

Lecture 15

Electrochemical Biosensors: pH, PO_2 , and PCO_2

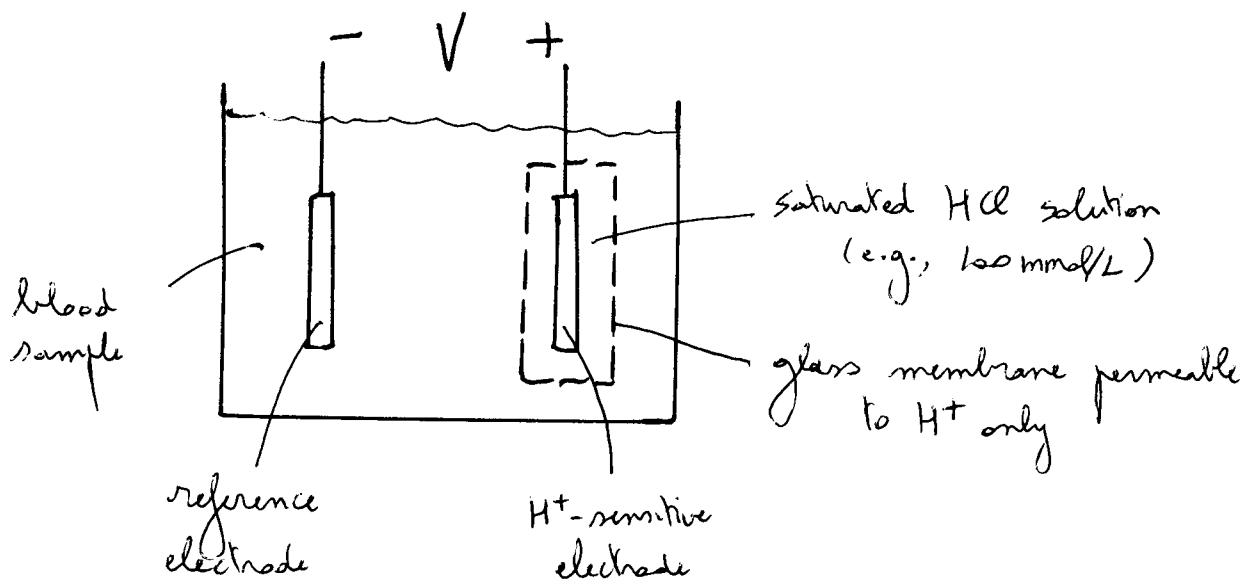
References

Webster, Ch. 10 (Sec. 10.1-10.2).

- Electrochemical sensors: measure pH, P_{O_2} , P_{CO_2} , ... as voltages and currents resulting from the underlying redox reactions.

• pH electrode: $H_2O \rightleftharpoons H^+ + OH^-$

$$[H^+] \cdot [OH^-] = (10^{-7} \frac{\text{mol}}{\text{L}})^2 \text{ at room temperature}$$



$$V = E_{H^+ \text{ el.}} - E_{\text{ref. el.}} + E_{\text{Nernst}}$$

= 0 for two Ag/AgCl electrodes

but non-zero if a calomel reference electrode is used!

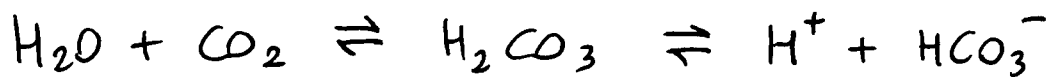
$$= \underbrace{\frac{RT}{F} \ln(10)}_{= 62 \text{ mV at room temperature}} \cdot \log_{10} \frac{[H^+]_{\text{sample}}}{[H^+]_{\text{HCl}}} = 62 \text{ mV} \cdot (\text{pH}_{\text{HCl}} - \text{pH}_{\text{sample}})$$

= 1 for $0.1 \frac{\text{mol}}{\text{L}}$ HCl in the glass bulb

- P_{CO_2} , partial pressure of CO_2 :

Typical range : 40 ± 3 mmHg awake
 44 ± 3 mmHg asleep

→ measured through linear relationship between $\log P_{CO_2}$ and pH in a saturated solution of sodium bicarbonate (NaHCO₃, or baking soda) :



At equilibrium : ([H₂O] is approximately constant)

$$\frac{[H^+][HCO_3^-]}{[CO_2]} = k$$

approximately constant,
 function of temperature

$$[CO_2] = a \cdot P_{CO_2} \quad a \approx 0.03 \frac{\text{mmol/l}}{\text{mmHg}}$$

$$\Rightarrow \log_{10} P_{CO_2} \approx -pH + \log_{10} [HCO_3^-] - \log_{10} k - \log_{10} a$$

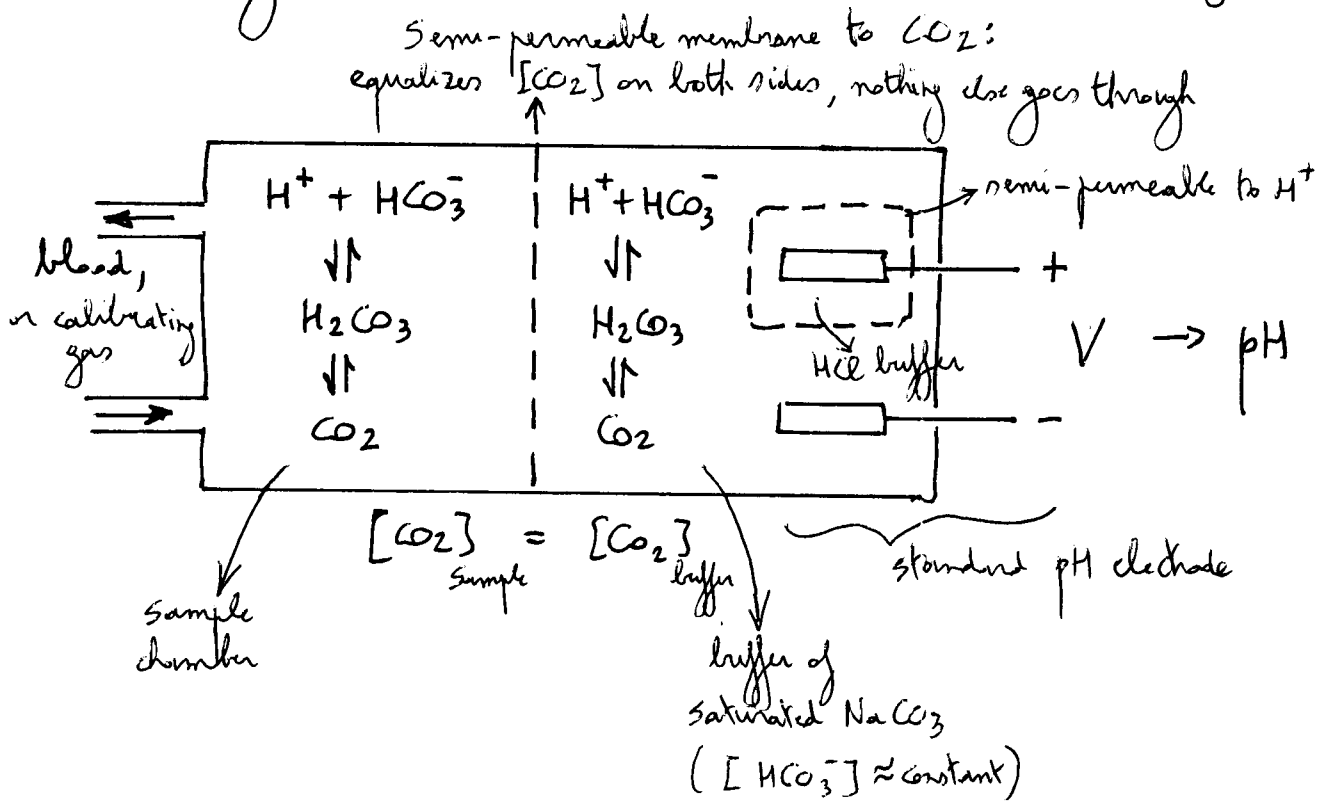
↓
 Indirect measure
 of P_{CO_2} ...

↓
 ... from
 measure of pH ...

↓
 ... in a buffered
 saturated solution
 of NaHCO₃ for
 which $[HCO_3^-] \approx \text{constant}$

Severinghaus PCO_2 electrode:

(Fig. 10.3)



$$\Rightarrow \log_{10} PCO_2 = -pH + \text{constant}$$

measured by
pH electrode

calibrated by
using a sample with
known PCO_2

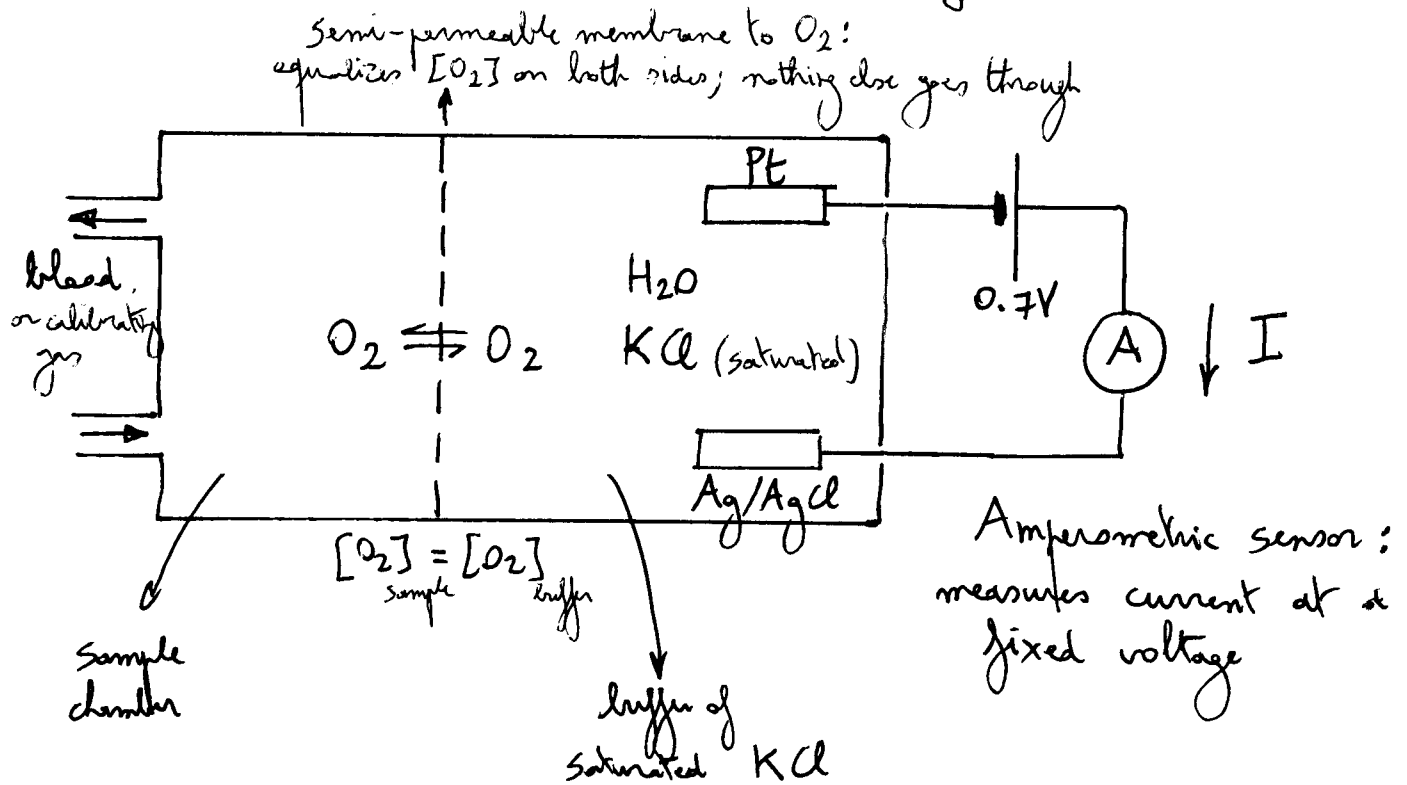
$$\text{or } \log_{10} PCO_2 = \frac{V}{62 \text{ mV}} + \text{constant}^?$$

different constant including
effect of $[HCl]$ in pH
buffer; calibrated in
a single step

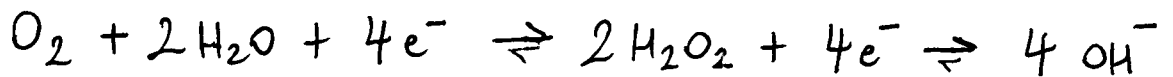
- P_{O_2} , partial pressure of O_2 :

Clark P_{O_2} electrode

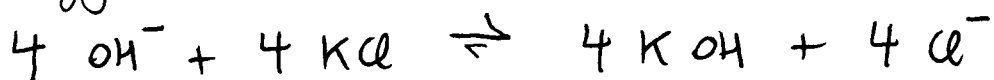
(Figs. 10.4 and 10.5)



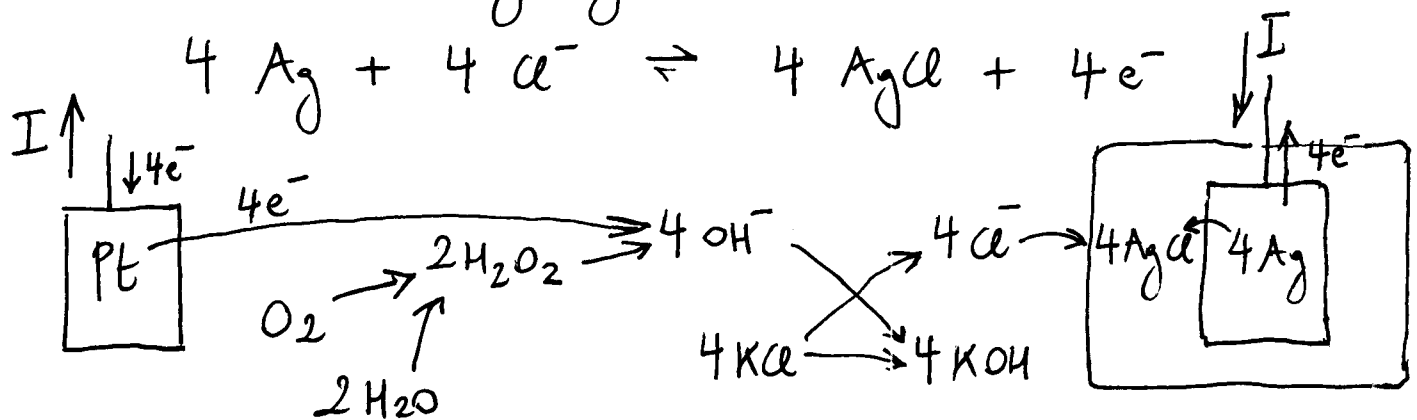
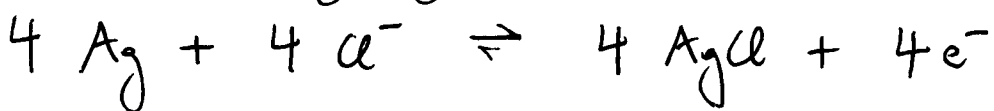
Reduction at the Pt CATHODE:



KCl buffer solution:

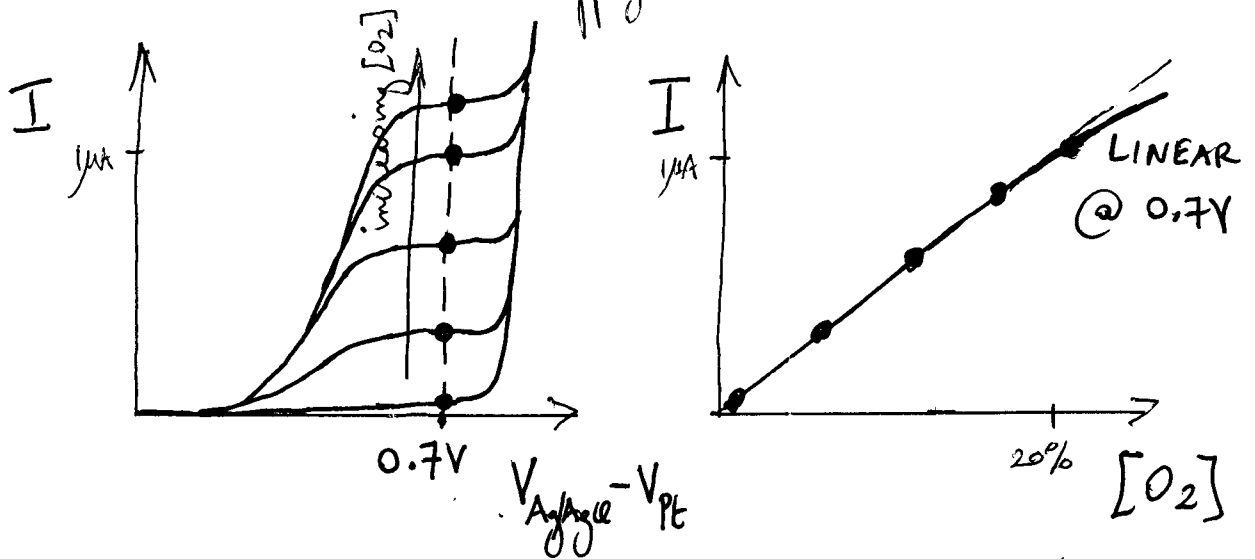


Oxidation at the Ag/AgCl ANODE:



To measure P_{O_2} , we want $[O_2]$ to be the reaction rate limiting factor:

- Saturated KCl solution as buffer
- Non-polarizable Ag/AgCl electrode
- Polarized Pt electrode requires a polarization potential of $\approx 0.7V$ in order to supply electrons to the solution:



(Fig. 10.5)

\Rightarrow For a polarizing voltage $\approx 0.7V$, the current I is approximately linear in $[O_2]$ (or P_{O_2}):

$$I \approx 4 \cdot F \cdot [O_2] \cdot \phi \quad [A = \frac{C}{s}]$$

4 electrons flow for every O_2 consumed.

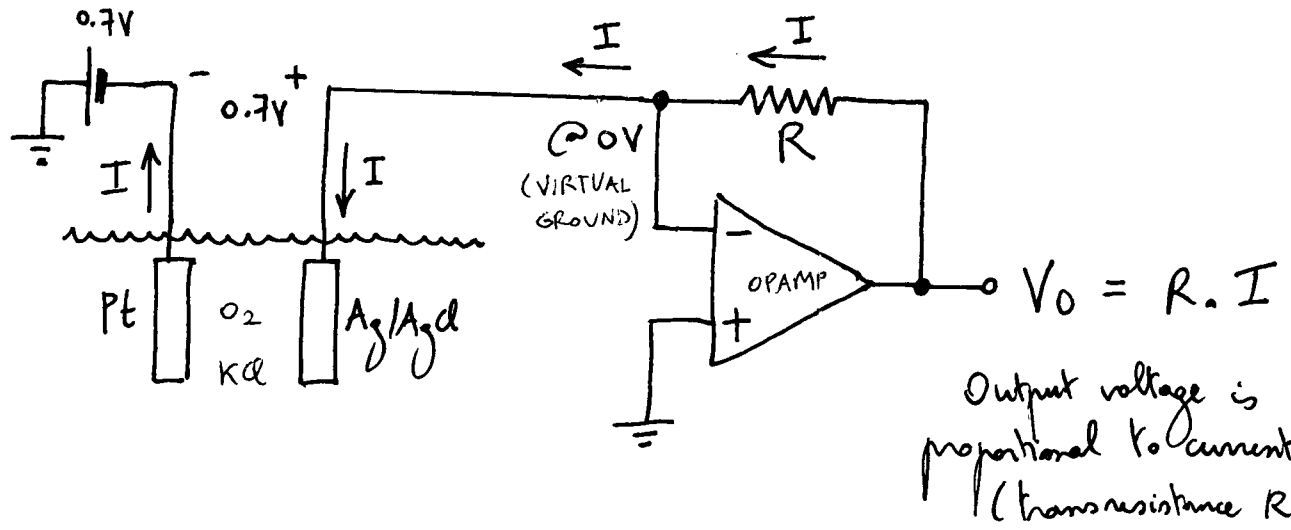
FARADAY'S CONSTANT $[\frac{C}{mol}]$
 Change of $\frac{1}{2}$ mol of electrons (protons)

$F = q \cdot N_A$
 $96,485 \frac{C}{mol} = 1.6 \cdot 10^{-19} C \cdot 6.0 \cdot 10^{23} \frac{1}{mol}$
 Proton Charge Avogadro

oxygen concentration $[\frac{mol}{l}]$

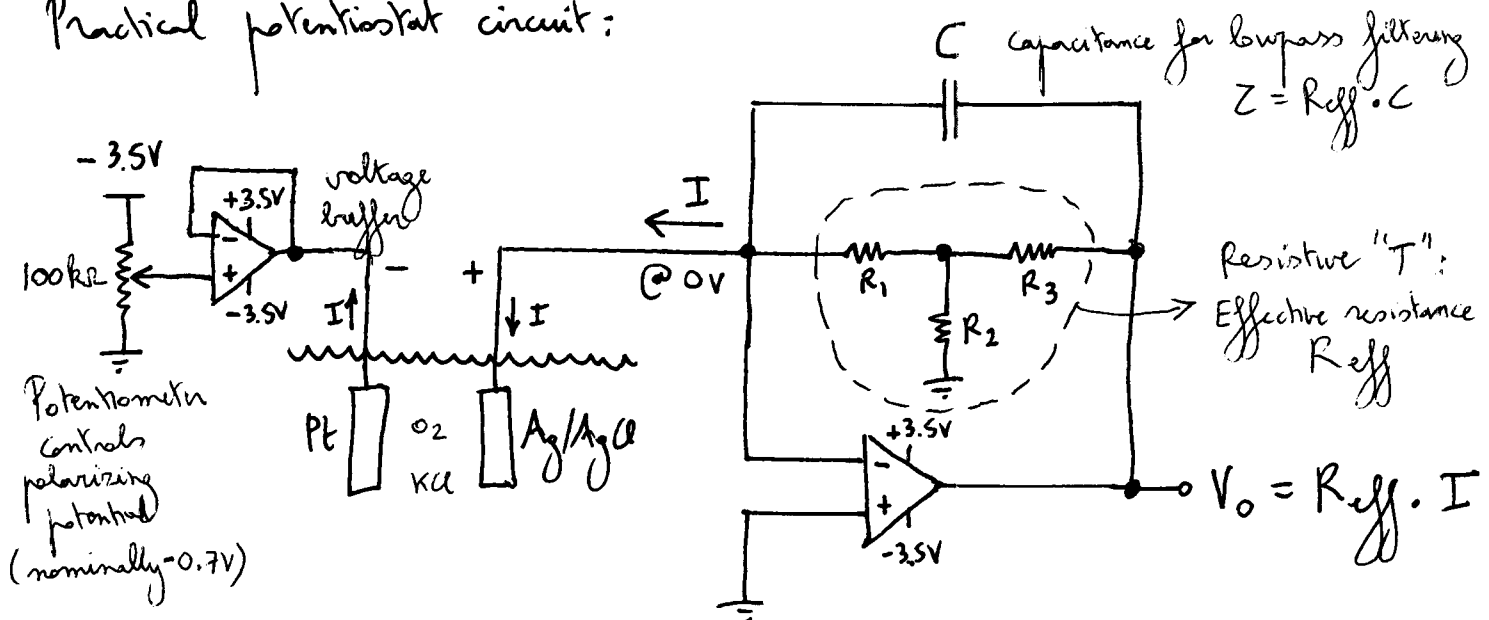
sample flow rate $[\frac{l}{s}]$

A POTENTIOSTAT measures the current I while applying a polarizing voltage (0.7V) between the electrodes:



R is large (several $M\Omega$) for high sensitivity (several mV per nA)

Practical potentiostat circuit:



Resistive "T" realizes very large effective resistance using lower resistances:

$$\begin{aligned}
 & \text{THÉVENIN} \quad R_1 \parallel R_3 \quad R_2 \parallel R_3 \quad \frac{R_2}{R_2+R_3} V_0 \\
 & \Rightarrow \frac{R_2}{R_2+R_3} V_0 = \left(R_1 + \frac{R_2 R_3}{R_2+R_3} \right) \cdot I \\
 & \text{or } R_2 \cdot V_0 = (R_1 R_2 + R_1 R_3 + R_2 R_3) \cdot I
 \end{aligned}$$

e.g.:

$$R_1 = R_3 = 1M\Omega, R_2 = 10k\Omega \Rightarrow R_{eff} = 100M\Omega$$

$$\Rightarrow R_{eff} = \frac{R_1 R_2 + R_1 R_3 + R_2 R_3}{R_2} \approx \frac{R_1 R_3}{R_2} \text{ for } R_1, R_3 \gg R_2$$