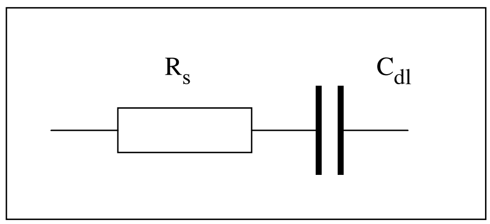
Chem 243 Cumulative Exam. R. Corn. Spring 2006.

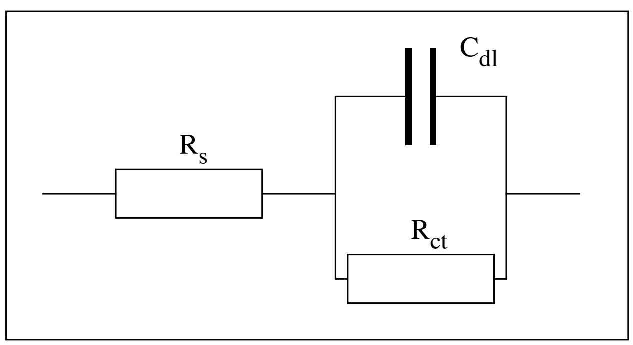
1) Electrochemical Impedance Spectroscopy (40 points)

For the following two electrochemical circuits, please
i) derive equations for the complex impedance Z(ω);
ii) derive equations for the Real and Imaginary parts of Z(ω);
iii) sketch the Nyquist Impedance plot you would expect to see from this cell.

(Hint: Z(ω) = 1/jωC for a Capacitor)
a) Ideal Polarized Electrode:



b) Randles Cell:



2) Classical Complex Susceptibility (30 points)

Consider the equation of motion for the position x(t) of a charged particle in a damped harmonic oscillator potential with a driving force -eE(t):

$$m\frac{d^2x}{dt^2} + m\Gamma\frac{dx}{dt} + m\omega_0^2 x = -eE(t)$$

a) Using the initial conditions x(t=0) = 0 and x'(t=0) = 0, use Laplace transforms to find the transfer function **H**(s) that relates the Laplace transform **x**(s) to the Laplace transform **E**(s) (note: bold indicates the LaPlace Transform; e.g. x(t) vs. **x**(s)):

$$\mathbf{x}(s) = \mathbf{H}(s)\mathbf{E}(s)$$

b) Let E(t) = $E_0\cos(\omega t)$ and then find the transfer function H(ω). (Hint: for this driving field, s goes to jω). Please sketch this function H as a function of ω.

c) How is this function H(ω) related to the classical complex susceptibility χ(ω)?

3) Langmuir Adsorption and Desorption Kinetics (30 points)

The vast majority of surface bioaffinity measurements utilize the specific adsorption of target biomolecules (*T*) from solution onto a surface that has been chemically modified with probe biomolecules (*P*). If the target and probe interact in a simple 1:1 ratio, then in the absence of bulk transport the surface reaction can be represented in the form:

$$T + P \underset{k_d}{\overset{k_a}{\rightleftharpoons}} TP \qquad (1)$$

where *TP* is the surface bound target-probe complex. Both *P* and *TP* are surface species, and in the Langmuir approximation their surface concentrations Γ_P and Γ_{TP} are linked to the total concentration of surface sites Γ_{tot} by eq 2:

$$\Gamma_P + \Gamma_{TP} = \Gamma_{tot} \qquad (2)$$

A) If we define θ as the fraction of occupied surface sites, $\theta = \Gamma_{TP}/\Gamma_{tot}$, write down the differential equation for the time evolution of θ ($d\theta/dt =$…) using k_a and k_d. and the bulk concentration [T].

B) Find the steady state equilibrium surface coverage θ_{eq}, which is obtained in the steady state approximation ($d\theta/dt = 0$). This equation defines the Langmuir adsorption coefficient $K_{ads} = k_a/k_d$. What is θ_{eq} at a bulk concentration equal to $1/K_{ads}$?.

C) Solve the differential equation in part (A) to determine the time dependence of the fractional surface coverage, *θ(t)*, for the case where $\theta = 0$ at $t = 0$ and the bulk concentration [T] = T_0. Hint: you can use Laplace transform methods to solve the differential equation.