ANALYTICAL CHALLENGE

Solution to redox titration challenge

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Solution

The problem at hand is to simulate the process of titrating V_0 mL of a NaIO solution ($C_0 = 0.01$ mol/L) with V mL of an HCl solution ($C = 0.10$ mol/L) [1]. The mathematical setup of the problem is given in Fig. 1 and the resulting graphs for the titration plots are shown in Figs. 2 and 3.

From Fig. 2 we can establish that the equivalence point, corresponding to the inflection point of the titration curves $E = E(\Phi)$ and $pH = pH(\Phi)$, occurs at $\Phi = 0.801$. Knowing the four parameters—pH, pI, pCl, and E—at each titration point allows us to calculate the concentration of any other species. For example, we can determine that solid iodine emerges in the equilibrium solid phase at $\Phi > 0.465$.

This article is the solution to the Analytical Challenge to be found at http://link.springer.com/article/10.1007/s00216-016-0020-0
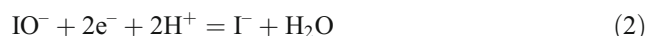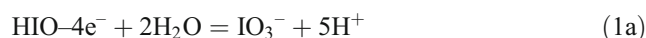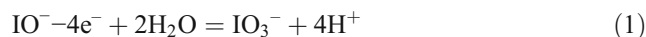
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Inspection of Fig. 3 allows us to evaluate the course of many processes during the titration. At the beginning of titration ($\Phi = 0$) we see that the concentrations of IO^- and HIO are vanishingly small (HIO is formed by hydrolysis $IO^- + H_2O = HIO + OH^-$ and $[HIO] > [IO^-]$ because HIO is a very weak acid). This suggests that both IO^- and HIO have disproportionated. As a result, the iodine species with oxidation numbers below and above +1 are formed simultaneously. We see from Fig. 3 that initially I^- and IO_3^- are the two predominant species. They are formed from the following half-reactions:

$$IO^- - 4e^- + 2H_2O = IO_3^- + 4H^+ \tag{1}$$

$$HIO - 4e^- + 2H_2O = IO_3^- + 5H^+ \tag{1a}$$

$$IO^- + 2e^- + 2H^+ = I^- + H_2O \tag{2}$$

$$HIO + 2e^- + H^+ = I^- + H_2O \tag{2a}$$

From here we obtain the schemes of predominating reactions of the disproportionating species, HIO and IO^-, at the start and in close vicinity of $\Phi = 0$:

$$3IO^- = IO_3^- + 2I^- \text{ (from 1 and 1a)}$$

$$3HIO = IO_3^- + 2I^- + 3H^+ \text{ (from 2 and 2a)}$$
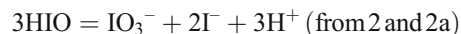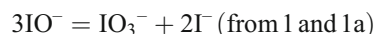
With the increase of Φ, the share of I_2 grows and, at $\Phi = 0.465$, the excess of I_2 forms the precipitate.

Fig. 1 The R code for simulating the titration of NaIO with HCl

```
## Titration of NaIO with HCl

## Input data
        V0 = 10
        C0 = 0.01
        C1 = 0.1

## Introductory data
       ZCl = 17
        ZI = 53
         A = 16.92
       pKw = 14
        Kw = 10^(-14)

## Function to be minimized
f <- function(x) {
        pH = x[1]
        pI = x[2]
       pCl = x[3]
         E = x[4]
         H = 10^(-pH)
        OH = Kw/H
         I = 10^(-pI)
        Cl = 10^(-pCl)

# Corresponding concentrations arising from equilibrium constants
        I2 = I^2*10^(2*A*(E - 0.621))
        I3 = I^3*10^(2*A*(E - 0.545))
        IO = I*10^(2*A*(E - 0.49) + 2*pH - 2*pKw)
       IO3 = I*10^(6*A*(E - 1.08) + 6*pH)
     H5IO6 = I*10^(8*A*(E - 1.24) + 7*pH)
     H3IO6 = I*10^(8*A*(E - 0.37) + 9*pH - 9*pKw)
       HIO = IO*10^(10.6 - pH)
      HIO3 = IO3*10^(0.79 - pH)
     H4IO6 = H3IO6*10^(3.3 - pH)
       Cl2 = Cl^2*10^(2*A*(E - 1.359))
       ClO = Cl*10^(2*A*(E - 0.88) + 2*pH - 2*pKw)
     ClO2m = Cl*10^(4*A*(E - 0.77) + 4*pH - 4*pKw)
      HClO = ClO*10^(7.3 - pH)
     HClO2 = Cl*10^(4*A*(E - 1.56) + 3*pH)
      ClO2 = Cl*10^(5*A*(E - 1.50) + 4*pH)
      ClO3 = Cl*10^(6*A*(E - 1.45) + 6*pH)
      ClO4 = Cl*10^(8*A*(E - 1.38) + 8*pH),
       ICl = I2^(0.5)*10^(A*(E - 1.105) - pCl)
      I2Cl = I2*10^(0.2 - pCl)
      ICl2 = ICl*10^(2.2 - pCl)
        Na = C0*V0/(V0 + V)

# Solubility of I2
   ifelse(I2 > 1.33e-3, {I2s = I2 - 1.33e-3; I2 = 1.33e-3}, {I2s = 0})

# The four balance equations
   z <- as.matrix(rep(NA, 4))

# 1 Charge balance
z[1] <- H - OH + Na - I - I3 - IO - IO3 - H4IO6 - 2*H3IO6 - Cl - ClO -
ClO2m - ClO3 - ClO4 - I2Cl - ICl2

# 2 Concentration balance for all iodine species
z[2] <- I + 3*I3 + 2*I2 + 2*I2s + HIO + IO + HIO3 + IO3 + H5IO6 + H4IO6
+ H3IO6 + 2*I2Cl + ICl + ICl2 - C0*V0/(V0 + V)

# 3 Concentration balance for all chlorine species
z[3] <- Cl + 2*Cl2 + HClO + ClO + HClO2 + ClO2m + ClO2 + ClO3 + ClO4 +
I2Cl + ICl + 2*ICl2 - C*V/(V0 + V)

# 4 Generalized electron balance involving all iodine and chlorine
species
z[4] <- (ZI + 1)*I + (3*ZI + 1)*I3 + 2*ZI*(I2 + I2s) + (ZI - 1)*(HIO +
IO) + (ZI - 5)*(HIO3 + IO3) + (ZI - 7)*(H5IO6 + H4IO6 + H3IO6) + (ZCl +
1)*Cl + 2*ZCl*Cl2 + (ZCl - 1)*(HClO + ClO) + (ZCl - 3)*(HClO2 + ClO2m)
+ (ZCl - 4)*ClO2 + (ZCl - 5)*ClO3 + (ZCl - 7)*ClO4 + (2*ZI + ZCl +
1)*I2Cl + (ZI + ZCl)*ICl + (ZI + 2*ZCl + 1)*ICl2 - ((ZI - 1)*C0*V0 +
(ZCl + 1)*C*V)/(V0 + V)

return(z)
}

## The titration curve
library(pracma)

V.init = 0.0001 # starting volume of HCl
max.it = 2000   # number of steps in the titration curve
par.0 = c(8.31,2.2,4.5,0.58) # initial values for pH, pI, pCl, and E
results <- matrix(rep(NA, max.it), ncol=5, nrow=max.it)

for(i in 1:max.it){
  V = V.init + 0.0005*(i-1)
  par.0 <- gaussNewton(par.0, f, maxiter=50000, tol=1.e-25)$xs
  results[i,] <- c(V, par.0)
}

## plot changes of pH vs titration progress
plot(results[,1], results[,2])

## plot changes of E vs titration progress
plot(results[,1], results[,5])
```
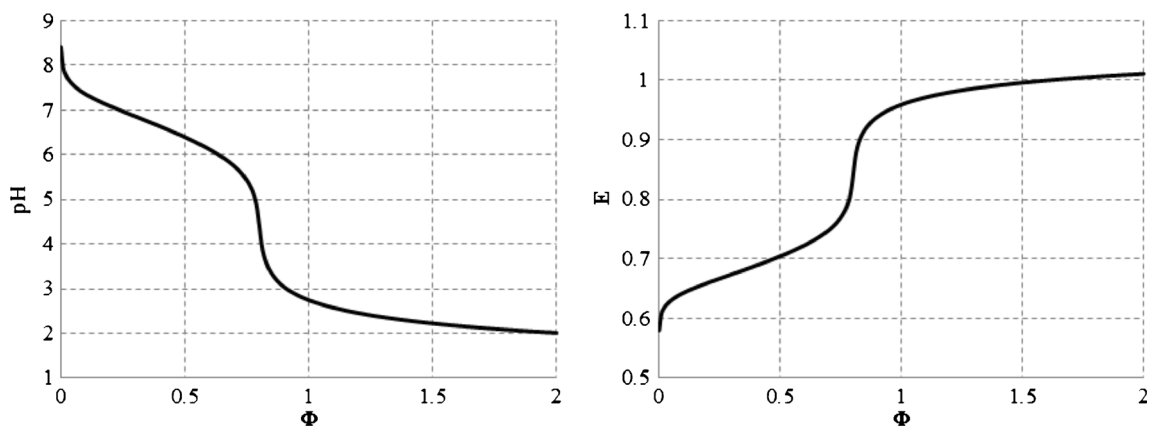
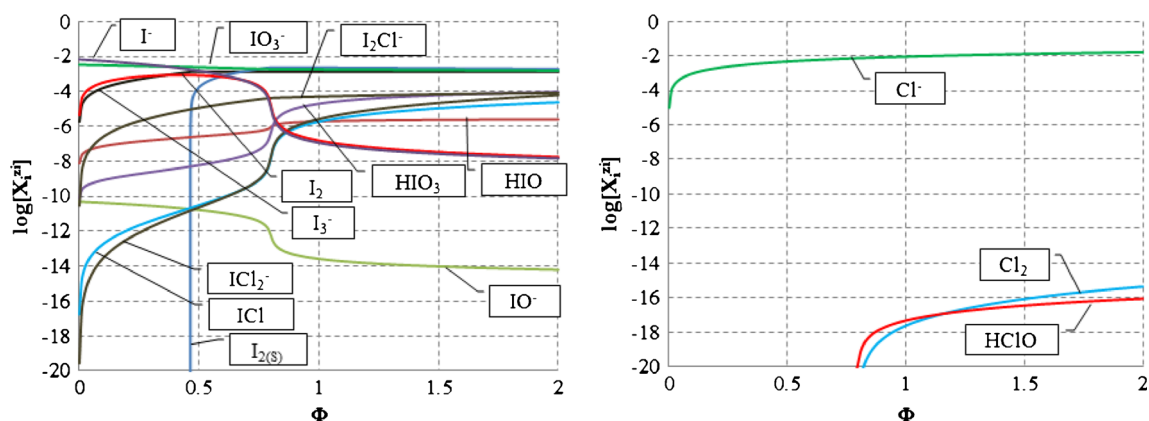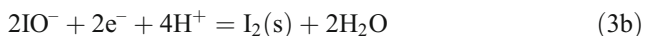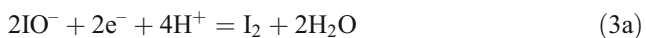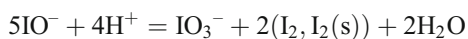Fig. 2 Changes of pH and E during the titration of NaIO with HCl

Fig. 3 Changes of chlorine and iodine species concentration during the titration of NaIO with HCl

$$2IO^- + 2e^- + 4H^+ = I_2 + 2H_2O \qquad (3a)$$

$$2IO^- + 2e^- + 4H^+ = I_2(s) + 2H_2O \qquad (3b)$$

From Eqs. (1), (3a), and (3b) we have:

$$5IO^- + 4H^+ = IO_3^- + 2(I_2, I_2(s)) + 2H_2O$$

This equation explains the inflection point of the titration curve at $\Phi \approx 4/5$, although several other reactions clearly take place. In this system, chloride ions (introduced by HCl) could also be considered a priori as a reducing agent. Such a possibility was assumed a priori when the balances involving all (known) products of chloride oxidation and complexation (I_2Cl^-, ICl, and ICl_2^-) were included. This way, full "democracy" was assumed with no simplifications. However, from the calculations we see that HCl acts primarily as a disproportionating, and not reducing agent.

References

1. Meija J, Michałowska-Kaczmarczyk AM, Michałowski T. Anal Bioanal Chem. 2017;409:11–13.