.11)
$\Delta_r G^\circ = \sum \nu_i \Delta_f G^\circ(\text{products}) - \sum \nu_i \Delta_f G^\circ(\text{reactants})$	{Standard Gibbs energy change of a reaction}	(6.12)
$\left[\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}$	{Gibbs-Helmholtz equation}	(6.15)
$\Delta G = nRT \ln \frac{P_2}{P_1}$	{Change in G due to change in P }	(6.17)
$\bar{G} = \bar{G}^\circ + RT \ln \frac{P}{1 \text{ bar}}$	{Molar Gibbs energy of a gas}	(6.18)
$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta V}$	{Clapeyron equation}	(6.19)
$\ln \frac{P_2}{P_1} = \frac{\Delta \bar{H}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	{Clausius-Clapeyron equation}	(6.21)
$\ln P = -\frac{\Delta \bar{H}}{RT} + \text{constant}$	{Clausius-Clapeyron equation}	(6.22)
$f = c - p + 2$	{The phase rule}	(6.23)
$f = \left(\frac{\partial U}{\partial N} \right)_T = T \left(\frac{\partial S}{\partial l} \right)_T$	{Restoring force of a stretched rubber band}	(6.27)

Key Equations

$\Delta_r G = -RT \ln K_P$	{Relation between $\Delta_r G^\circ$ and K_P }	(9.7)
$\Delta_r G = \Delta_r G^\circ + RT \ln Q$	{Gibbs energy change of a reaction}	(9.9)
$\gamma = \frac{f}{P}$	{Fugacity coefficient}	(9.11)
$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	{van't Hoff equation}	(9.18)
$\ln K = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$	{van't Hoff equation}	(9.19)

Key Equations

$\Lambda_m = \frac{(1000 \text{ cm}^3 \text{ L}^{-1})\kappa}{c}$	(Molar or equivalent conductance)	(8.4)
$\Lambda_m = \lambda_m^+ + \lambda_m^-$	(Kohlrausch's law of independent migration)	(8.6)
$\frac{1}{\Lambda} = \frac{1}{K_1 \Lambda_1^2} (\Delta c)^{-1} + \frac{1}{\Lambda_0}$	(Ostwald dilution law)	(8.9)
$F = \frac{qS_m(\rho)}{4\pi\epsilon_0 r^2}$	(Coulomb's law)	(8.12)
$m = (m^+ m^-)^{1/2}$	(Mean ionic molality)	(8.17)
$a_{\pm} = (a_+^+ a_-^-)^{1/2}$	(Mean ionic activity)	(8.20)
$a_{\pm} = \gamma_{\pm} m_{\pm}$	(Definition of γ_{\pm})	(8.21)
$\gamma_{\pm} = (\gamma_+^+ \gamma_-^-)^{1/2}$	(Mean ionic activity coefficient)	(8.22)
$I = \frac{1}{2} \sum_i m_i z_i^2$	(Ionic strength)	(8.25)
$\log \gamma_{\pm} = -0.509 z_{\pm}^2 \sqrt{I}$	(Debye-Hückel limiting law)	(8.26)
$\log \frac{S}{S^0} = 0.509 z_{\pm}^2 \sqrt{I}$	(Salting-in effect)	(8.28)
$\log \frac{S}{S^0} = -K' I$	(Salting-out effect)	(8.29)

Key Equations

$E = E_{\text{cathode}} - E_{\text{anode}}$	(Standard emf of a cell)	(10.1)
$\Delta_r G = -vFE$	(Relating $\Delta_r G$ to the emf of a cell)	(10.2)
$E = \frac{\Delta_r G^0}{vF}$	(Relating $\Delta_r G^0$ to the standard emf of a cell)	(10.4)
$E = \frac{RT \ln K}{vF}$	(Relating E^0 to the equilibrium constant)	(10.5)
$E = E^0 - \frac{RT}{vF} \ln \frac{a_{\text{O}} a_{\text{R}}^{\nu}}{a_{\text{O}}^{\nu} a_{\text{R}}}$	(The Nernst equation)	(10.7)
$E = E^0 - \frac{0.0257 \text{ V}}{v} \ln \frac{a_{\text{O}} a_{\text{R}}^{\nu}}{a_{\text{O}}^{\nu} a_{\text{R}}}$	(The Nernst equation at 298 K)	(10.8)
$\Delta_r S = vF \left(\frac{\partial E}{\partial T} \right)_P$	(Relating $\Delta_r S$ to the temperature coefficient of E)	(10.9)
$\Delta_r H = vFE^0 - vFT \left(\frac{\partial E}{\partial T} \right)_P$	(Standard enthalpy change of an electrochemical reaction)	(10.10)

Key Equations

$[A] = [A]_0 - kt$	(Rate law for zero-order reaction)	(12.4)
$\ln \frac{[A]}{[A]_0} = -kt$	(Rate law for first-order reaction)	(12.6)
$[A] = [A]_0 e^{-kt}$	(Rate law for first-order reaction)	(12.7)
$t_{1/2} = \frac{\ln 2}{k}$	(Half-life of first-order reaction)	(12.8)
$t_{1/2} = \frac{1}{k[A]_0^{n-1}}$	(General expression for half-life)	(12.9)
$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	(Rate law for second-order reaction)	(12.11)
$k = A e^{-E_a/RT}$	(Arrhenius equation)	(12.23)
$\ln k = \ln A - \frac{E_a}{RT}$	(Arrhenius equation)	(12.24)
$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$	(Arrhenius equation)	(12.25)
$\mu = \frac{m_A m_B}{m_A + m_B}$	(Reduced mass)	(12.28)
$k = P z e^{-E_a/RT}$	(Modified Arrhenius equation)	(12.31)
$k = \frac{k_B T}{h} e^{AS} e^{-R_e^{-1} M^{-1/2} RT} (M^{1/2})$	(Thermodynamic formulation of reaction rate)	(12.36)
$\log \frac{k}{k_0} = -\gamma \Delta G B \sqrt{I}$	(Kinetic salt effect)	(12.44)
$k_D = \frac{8}{3} \frac{RT}{\eta}$	(Diffusion-controlled rate constant)	(12.45)