Notes to class

- Take a look at pset
  - More involved derivations, OH your friend
- Lecture not on test but good for understanding

Lecture Overview

How to use a potentiostat?
How does a potentiostat work?
- Not how a modern one works, but how to visualize it / understand how one could do it. (McGyver)

Background: Intro physics

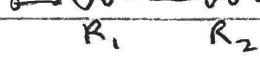
- IR circuits

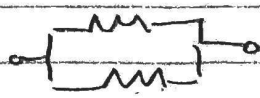
$$V = IR$$

$$\sum_{loop} V = 0 \qquad \sum_{junction} I = 0$$

Kirchhoff's laws

- Equivalent resistance

- series  $R_{eq} = R_1 + R_2$

- parallel 

$$\frac{1}{R_{eq}} = \frac{1}{R_1} + \frac{1}{R_2}$$

$$R_{eq} = \frac{R_1 R_2}{R_1 + R_2}$$

Q: $R_1 >> R_2$, series $R_{eq} = R_1$
parallel $R_{eq} = R_2$

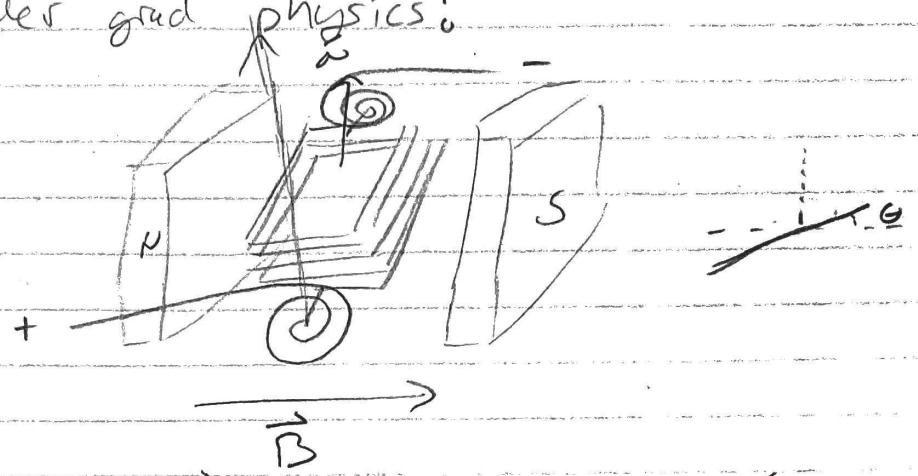
Definitions:

- Galvantometer - measures current (aka ammeter)
- Potentiometer - measures voltage (aka voltmeter)
- Galvanostat - applies a current
- Potentiostat - applies a voltage

How Does Voltmeter Work?

- Digital Voltmeters used everywhere (IC)
- Under grad physics!

Draw draw



Coil in $\vec{B}$: $|\vec{\mu}| = nIA$ (Right hand rule)

$|\vec{\tau}_{coil}| = |\vec{\mu} \times \vec{B}| = nIAB\sin\theta$

τ actually $\cos\theta$

Balanced by springs:

$\tau_{spring} = -\kappa\theta$ (Hooke's law)

Thin steel wire $\kappa \approx 0.005$ J/

Solve: Fridge magnet: 5mT, use B = 100mT

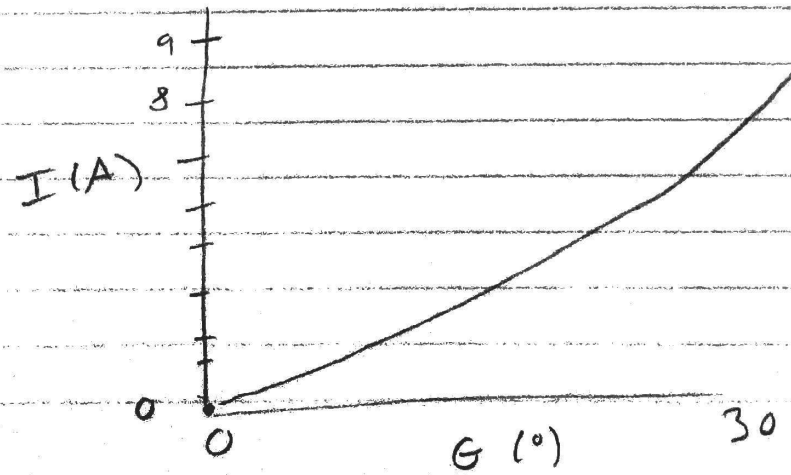
coil = 10 cm × 10 cm = 0.01 m²

$\Sigma\tau = 0 = 20\,I\,(0.01)(.1)\cos\theta - 0.005\frac{180}{\pi}\theta$

$\cos\theta \approx 1$

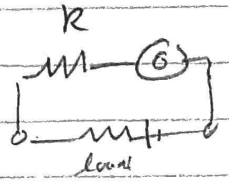
$\theta \approx 0.07I$ (rad)

$\approx 4I$ (degrees)



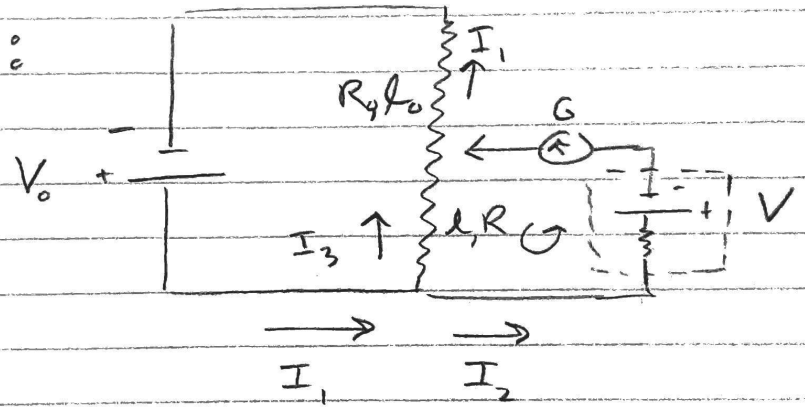
Surprisingly accurate! and linear
d'Arsonval + Deprez 1882
Could detect 0.01 mA
(Wikipedia)

Q: How turn into a volt meter?
- can add large R in series



Problems: Draws current unless big, then I too small

Solution:

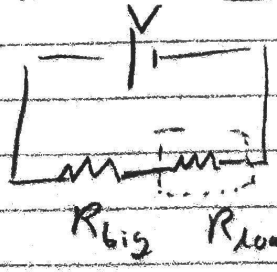


when $I_2 = 0$, $I_1 = I_3 = \frac{V_0}{R_0}$

$$V = I_3 R = \left(\frac{V_0}{R_0}\right) R_0 \left(\frac{l}{l_0}\right) = \left(\frac{V_0}{l_0}\right) l$$

No current through cell and
no need to calibrate galvanometer

Now, assuming we can measure voltage,
How to build basic galvanostat



$$I = \frac{V}{R_{big} + R_{load}}$$

If $R_{big} >> R_{load}$, $I_{approx} \approx \frac{V}{R_{big}}$

How much bigger does R_{big} need to be for I_{approx} within 1% of I_{real}?

$$\left| \frac{I_{real} - I_{approx}}{I_{real}} \right| < 0.01$$

$$\left| 1 - \frac{R_{big} + R_{load}}{R_{big}} \right| = \left| \frac{R_{load}}{R_{big}} \right| < 0.01$$

$$R_{big} > 100 R_{load}$$

Voltage applied is fixed, but can change resistance (manually or through circuit)

Assume $R_{load} < 100\ \Omega$

Q: What V needed to apply (within 1%) .1 mA, 1 mA, 10 mA? What R_{bias}?

$R_{big} > 10\ K\Omega$

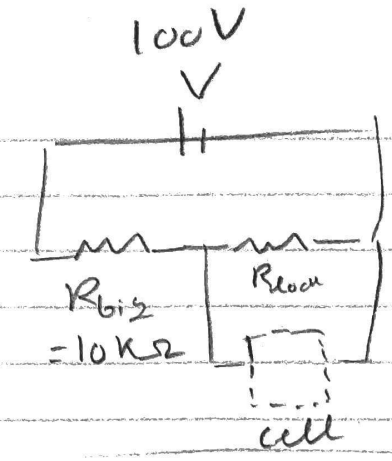
R_{big} (10 mA) $\approx$ V

$V \approx 100$ V

$R = 10\ K\Omega,\ 100\ K\Omega,\ 1\ M\Omega$

How to turn into potentiostat?

- Need known current, but that requires above...
- Not easy, needs high voltage
- If $R_{load} < 100\ \Omega$



I = 10 mA

R_{load} can vary to let
0 - 1 V

But $R_{cell} < 1\Omega$

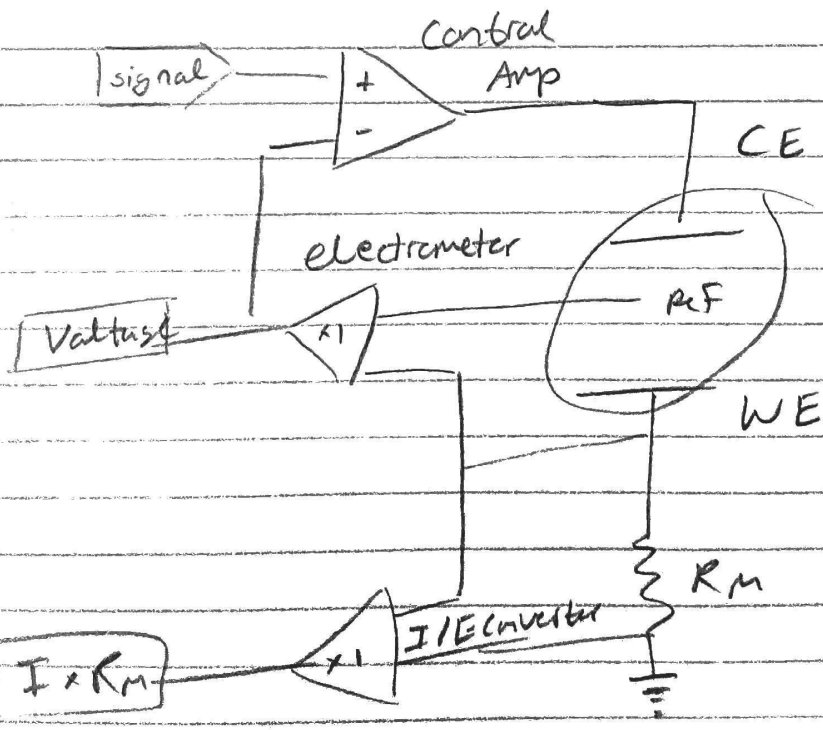
Not EASY

In practice, use op-amps etc.

Potentiostats in real life

- WE, CE, Ref, CA

GAMRY



Draw Flow of current

- Electrometer (high impedence ⇒ 0 current)
  - capacitors, etc, to balance w/ circuit to make sure doesn't interfere
  - Measures Voltage diff

NOT

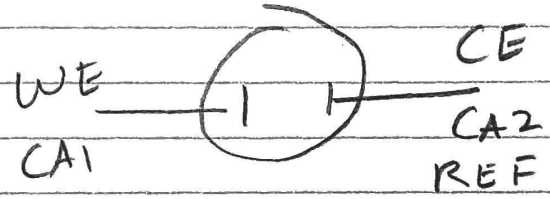
- Current-to-voltage converter
  - Measure voltage across known R_M
- Control amplifier
  - negative Feedback loop

APPLY VOLTAGE, MEASURE I

CAN USE I as signal too

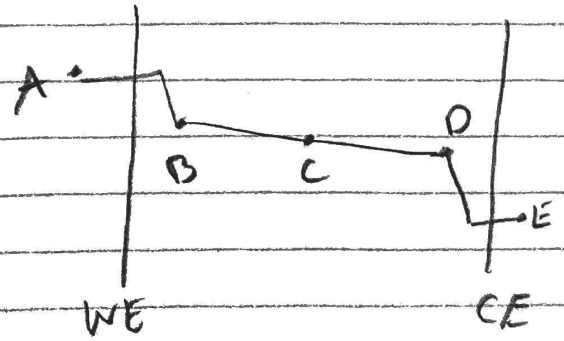
Electrode Setup

2 Electrode



CAN have just 1 CA (Gamry)
or both (Biologic)

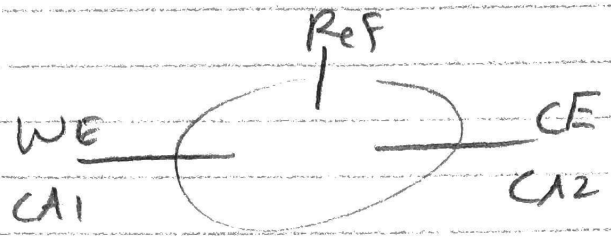
i.e. Batteries, super capacitors, Fuel cells.



Measures A ↔ E

Remember, Voltage out is WE - Ref
But voltage applied is
WE/(CA1) - CE/(CA2)

3 electrod



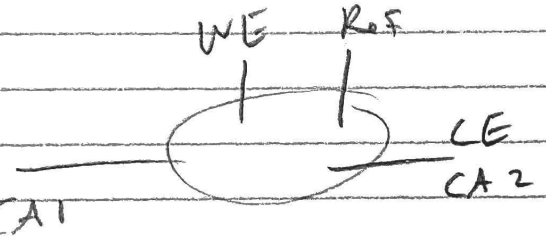
OFten what are think of in echem

COMMON

HalF-cell

measure $A \rightleftarrows B$

4 electrode



For high solutin resistance,

Want to measure in solutin
(sometimes have CE, sometimes not)

Q: Cell in paper applies 2V across whole cell, but I want info on just WE, how do I set up if:

CA1, WE, Ref, CE, CA2

or CA1, WE, Ref, CE/CA1

- Can only set voltage between WE and Ref
- can measure between WE & Ref or CE and Ref
  Ref & CE

$WE - REF = 2V$

$WE - CE = WE - Ref - (CE - Ref)$