High Temperature Materials
Midterm

1) For the following questions choose correct answer and/or fill in the blanks. (5 each)

i) In general the diffusivity of defects are higher/lower (choose one) than the atomic defects because ____.

ii) The Nernst-Einstein relationship relates __________________________ to ____.

iii) The oxidation of a metal does/does not (choose one) depend on the nature of the oxide that forms on its surface because _____________________________

iv) The Pilling-Bedworth ratio is the ratio of _____________ to _______________

A P-B ratio < 1 implies that the oxide layer formed is/is not (choose one) protective because ____

v) Ambipolar diffusion is/is not (choose one) important when dealing with creep. In that case the rate-limiting step is the slower/faster (choose one) _________ ___________________

vi) A simple way to determine whether an oxide is an n-type or p-type semiconductor is to measure ____.

vii) If the activity of O_2 at the Ni/NiO interface is 10^{-28} atm at 1000 °C, the activity of Ni at the same interface is calculated to be _________________________________

viii) To increase the electron (*n*-type) conductivity of ZnO, I would you add Al_2O_3/Li_2O (choose one) because _______________________________________.

10 2) i) Explain ambipolar diffusion in your own words. Use oxidation as an illustrative example.
20 ii) Explain in broad terms Wagner's treatment of parabolic oxidation. In other words, state the assumptions he made to obtain the following expression:

$$J_{M^\bullet} = \frac{-\sigma_{def} t_e}{(ze)^2} \frac{d\tilde{\mu}_{M^\bullet}}{dx} = \frac{-\sigma_{def}\sigma_e}{(ze)^2(\sigma_{def}+\sigma_e)} \frac{d\tilde{\mu}_{M^\bullet}}{dx} \quad (7.73)$$

Make sure you define all terms.

20 iii) How does one measure K_x. In broad terms explain how this value is related to expression shown above.

3) The diffusivity of oxygen vacancies in TiO_2 was measured to be:

$$D_{VO}\ (m^2/s) \approx 2 \times 10^{-3} \exp - 251(kJ)/RT$$

a) What information do you need to know in order to calculate the diffusivity of oxygen ions in this oxide? Be specific. **10**
b) Careful chemical analysis of the TiO_2 for which the oxygen diffusivity was measured above contained150 ppm Al_2O_3. Does that help you in solving part a. Please make sure you state all assumptions. **15**
c) If you determine that the oxidation of Ti is rate limited by the diffusion of oxygen vacancies through a titania layer, would you alloy the Ti with Al or Nb to enhance its oxidation resistance? Explain. **15**

Information you may find useful: Density of TiO_2 = 4.25 g/cm^3.

4) 30 pts.

In a now classic paper,[102] Kingery *et al.* measured the conductivity of $Zr_{0.85}Ca_{0.15}O_{1.85}$ as a function of oxygen partial pressure and temperature. They found that the conductivity (S/m) was independent of oxygen partial pressure and obeyed the relation

$$\sigma = 1.5 \times 10^5 \exp\left(-\frac{1.26\,\text{eV}}{kT}\right)$$

The diffusion coefficient of the oxygen ions (m^2/s) was also measured in a *separate* experiment on the same material and was found to obey

$$D = 1 \times 10^{-6} \exp\left(-\frac{1.22\,\text{eV}}{kT}\right)$$

What conclusions can be reached regarding the conduction mechanisms in this oxide and its defect structure? Information you may find useful: density of zirconia $\approx$ 6.1 g/cm^3 and molecular weight of Zr is 91.22 g/mol.

5) **10 + 20**

Cuprous chloride is an electronic *p*-type conductor at high Cl pressures. As the chlorine pressure decreases, ionic conductivity takes over.

(*a*) Suggest a mechanism or combination of mechanisms to explain this behavior.
(*b*) Obtain a relationship between conductivity and the defect population for your proposed mechanism(s) that is consistent with the experimental observations. *Hint*: Consider two mechanisms, one stoichiometric and the other nonstoichiometric.

TAKE HOME

10 1) i) Consider the case of an oxide that is predominantly an ionic conductor and its electron partial conductivity is higher than the conduction due to its holes. Derive a simplified expression for the flux of neutral species across such a membrane.

10 ii) Provide an example where the flux expression calculated in part i is important technologically. Be specific and make sure you clearly state the driving force(s), if any, for the resulting flux.

iii) Derive an expression for the oxidation of a metal that forms a p-type electronically conducting oxide. Show that the parabolic rate constant of such an oxide is/is not (choose one) a strong function of ambient partial pressure of oxygen. **10**

iv) Relate if possible the permeation flux through an oxide to K_x across that oxide.

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Solution to part d.

$\Delta x^2 = 2\ K_x\ t$

$d\ (\Delta x/dt) = K_x /\sqrt{2t} = J_M\ \Omega$

$J_M = \sqrt{K_x} / \Omega\ \sqrt{2t}$