

Lecture #4 of 17

Looking forward... our review of Chapter “0”

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation (*halfway complete*)
- **Common reference electrodes**
- **Standard and Absolute potentials**
- **Latimer and Pourbaix diagrams**
- *Calculating E_{cell} under non-standard-state conditions*
- *Conventions*

Quick Check on Your Understanding

You try!

(a) What is the standard E_{cell} for a galvanic cell based on zinc and silver?

$$E_{\text{cell}} = +0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V}$$

(b) If one wanted to electrolytically charge the cell from part a (before any reactions took place), what potential would one have to provide?

electro-chemical series

Potassium	-2.92
Calcium	-2.87
Sodium	-2.71
Magnesium	-2.37
Aluminium	-1.66
Zinc	-0.76
Iron	-0.44
Tin	-0.14
Lead	-0.13
Hydrogen	0.00
Copper	+0.34
Silver	+0.80
Mercury	+0.85
Gold	+1.68

$$E_{\text{bias}} < -1.56 \text{ V... such that } E_{\text{cell}} + E_{\text{bias}} < 0 \text{ (this is the observed value)}$$

RECALL: International Union of Pure and Applied Chemistry (IUPAC)

(Accepted) Nomenclature and Terminology that you've learned, but may have forgotten

- Coulomb (in units of $C = A \cdot s$) is the unit of charge (96,485 C are in a mole of singly charged species = Faraday constant, $F \approx 96,500 \text{ C/mol} \approx 10^5 \text{ C/mol}$)
differentiate, with respect to time **integrate, over time**
- Electricity is the flow of current (I ; in units of $A = C/s$) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g. e^- , H^+)

- (Electrode) (electric) potential (V or E ; in units of $V = J/C$) is written as a reduction

This relates to Gibbs free energy as $\Delta G = -RT \ln K = -nFE_{\text{cell}}$ (electrical work per mole), and...

... partial molar Gibbs free energy is the electrochemical potential ($\bar{\mu}$, in units of J/mol)

- Chemical potential (μ , in units of J/mol)
- Galvani/Inner (electric) potential (ϕ , in units of V)

... and in summary, $\bar{\mu} = \mu + zF\phi$

Also, standard state is a solvent, a solid, and a species at unit activity (~1 M solutes, ~1 bar gases)

Also, $E = IR$ (Ohm's law) when resistance is constant

- Galvanic cells produce power (P ; in units of $W = A \times V = C/s \times J/C = J/s$) by spontaneous redox reactions

opposites

- Electrolytic cells require a power input to drive redox reactions; thus, the reactions are thermodynamically unfavorable

- A battery has an anode/anolyte and a cathode/catholyte, but these descriptors change depending on whether the battery is being discharged (galvanic) or charged (electrolytic); negative electrode/negolyte and positive electrode/posolyte are better

Electrochemical potential of species i in phase β is an energy (J/mol),

$$\bar{\mu}_i^\beta = \left(\frac{\partial G}{\partial n_i^\beta} \right)_{T,p,n_{j \neq i}} = \mu_i^\beta + z_i F \phi^\beta, \text{ where}$$

RECALL:

G (Gibbs free energy (J))

n_i (amount of species i (mol))

$\mu_i = \mu_i^0 + RT \ln a_i$ (chemical potential (J/mol))

z_i (valency of species i)

$F \approx 10^5$ (Faraday constant (C/mol))

ϕ^β (Galvani/inner electric potential (V))

a_i (activity of species i)

For an uncharged species $\bar{\mu}_i^\beta = \mu_i^\beta$.

... more on this later...

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$,

But first... what is Q , again? ... the reaction quotient!



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$,

But first... what is Q , again? ... the reaction quotient!

$$Q = \frac{\prod_p a_p^{v_p}}{\prod_r a_r^{v_r}} = \frac{\prod_p \left(\gamma_p \frac{c_p}{c_p^0} \right)^{v_p}}{\prod_r \left(\gamma_r \frac{c_r}{c_r^0} \right)^{v_r}}$$

$$Q = \frac{\prod_p c_p^{v_p}}{\prod_r c_r^{v_r}}, \text{ for dilute solutions... **which we never have!**}$$

a_p is the activity of product p

a_r is the activity of reactant r

v_i is the stoichiometric number of i

γ_i is the activity coefficient of i

c_i is the concentration of i

c_i^0 is the standard state concentration of i

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$,

$$-nFE = -nFE^0 + RT \ln Q$$

Reaction quotient as product and quotient of species' activities

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = E^0 - \frac{RT \log Q}{nF \log e}$$

$$E = E^0 - \frac{RT}{0.4343nF} \log Q$$

$$E = E^0 - \frac{2.3026RT}{nF} \log Q$$

... and at 298.15 K, $E = E^0 - \frac{0.05916 \text{ V}}{n} \log Q$

Physicist



Walther Hermann Nernst (1864–1941) Nobel Prize (Chemistry, 1920) from Wiki

Memorize ~60 mV per order in \log_{10} , but do not forget n and that this is at 25 °C!

Looking forward... our review of Chapter “0”

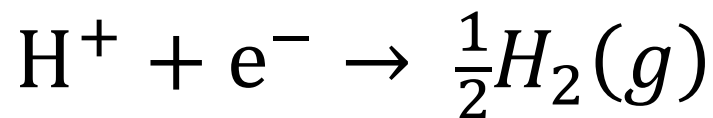
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Half reactions must be referenced to something...

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

Since the method of half-reactions ultimately results in us taking their difference, we can add an arbitrary constant to all half reactions... By one (somewhat arbitrary) convention, it is often assumed that E° for the standard hydrogen electrode (**SHE**) is equal to zero.

Half-Reaction for Hydrogen gas (H_2):



Potential

Standard Potential

$$E_{\text{H}_2} = E_{\text{H}_2}^{\circ} + \frac{RT}{F} \ln \frac{\sqrt{p_{\text{H}_2}}}{[\text{H}^+]}$$

Rigorously, these two terms in Q need to be divided by the standard-state condition, and include activity coefficients

$$E_{\text{H}_2}^{\circ} = 0 \text{ vs. SHE}$$

Thus, the potentials for half-cell reactions are actually full-cell potential (difference(s)) versus SHE, or other!

Given this value, what is this experimental reduction potential versus?

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

Since the method of half-reactions ultimately results in us taking their difference, we can add an arbitrary constant to all half reactions... By one (somewhat arbitrary) convention, it is often assumed that E° for the standard hydrogen electrode (**SHE**) is equal to zero.

- * **Normal hydrogen electrode (NHE)** is an empirical SHE ($[\text{H}^+] = 1$; not standard state)
- * **Standard hydrogen electrode (SHE)** is a hypothetical, perfect NHE ($a = 1$; not empirical)
- * **Reversible hydrogen electrode (RHE)** is the SHE but the same regardless of pH
- * And generally, **formal potentials (E°)** take into consideration non-idealities and changes in ionic strengths so that the reaction quotient only has concentrations, and not activities

$$E_{\text{H}_2} = E_{\text{H}_2}^{\circ} + \frac{RT}{F} \ln \frac{\sqrt{p_{\text{H}_2}}}{[\text{H}^+]} \quad E_{\text{H}_2}^{\circ} = 0$$

Outmoded Terminology: The Normal Hydrogen Electrode

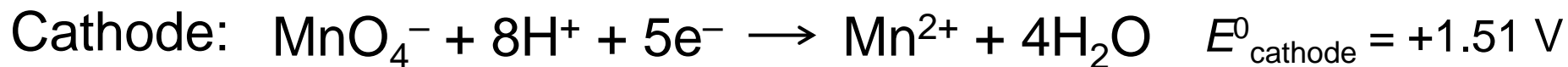
R. W. Ramette
Carleton College, Northfield, MN 55057

EXAMPLE: Write a balanced chemical equation and calculate the standard cell potential for the galvanic cell:
 $\text{Zn(s)} \mid \text{Zn}^{2+} (1 \text{ M}) \parallel \text{MnO}_4^- (1 \text{ M}), \text{Mn}^{2+} (1 \text{ M}), \text{H}^+ (1 \text{ M}) \mid \text{Pt(s)}$

Look up half-reactions and standard reduction potentials in an Electrochemical Series table (CRC, B&F Appendix C, WWW):



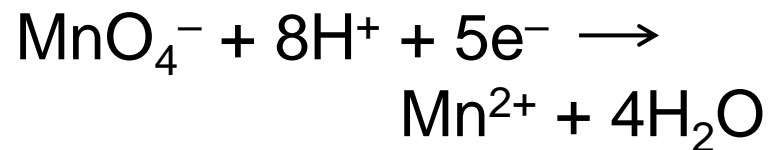
Note: Although strictly correct, do not use “ $-E^0$ ” as the “ E^0 for oxidation”



Note: Be careful to choose the correct half-reaction with MnO_4^-

$\text{Mn}^{2+} + 2 e \rightleftharpoons \text{Mn}$	-1.185
$\text{Mn}^{3+} + e \rightleftharpoons \text{Mn}^{2+}$	1.5415
$\text{MnO}_2 + 4 \text{H}^+ + 2 e \rightleftharpoons \text{Mn}^{2+} + 2 \text{H}_2\text{O}$	1.224
$\text{MnO}_4^- + e \rightleftharpoons \text{MnO}_4^{2-}$	0.558
$\text{MnO}_4^- + 4 \text{H}^+ + 3 e \rightleftharpoons \text{MnO}_2 + 2 \text{H}_2\text{O}$	1.679
$\text{MnO}_4^- + 8 \text{H}^+ + 5 e \rightleftharpoons \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	1.507
$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 e \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$	0.595
$\text{MnO}_4^{2-} + 2 \text{H}_2\text{O} + 2 e \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$	0.60
$\text{Mn}(\text{OH})_2 + 2 e \rightleftharpoons \text{Mn} + 2 \text{OH}^-$	-1.56
$\text{Mn}(\text{OH})_3 + e \rightleftharpoons \text{Mn}(\text{OH})_2 + \text{OH}^-$	0.15
$\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + e \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}$	1.485

* All values versus SHE



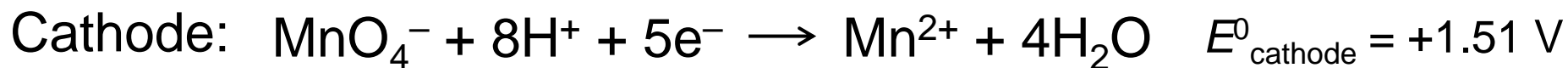
$\text{Zn}^{2+} + 2 e \rightleftharpoons \text{Zn}$	-0.7618
$\text{Zn}^{2+} + 2 e \rightleftharpoons \text{Zn}(\text{Hg})$	-0.7628
$\text{ZnO}_2^{2-} + 2 \text{H}_2\text{O} + 2 e \rightleftharpoons \text{Zn} + 4 \text{OH}^-$	-1.215
$\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O} + 2 e = \text{Zn}(\text{Hg}) + \text{SO}_4^{2-} + 7 \text{H}_2\text{O} (\text{Saturated ZnSO}_4)$	-0.7993
$\text{ZnOH}^+ + \text{H}^+ + 2 e \rightleftharpoons \text{Zn} + \text{H}_2\text{O}$	-0.497
$\text{Zn}(\text{OH})_4^{2-} + 2 e \rightleftharpoons \text{Zn} + 4 \text{OH}^-$	-1.199
$\text{Zn}(\text{OH})_2 + 2 e \rightleftharpoons \text{Zn} + 2 \text{OH}^-$	-1.249
$\text{ZnO} + \text{H}_2\text{O} + 2 e \rightleftharpoons \text{Zn} + 2 \text{OH}^-$	-1.260

EXAMPLE: Write a balanced chemical equation and calculate the standard cell potential for the galvanic cell:
 $\text{Zn(s)} \mid \text{Zn}^{2+} (1 \text{ M}) \parallel \text{MnO}_4^- (1 \text{ M}), \text{Mn}^{2+} (1 \text{ M}), \text{H}^+ (1 \text{ M}) \mid \text{Pt(s)}$

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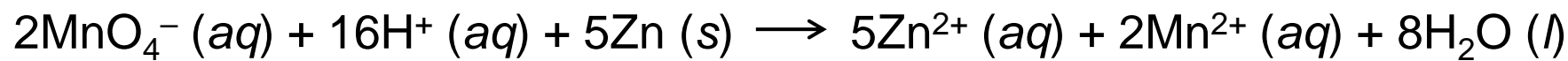


Note: Although strictly correct, do not use “ $-E^0$ ” as the “ E^0 for oxidation”



Note: Be careful to choose the correct half-reaction with MnO_4^-

To get the balanced overall reaction?... multiply the anode reaction by 5 and subtract it from 2 times the cathode reaction:



$$E_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = 1.51 \text{ V} + 0.76 \text{ V} = +2.27 \text{ V}$$

(remember this?)

CRC Handbook of Chemistry and Physics, 92nd Edition

$\text{Mg}^+ + e \rightleftharpoons \text{Mg}$	-2.70
$\text{Na}^+ + e \rightleftharpoons \text{Na}$	-2.71
$\text{Yb}^{2+} + 2 e \rightleftharpoons \text{Yb}$	-2.76
$\text{Bk}^{3+} + e \rightleftharpoons \text{Bk}^{2+}$	-2.8
$\text{Ho}^{3+} + e \rightleftharpoons \text{Ho}^{2+}$	-2.8
$\text{Ra}^{2+} + 2 e \rightleftharpoons \text{Ra}$	-2.8
$\text{Eu}^{2+} + 2 e \rightleftharpoons \text{Eu}$	-2.812
$\text{Ca}^{2+} + 2 e \rightleftharpoons \text{Ca}$	-2.868
$\text{Sr}(\text{OH})_2 + 2 e \rightleftharpoons \text{Sr} + 2 \text{OH}^-$	-2.88
$\text{Sr}^{2+} + 2 e \rightleftharpoons \text{Sr}$	-2.899
$\text{Fr}^+ + e \rightleftharpoons \text{Fr}$	-2.9
$\text{La}(\text{OH})_3 + 3 e \rightleftharpoons \text{La} + 3 \text{OH}^-$	-2.90
$\text{Ba}^{2+} + 2 e \rightleftharpoons \text{Ba}$	-2.912
$\text{K}^+ + e \rightleftharpoons \text{K}$	-2.931
$\text{Rb}^+ + e \rightleftharpoons \text{Rb}$	-2.98
$\text{Ba}(\text{OH})_2 + 2 e \rightleftharpoons \text{Ba} + 2 \text{OH}^-$	-2.99
$\text{Er}^{3+} + e \rightleftharpoons \text{Er}^{2+}$	-3.0
$\text{Ca}(\text{OH})_2 + 2 e \rightleftharpoons \text{Ca} + 2 \text{OH}^-$	-3.02
$\text{Cs}^+ + e \rightleftharpoons \text{Cs}$	-3.026
$\text{Li}^+ + e \rightleftharpoons \text{Li}$	-3.040
$3 \text{N}_2 + 2 \text{H}^+ + 2 e \rightleftharpoons 2 \text{HN}_3$	-3.09
$\text{Pr}^{3+} + e \rightleftharpoons \text{Pr}^{2+}$	-3.1
$\text{Ca}^+ + e \rightleftharpoons \text{Ca}$	-3.80
$\text{Sr}^+ + e \rightleftharpoons \text{Sr}$	-4.10

*** All values versus SHE***** How negative can E° be?**

Q: What processes occur in electrochemistry? ... one more ...

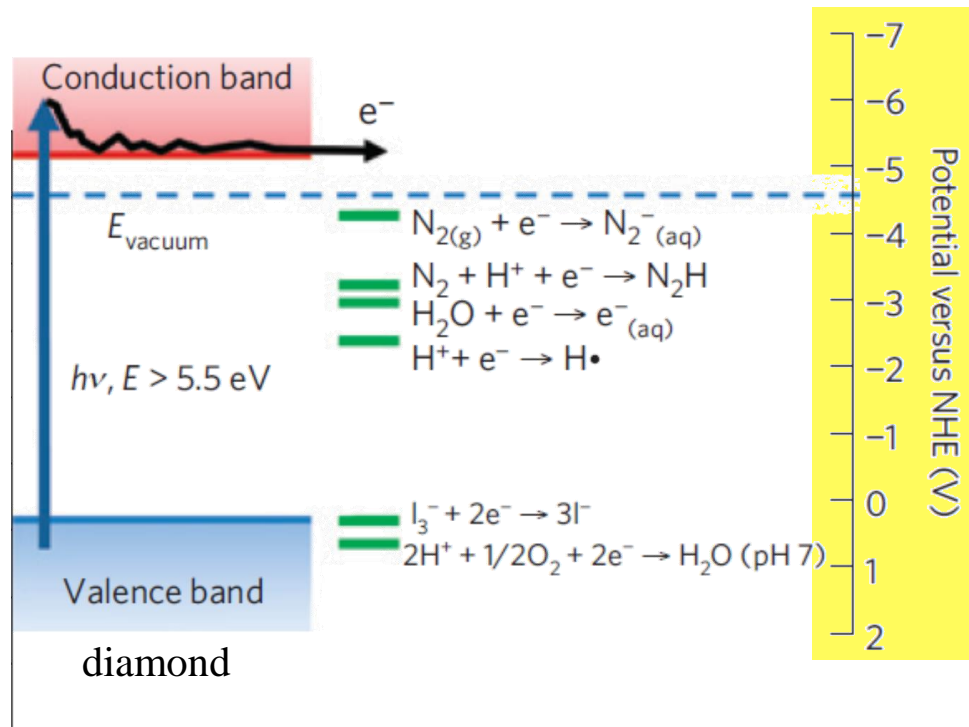
A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

Example: solvated electrons

Prof. Robert Hamers (Univ. of Wisconsin)



<http://hamers.chem.wisc.edu/people>



During the first part of the twentieth century, E. C. Franklin and C. A. Kraus probably did more to elucidate the chemistry of liquid ammonia solutions than everybody else combined... It is perhaps little known that their work was prompted by the research and insight of H. P. Cady, carried out while he was an undergraduate! Whilst working on cobalt ammine complexes, Cady proposed that ammonia in these (and other “double salts”) must function in a manner akin to water in salts with water of crystallization. He suggested further that liquid ammonia would probably be found to resemble water in its physical and chemical properties—thus adding a second to our list of ionizing solvents. Cady’s undergraduate work, carried out without supervision, published in 1897, was perhaps the first physical chemistry study of liquid ammonia solutions.

Zurek, Edwards, & Hoffman, *Angew. Chem. Int. Ed.*, 2009, 48, 8198

In the case of the sodium solution, no signs of a polarization current could be detected with a sensitive galvanometer, and it will be noticed that the molecular conductivity rises with the concentration, contrary to that of electrolytes. As has been mentioned above no gas is given off when the solution is submitted to electrolysis. The sodium is not affected by the current, nor is there any deposit on the electrodes. In spite of the fact that the sodium is in solution, the solution seems to conduct like a metal and not like an electrolyte.

Salt used	Dissolved in ammonia	
	V	μ
Metallic sodium, ¹ 23 being taken as the molecular weight,	4.28	393.
	3.97	413.
	3.8	448.

Cady, *J. Phys. Chem.*, 1897, 1, 707

Q: What is electrochemistry? ... one more ...

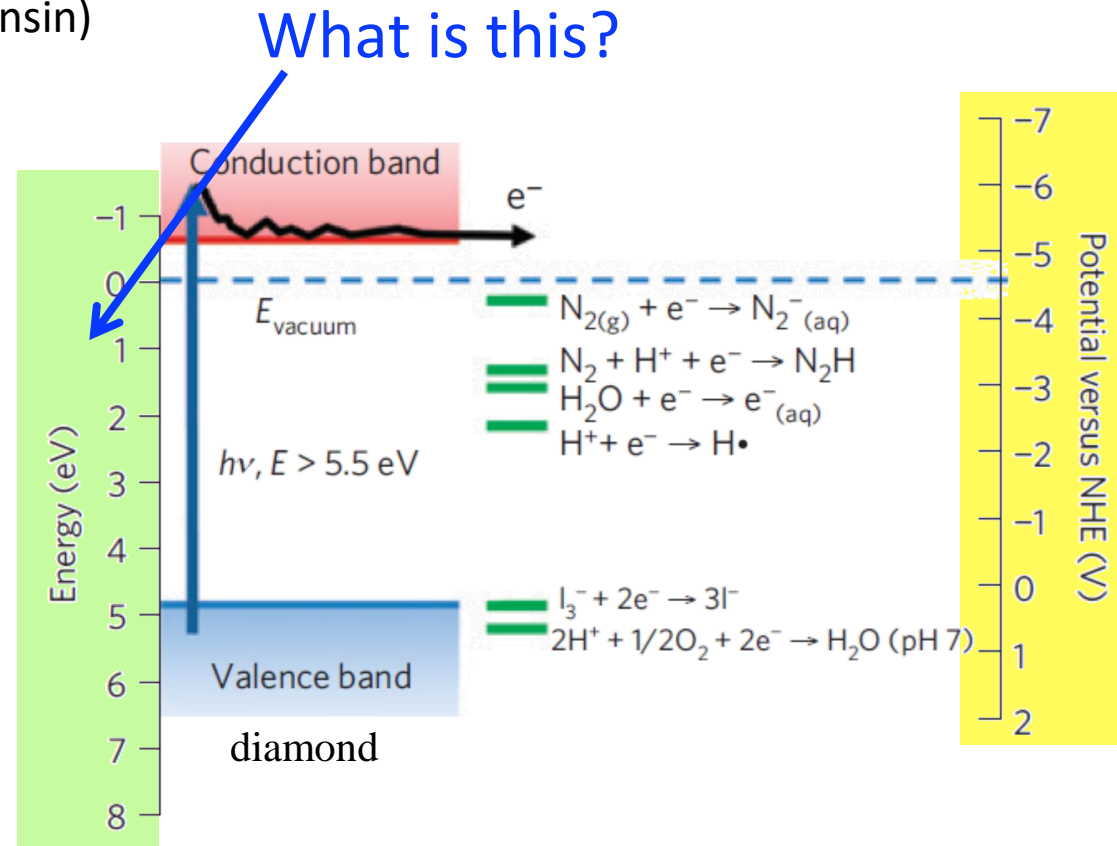
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Absolute potentials can be measured / approximated...
very carefully...

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROCHEMISTRY*



THE ABSOLUTE ELECTRODE POTENTIAL: AN EXPLANATORY NOTE

(Recommendations 1986)

Prof. Sergio Trasatti
(Università de Milano, Italy)

On the basis of the values in Table 1 the recommended absolute potential of the standard hydrogen electrode, as results from both eqns.(12) and (15) with the same accuracy, is:
(Note k)

$$E^{\circ}(\text{H}^+/\text{H}_2)^{\text{H}_2\text{O}}(\text{abs}) = (4.44 \pm 0.02) \text{ V} \quad \text{at } 298.15 \text{ K} \quad (19)$$

Note k: It must be stressed that calculations based on eqns.(12) and (15) are only apparently independent since the quantities involved derive from the same set of experimental data. For instance, $\alpha_{\text{H}^+}^{\circ}$ is obtained from (ref. 15): $-\Delta_{\text{at}}G^{\circ} - \Delta_{\text{ion}}G^{\circ} + E_{16}^{\circ}F + \phi_{\text{Hg}}^{\circ}F$. It should be noted that, owing to the role of the decimal figures, eqn.(15) gives 4.448 V, *i.e.* 4.45 V. However, in view of the discussion concerning eqns.(10) and (11), the value calculated by means of eqn.(12) is to be preferred because it ensues directly from the experimental data.

Absolute potentials can be measured / approximated...
very carefully...

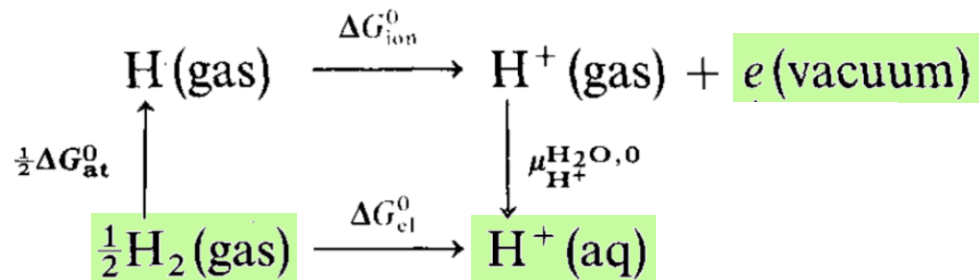
$$E^\circ(\text{H}^+/\text{H}_2)(\text{abs}) = (\Delta_{\text{at}}G^\circ + \Delta_{\text{ion}}G^\circ + \alpha_{\text{H}^+}^{\circ,S})/F \quad (12)$$

TABLE 1. Values of quantities needed to calculate the absolute potential of the standard hydrogen electrode in water (298.15 K)

$\frac{1}{2}\text{H}_2 \rightarrow \text{H}$	$\Delta_{\text{at}}G^\circ = 203.30 \text{ kJ mol}^{-1}$	ref. (17)
$\text{H} \rightarrow \text{H}^+ + \text{e}$	$\Delta_{\text{ion}}G^\circ = 1313.82 \text{ kJ mol}^{-1}$	(1,17)
$\text{H}^+(\text{vacuum}) \rightarrow \text{H}^+(\text{water})$	$\alpha_{\text{H}^+}^\circ = -(1088 \pm 2) \text{ kJ mol}^{-1}$	(15)
Potential of zero charge of Hg	$E_{\sigma=0}(\text{SHE}) = -(0.192 \pm 0.001) \text{ V}$	(18)
Electron work function of Hg	$\phi = (4.50 \pm 0.02) \text{ eV}$	(19)
E° of cell (16)	$E_{16}^\circ = -(0.0559 \pm 0.0002) \text{ V}$	(15)
Contact potential difference ^a	$\Delta_{\text{H}_2\text{O}}^{\text{Hg}}\psi = -(0.248 \pm 0.001) \text{ V}$	

^aFrom eqn. (18)

Born–Haber cycle:



Trasatti, *Electroanal. Chem. Interfac. Electrochem.*, 1974, 52, 313

Trasatti, *Pure & Appl. Chem.*, 1986, 58, 955

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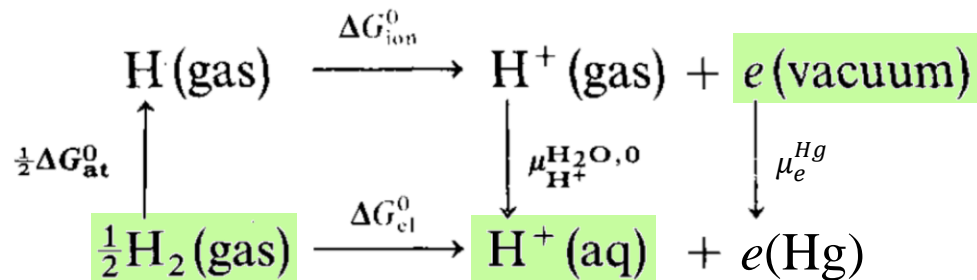
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Born–Haber cycle:
(two ways to solve this)



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... but we need an electrode!

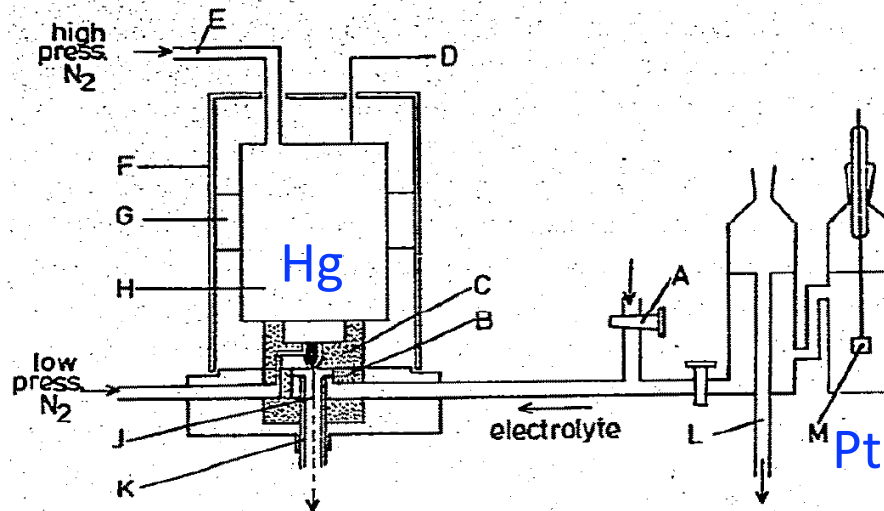
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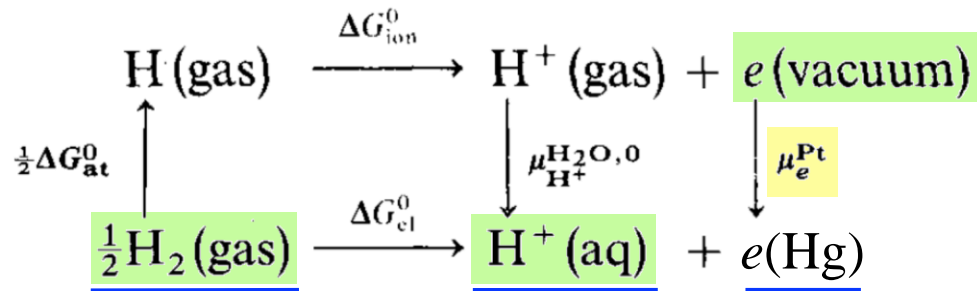
$$E_{16}^\circ = \Delta\psi^\circ(\text{Hg}, \text{H}_2) = E^\circ(\text{H}^+/\text{H}_2)(\text{abs}) - \phi^{\text{Hg}} \quad (17)$$

Hg | air | H⁺(sln) | (H₂)Pt

(16)



Born–Haber cycle:
(two ways to solve this)



Farrell and McTigue, *Electroanal. Chem. Interfac. Electrochem.*, 1982, 139, 37

Trasatti, *Electroanal. Chem. Interfac. Electrochem.*, 1974, 52, 313

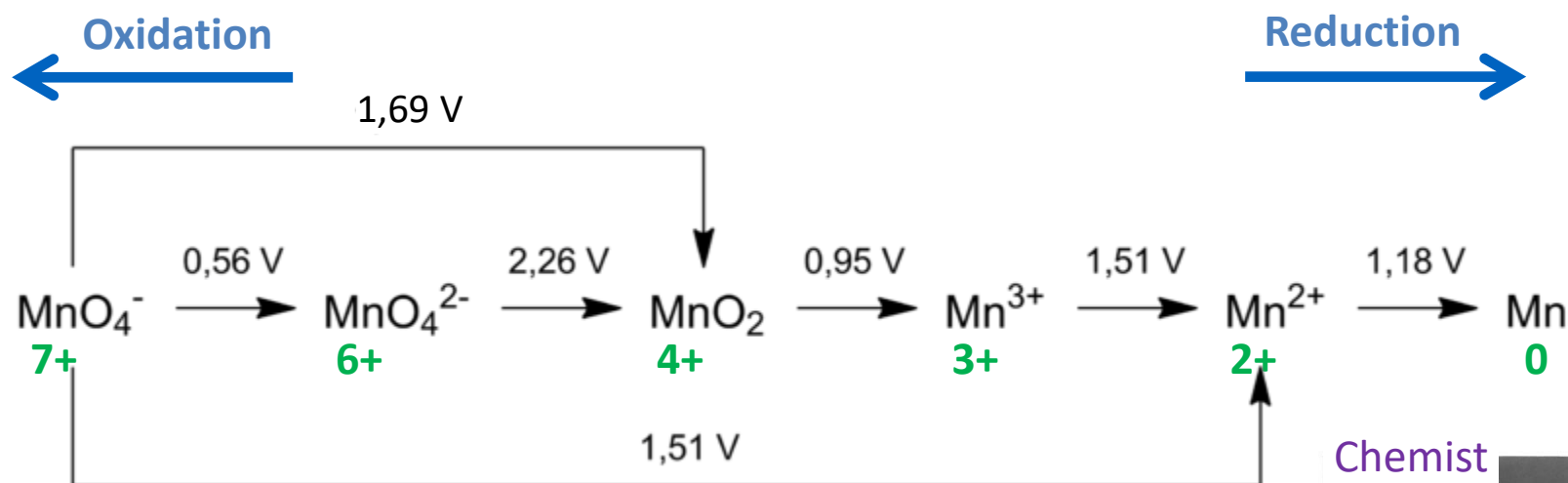
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... but we need an electrode!

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A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



Chemist

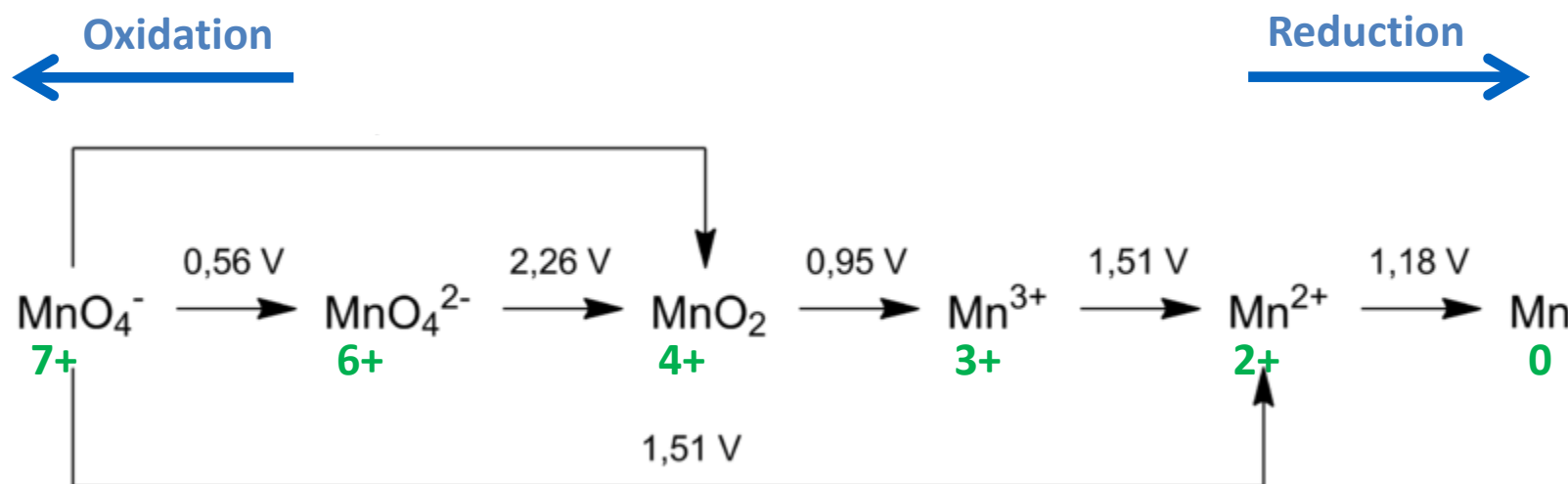


Wendell Mitchell Latimer
(1893–1955)

<http://academictree.org/chemistry/peopleinfo.php?pid=24644>

Latimer, The oxidation states of the elements and their potentials in aqueous solution, 1938

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



from Wiki

Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule (*the opposite is comproportionation (AKA: symproportionation)*)

(1) Does Mn^{2+} disproportionate? **NO.** $E^0 = E_{\text{red}} - E_{\text{ox}} = 1.18 - 1.51 = -0.33 \text{ V}$

(2) What is the standard reduction potential of MnO_4^- to MnO_2 ?

