

# CH 342 S02 Project Solution 18.Mar.02

> restart:

## Nernst Equation

Gibb's energy of cell and relation to cell potential yield Nernst equation.

> eqnEq := DrG = DrGo + Rg\*T\*ln(Q):

eqnFo := DrGo = -gamma\*F\*Eo: eqnF := DrG = -gamma\*F\*E:

eqnNernst := expand((-1/(gamma\*F))\*subs({DrGo = -gamma\*F\*Eo, DrG = -gamma\*F\*E}, eqnEq));

$$eqnNernst := E = Eo - \frac{Rg T \ln(Q)}{\gamma F}$$

## Reaction Coefficient

> Qproc := proc(a,X,g,n) product(a[X[i]]^g[i],i=1...n) end proc:

> Xs := table([Ap,Ti,A,Ti2p]): gs := table([-2,-1,2,1]):

> as := table([(Ap) = gAp\*bAp, (Ti) = 1, (A) = 1, (Ti2p) = gTi2p\*bTi2p]):

> Qs := Qproc(as,Xs,gs,4);

$$Qs := \frac{gTi2p bTi2p}{gAp^2 bAp^2}$$

Substitute formulations for molalities and reexpress Nernst equation.

> bTi2p := fr\*boap/2:

bAp := (1-fr)\*boap: Qs;

$$\frac{1}{2} \frac{gTi2p fr}{gAp^2 (1-fr)^2 boap}$$

> Ecells := subs({gamma=2,Q=Qs},rhs(eqNernst));

$$Ecells := Eo - \frac{1}{2} \frac{Rg T \ln\left(\frac{1}{2} \frac{gTi2p fr}{gAp^2 (1-fr)^2 boap}\right)}{F}$$

## Given Values

> readmylib(pchemconstants): Eos := 1.96: Ts := 25+273.15:

> Ecellc := subs({Eo=Eos,T=Ts},Ecells);

$$Ecellc := 1.96 - .01284636705 \ln\left(\frac{1}{2} \frac{gTi2p fr}{gAp^2 (1-fr)^2 boap}\right)$$

## Ideal Cell

```
> EcellIdeal := subs({gTi2p=1,gAp=1},Ecellc);
```

$$EcellIdeal := 1.96 - .01284636705 \ln\left(\frac{1}{2} \frac{fr}{(1-fr)^2 boap}\right)$$

```
> EcellEI := proc(bv) subs(boap=bv,EcellIdeal) end proc:
```

## Ideal Recharge Voltages

```
> EICRecharge := proc(bv,fc)
  evalf[3](subs({boap=bv,fr=fc},EcellIdeal));
end proc:
```

```
> EICRecharge := <EICRecharge(0.01,0.95),EICRecharge(0.1,0.95),EICRecharge(1,0.95)>;
```

$$EICRecharge := \begin{bmatrix} 1.83 \\ 1.86 \\ 1.89 \end{bmatrix}$$

## Recharge Voltages

0.010 m -> 1.83 V

0.10 m -> 1.86 V

1.0 m -> 1.89 V

## [-] Ideal Plots

```
> EcellAI1 := EcellEI(0.01);
EcellAI2 := EcellEI(0.1);
EcellAI3 := EcellEI(1);
```

$$EcellAI1 := 1.96 - .01284636705 \ln\left(50.00000000 \frac{fr}{(1-fr)^2}\right)$$

$$EcellAI2 := 1.96 - .01284636705 \ln\left(5.000000000 \frac{fr}{(1-fr)^2}\right)$$

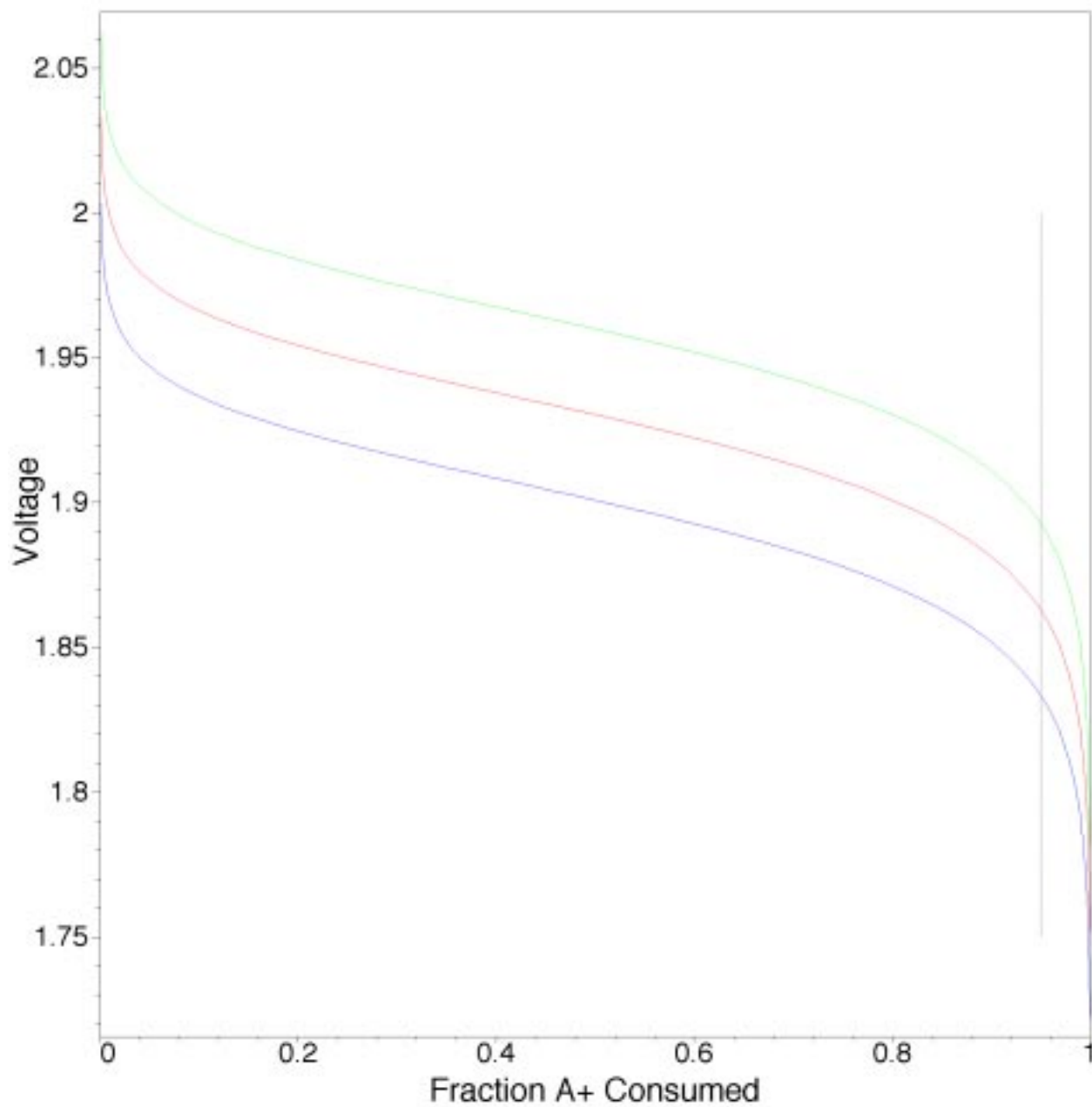
$$EcellAI3 := 1.96 - .01284636705 \ln\left(\frac{1}{2} \frac{fr}{(1-fr)^2}\right)$$

```
> jjw_newplot(`Ideal Cell Potentials`, `Fraction A+ Consumed`, `Voltage`);
```

Warning, the name changecoords has been redefined

```
> pEI1 := plot(EcellAI1,fr=0...1,color=blue):
pEI2 := plot(EcellAI2,fr=0...1,color=red):
pEI3 := plot(EcellAI3,fr=0...1,color=green):
pR := PLOT(CURVES([[0.95,1.75],[0.95,2]],LINESTYLE(2))):
> display({pEI1,pEI2,pEI3,pR});
```

### Ideal Cell Potentials



# Non-ideal Cell

## Activity Coefficients

> gTi2p := 1 + t\*bTi2p^2; gAp := 1+a\*bAp^2;

$$g_{Ti2p} := 1 + \frac{1}{4} t fr^2 boap^2$$

$$g_{Ap} := 1 + a (1 - fr)^2 boap^2$$

> Ecellc;

$$1.96 - .01284636705 \ln \left( \frac{1}{2} \frac{\left( 1 + \frac{1}{4} t fr^2 boap^2 \right) fr}{(1 + a (1 - fr)^2 boap^2)^2 (1 - fr)^2 boap} \right)$$

> EcellER := proc(av,tv,bv) subs({a=av,t=tv,boap=bv},Ecellc) end proc:

## Cell Potentials

> EcellR1 := EcellER(0.1,1,1);

EcellR2 := EcellER(1,0.1,1);

$$E_{cellR1} := 1.96 - .01284636705 \ln \left( \frac{1}{2} \frac{\left( 1 + \frac{1}{4} fr^2 \right) fr}{(1 + .1 (1 - fr)^2)^2 (1 - fr)^2} \right)$$

$$E_{cellR2} := 1.96 - .01284636705 \ln \left( \frac{1}{2} \frac{(1 + .02500000000 fr^2) fr}{(1 + (1 - fr)^2)^2 (1 - fr)^2} \right)$$

## Non-ideal Plots

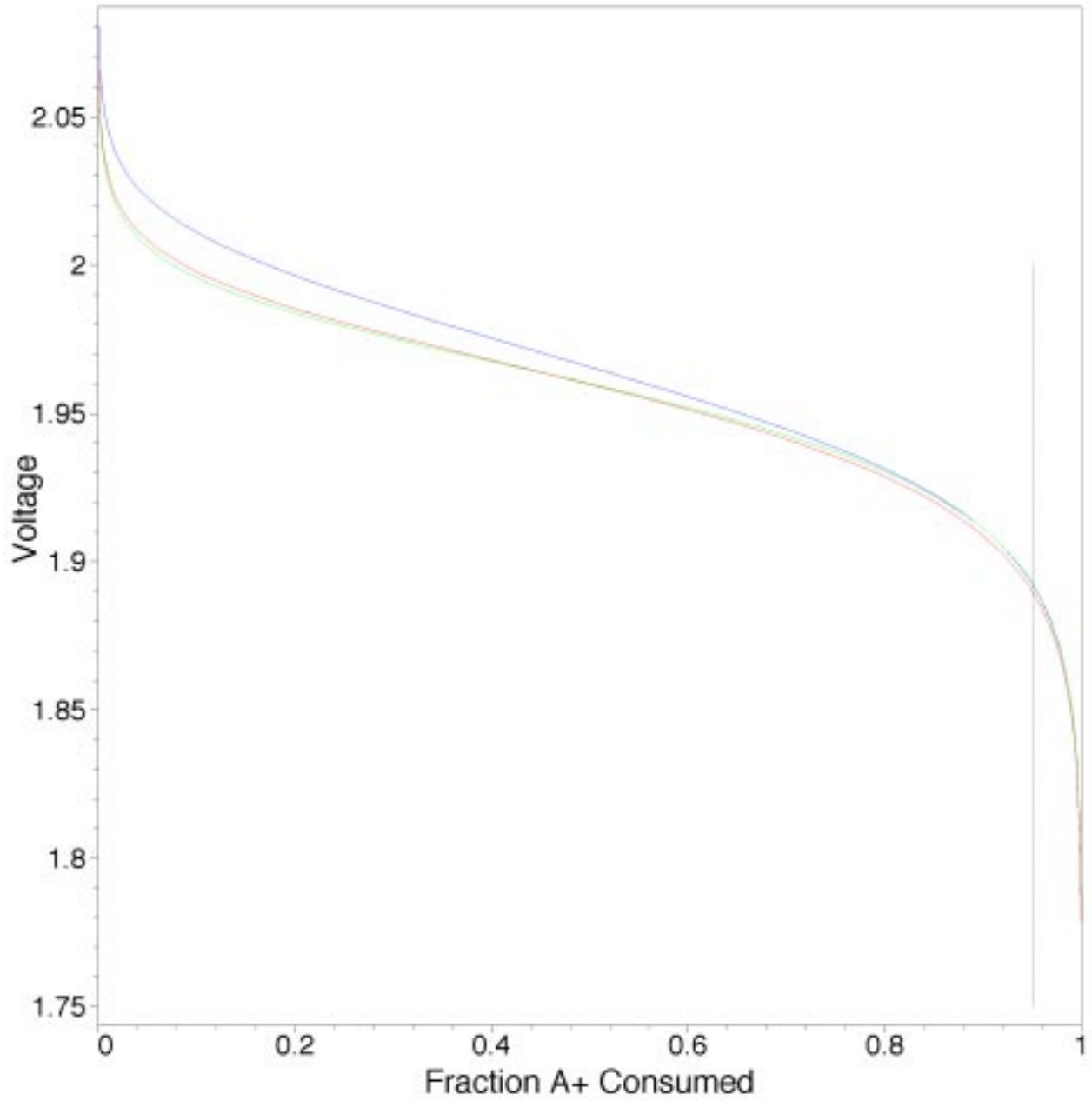
> pER1 := plot(EcellR1,fr=0...1,color=red):

pER2 := plot(EcellR2,fr=0...1,color=blue):

> jjw\_newplot(`Non-ideal Cell Voltage`, `Fraction A+ Consumed`, `Voltage`):

> display({pEI3,pER1,pER2,pR});

## Non-ideal Cell Voltage



## Recharge Voltages

For non-ideal cells, the values are all about the same as the ideal cell at 1.0 m  $\rightarrow$  1.89 V.

>