



Lecture #10 of 14

(3: TThF, 5: MTWThF, 4: MTWTh, 2: TW)

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

Charged Interfaces (*let's review ThFM*)

- Th: Vacuum level, Redox half-reactions, Nernst equation, History, Conventions, Electrodes
- **F: Potentiostat, Electric double layer, Electric potentials, Liquid-junction potentials, Donnan potential, Membrane potential**
- M: pH probe, Acidity scale, Titrations, Buffering, Henderson–Hasselbalch equation, *Latimer diagram, Pourbaix diagram*

Reaction	E°/V
$\text{Fr}^+ + e \rightleftharpoons \text{Fr}$	-2.9
$\text{Ga}^{3+} + 3 e \rightleftharpoons \text{Ga}$	-0.549
$\text{Ga}^+ + e \rightleftharpoons \text{Ga}$	-0.2
$\text{Ga}(\text{OH})_2^+ + \text{H}^+ + 3 e \rightleftharpoons \text{Ga} + \text{H}_2\text{O}$	-0.498
$\text{H}_2\text{GaO}_3^- + \text{H}_2\text{O} + 3 e \rightleftharpoons \text{Ga} + 4 \text{OH}^-$	-1.219
$\text{Gd}^{3+} + 3 e \rightleftharpoons \text{Gd}$	-2.279
$\text{Ge}^{2+} + 2 e \rightleftharpoons \text{Ge}$	0.24
$\text{Ge}^{4+} + 4 e \rightleftharpoons \text{Ge}$	0.124
$\text{Ge}^{4+} + 2 e \rightleftharpoons \text{Ge}^{2+}$	0.00
$\text{GeO}_2 + 2 \text{H}^+ + 2 e \rightleftharpoons \text{GeO} + \text{H}_2\text{O}$	-0.118
$\text{H}_2\text{GeO}_3 + 4 \text{H}^+ + 4 e \rightleftharpoons \text{Ge} + 3 \text{H}_2\text{O}$	-0.182
$2 \text{H}^+ + 2 e \rightleftharpoons \text{H}_2$	0.00000
$\text{H}_2 + 2 e \rightleftharpoons 2 \text{H}^-$	-2.23
$\text{HO}_2 + \text{H}^+ + e \rightleftharpoons \text{H}_2\text{O}_2$	1.495
$2 \text{H}_2\text{O} + 2 e \rightleftharpoons \text{H}_2 + 2 \text{OH}^-$	-0.8277
$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 e \rightleftharpoons 2 \text{H}_2\text{O}$	1.776
$\text{Hf}^{3+} + 4 e \rightleftharpoons \text{Hf}$	-1.55
$\text{HfO}^{2+} + 2 \text{H}^+ + 4 e \rightleftharpoons \text{Hf} + \text{H}_2\text{O}$	-1.724
$\text{HfO}_2 + 4 \text{H}^+ + 4 e \rightleftharpoons \text{Hf} + 2 \text{H}_2\text{O}$	-1.505
$\text{HfO}(\text{OH})_2 + \text{H}_2\text{O} + 4 e \rightleftharpoons \text{Hf} + 4 \text{OH}^-$	-2.50
$\text{Hg}_2^{2+} + 2 e \rightleftharpoons \text{Hg}$	0.851
$2 \text{Hg}^{2+} + 2 e \rightleftharpoons \text{Hg}_2^{2+}$	0.920
$\text{Hg}_2^{2+} + 2 e \rightleftharpoons 2 \text{Hg}$	0.7973
$\text{Hg}_2(\text{ac})_2 + 2 e \rightleftharpoons 2 \text{Hg} + 2(\text{ac})^-$	0.51163
$\text{Hg}_2\text{Br}_2 + 2 e \rightleftharpoons 2 \text{Hg} + 2 \text{Br}^-$	0.13923
$\text{Hg}_2\text{Cl}_2 + 2 e \rightleftharpoons 2 \text{Hg} + 2 \text{Cl}^-$	0.26808
$\text{Hg}_2\text{HPO}_4 + 2 e \rightleftharpoons 2 \text{Hg} + \text{HPO}_4^{2-}$	0.6359
$\text{Hg}_2\text{I}_2 + 2 e \rightleftharpoons 2 \text{Hg} + 2 \text{I}^-$	-0.0405

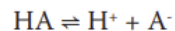
Reaction	E°/V
$\text{La}(\text{OH})_3 + 3 e \rightleftharpoons \text{La} + 3 \text{OH}^-$	-2.90
$\text{Li}^+ + e \rightleftharpoons \text{Li}$	-3.0401
$\text{Lr}^{3+} + 3 e \rightleftharpoons \text{Lr}$	-1.96
$\text{Lu}^{3+} + 3 e \rightleftharpoons \text{Lu}$	-2.28
$\text{Md}^{3+} + e \rightleftharpoons \text{Md}^{2+}$	-0.1
$\text{Md}^{3+} + 3 e \rightleftharpoons \text{Md}$	-1.65
$\text{Md}^{2+} + 2 e \rightleftharpoons \text{Md}$	-2.40
$\text{Mg}^+ + e \rightleftharpoons \text{Mg}$	-2.70
$\text{Mg}^{2+} + 2 e \rightleftharpoons \text{Mg}$	-2.372
$\text{Mg}(\text{OH})_2 + 2 e \rightleftharpoons \text{Mg} + 2 \text{OH}^-$	-2.690
$\text{Mn}^{2+} + 2 e \rightleftharpoons \text{Mn}$	-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
$\text{Mo}^{3+} + 3 e \rightleftharpoons \text{Mo}$	-0.200
$\text{MoO}_2 + 4 \text{H}^+ + 4 e \rightleftharpoons \text{Mo} + 4 \text{H}_2\text{O}$	-0.152
$\text{H}_3\text{Mo}_7\text{O}_{24}^{3-} + 45 \text{H}^+ + 42 e \rightleftharpoons 7 \text{Mo} + 24 \text{H}_2\text{O}$	0.082
$\text{MoO}_3 + 6 \text{H}^+ + 6 e \rightleftharpoons \text{Mo} + 3 \text{H}_2\text{O}$	0.075
$\text{N}_2 + 2 \text{H}_2\text{O} + 6 \text{H}^+ + 6 e \rightleftharpoons 2 \text{NH}_4\text{OH}$	0.092
$3 \text{N}_2 + 2 \text{H}^+ + 2 e \rightleftharpoons 2 \text{HN}_3$	-3.09
$\text{N}_5^+ + 3 \text{H}^+ + 2 e \rightleftharpoons 2 \text{NH}_4^+$	1.275

... the CRC Handbook has a lot of chemical information... including tables of values...
... such as those in the **Electrochemical Series...**

$\text{Hg}_2\text{O} + \text{H}_2\text{O} + 2 e \rightleftharpoons 2 \text{Hg} + 2 \text{OH}^-$	0.123	$\text{N}_2\text{O} + 2 \text{H}^+ + 2 e \rightleftharpoons \text{N}_2 + \text{H}_2\text{O}$	1.766
$\text{HgO} + \text{H}_2\text{O} + 2 e \rightleftharpoons \text{Hg} + 2 \text{OH}^-$	0.0977	$\text{H}_2\text{N}_2\text{O}_2 + 2 \text{H}^+ + 2 e \rightleftharpoons \text{N}_2 + 2 \text{H}_2\text{O}$	2.65
$\text{Hg}(\text{OH})_2 + 2 \text{H}^+ + 2 e \rightleftharpoons \text{Hg} + 2 \text{H}_2\text{O}$	1.034	$\text{N}_2\text{O}_4 + 2 e \rightleftharpoons 2 \text{NO}_2^-$	0.867
$\text{Hg}_2\text{SO}_4 + 2 e \rightleftharpoons 2 \text{Hg} + \text{SO}_4^{2-}$	0.6125	$\text{N}_2\text{O}_4 + 2 \text{H}^+ + 2 e \rightleftharpoons 2 \text{NHO}_2$	1.065
$\text{Ho}^{2+} + 2 e \rightleftharpoons \text{Ho}$	-2.1	$\text{N}_2\text{O}_4 + 4 \text{H}^+ + 4 e \rightleftharpoons 2 \text{NO} + 2 \text{H}_2\text{O}$	1.035
$\text{Ho}^{3+} + 3 e \rightleftharpoons \text{Ho}$	-2.33	$2 \text{NH}_3\text{OH}^+ + \text{H}^+ + 2 e \rightleftharpoons \text{N}_2\text{H}_5^+ + 2 \text{H}_2\text{O}$	1.42
$\text{Ho}^{3+} + e \rightleftharpoons \text{Ho}^{2+}$	-2.8	$2 \text{NO} + 2 \text{H}^+ + 2 e \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O}$	1.591
$\text{I}_2 + 2 e \rightleftharpoons 2 \text{I}^-$	0.5355	$2 \text{NO} + \text{H}_2\text{O} + 2 e \rightleftharpoons \text{N}_2\text{O} + 2 \text{OH}^-$	0.76
$\text{I}_3^- + 2 e \rightleftharpoons 3 \text{I}^-$	0.536	$\text{HNO}_2 + \text{H}^+ + e \rightleftharpoons \text{NO} + \text{H}_2\text{O}$	0.983
$\text{H}_3\text{IO}_6^{2-} + 2 e \rightleftharpoons \text{IO}_3^- + 3 \text{OH}^-$	0.7	$2 \text{HNO}_2 + 4 \text{H}^+ + 4 e \rightleftharpoons \text{H}_2\text{N}_2\text{O}_2 + 2 \text{H}_2\text{O}$	0.86
$\text{H}_5\text{IO}_6 + \text{H}^+ + 2 e \rightleftharpoons \text{IO}_3^- + 3 \text{H}_2\text{O}$	1.601	$2 \text{HNO}_2 + 4 \text{H}^+ + 4 e \rightleftharpoons \text{N}_2\text{O} + 3 \text{H}_2\text{O}$	1.297
$2 \text{HIO} + 2 \text{H}^+ + 2 e \rightleftharpoons \text{I}_2 + 2 \text{H}_2\text{O}$	1.439	$\text{NO}_2^- + \text{H}_2\text{O} + e \rightleftharpoons \text{NO} + 2 \text{OH}^-$	-0.46
$\text{HIO} + \text{H}^+ + 2 e \rightleftharpoons \text{I}^- + \text{H}_2\text{O}$	0.987	$2 \text{NO}_2^- + 2 \text{H}_2\text{O} + 4 e \rightleftharpoons \text{N}_2\text{O}_2^{2-} + 4 \text{OH}^-$	-0.18
$\text{IO}^- + \text{H}_2\text{O} + 2 e \rightleftharpoons \text{I}^- + 2 \text{OH}^-$	0.485	$2 \text{NO}_2^- + 3 \text{H}_2\text{O} + 4 e \rightleftharpoons \text{N}_2\text{O} + 6 \text{OH}^-$	0.15
$2 \text{IO}_3^- + 12 \text{H}^+ + 10 e \rightleftharpoons \text{I}_2 + 6 \text{H}_2\text{O}$	1.195	$\text{NO}_3^- + 3 \text{H}^+ + 2 e \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$	0.934
$\text{IO}_3^- + 6 \text{H}^+ + 6 e \rightleftharpoons \text{I}^- + 3 \text{H}_2\text{O}$	1.085	$\text{NO}_3^- + 4 \text{H}^+ + 3 e \rightleftharpoons \text{NO} + 2 \text{H}_2\text{O}$	0.957
$\text{IO}_3^- + 2 \text{H}_2\text{O} + 4 e \rightleftharpoons \text{IO}^- + 4 \text{OH}^-$	0.15	$2 \text{NO}_3^- + 4 \text{H}^+ + 2 e \rightleftharpoons \text{N}_2\text{O}_4 + 2 \text{H}_2\text{O}$	0.803
$\text{IO}_3^- + 3 \text{H}_2\text{O} + 6 e \rightleftharpoons \text{IO}^- + 6 \text{OH}^-$	0.26	$\text{NO}_3^- + \text{H}_2\text{O} + 2 e \rightleftharpoons \text{NO}_2^- + 2 \text{OH}^-$	0.01
$\text{In}^+ + e \rightleftharpoons \text{In}$	-0.14	$2 \text{NO}_3^- + 2 \text{H}_2\text{O} + 2 e \rightleftharpoons \text{N}_2\text{O}_4 + 4 \text{OH}^-$	-0.85
$\text{In}^{2+} + e \rightleftharpoons \text{In}^+$	-0.40	$\text{Na}^+ + e \rightleftharpoons \text{Na}$	-2.71
$\text{In}^{3+} + e \rightleftharpoons \text{In}^{2+}$	-0.49	$\text{Nb}^{3+} + 3 e \rightleftharpoons \text{Nb}$	-1.099
$\text{In}^{3+} + 2 e \rightleftharpoons \text{In}^+$	-0.443	$\text{NbO}_2 + 2 \text{H}^+ + 2 e \rightleftharpoons \text{NbO} + \text{H}_2\text{O}$	-0.646
$\text{In}^{3+} + 3 e \rightleftharpoons \text{In}$	-0.3382	$\text{NbO}_2 + 4 \text{H}^+ + 4 e \rightleftharpoons \text{Nb} + 2 \text{H}_2\text{O}$	-0.690
$\text{In}(\text{OH})_3 + 3 e \rightleftharpoons \text{In} + 3 \text{OH}^-$	-0.99	$\text{NbO} + 2 \text{H}^+ + 2 e \rightleftharpoons \text{Nb} + \text{H}_2\text{O}$	-0.733
$\text{In}(\text{OH})_4^- + 3 e \rightleftharpoons \text{In} + 4 \text{OH}^-$	-1.007	$\text{Nb}_2\text{O}_5 + 10 \text{H}^+ + 10 e \rightleftharpoons 2 \text{Nb} + 5 \text{H}_2\text{O}$	-0.644
$\text{In}_2\text{O}_3 + 3 \text{H}_2\text{O} + 6 e \rightleftharpoons 2 \text{In} + 6 \text{OH}^-$	-1.034	$\text{Nd}^{3+} + 3 e \rightleftharpoons \text{Nd}$	-2.323
$\text{Ir}^{3+} + 3 e \rightleftharpoons \text{Ir}$	1.156	$\text{Nd}^{2+} + 2 e \rightleftharpoons \text{Nd}$	-2.1
$[\text{IrCl}_6]^{2-} + e \rightleftharpoons [\text{IrCl}_6]^{3-}$	0.8665	$\text{Nd}^{3+} + e \rightleftharpoons \text{Nd}^{2+}$	-2.7
$[\text{IrCl}_6]^{3-} + 3 e \rightleftharpoons \text{Ir} + 6 \text{Cl}^-$	0.77	$\text{Ni}^{2+} + 2 e \rightleftharpoons \text{Ni}$	-0.257
$\text{Ir}_2\text{O}_3 + 3 \text{H}_2\text{O} + 6 e \rightleftharpoons 2 \text{Ir} + 6 \text{OH}^-$	0.098	$\text{Ni}(\text{OH})_2 + 2 e \rightleftharpoons \text{Ni} + 2 \text{OH}^-$	-0.72
$\text{K}^+ + e \rightleftharpoons \text{K}$	-2.931	$\text{NiO}_2 + 4 \text{H}^+ + 2 e \rightleftharpoons \text{Ni}^{2+} + 2 \text{H}_2\text{O}$	1.678
$\text{La}^{3+} + 3 e \rightleftharpoons \text{La}$	-2.379	$\text{NiO}_2 + 2 \text{H}_2\text{O} + 2 e \rightleftharpoons \text{Ni}(\text{OH})_2 + 2 \text{OH}^-$	-0.490

Can you identify what the reference potential is for this list of standard(-state) reduction potentials? *(it's like the infinite vacuum)*

This table lists the dissociation (ionization) constants of over 1070 organic acids, bases, and amphoteric compounds. All data apply to dilute aqueous solutions and are presented as values of pK_a , which is defined as the negative of the logarithm of the equilibrium constant K_a for the reaction

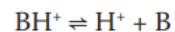


i.e.,

$$K_a = [H^+][A^-]/[HA]$$

where $[H^+]$, etc. represent the concentrations of the respective species in mol/L. It follows that $pK_a = pH + \log[HA] - \log[A^-]$, so that a solution with 50% dissociation has pH equal to the pK_a of the acid.

Data for bases are presented as pK_a values for the conjugate acid, i.e., for the reaction



In older literature, an ionization constant K_b was used for the reaction $B + H_2O \rightleftharpoons BH^+ + OH^-$. This is related to K_a by

$$pK_a + pK_b = pK_{water} = 14.00 \quad (\text{at } 25^\circ\text{C}) \quad \dots \quad pBLAH = -\log a_{BLAH}$$

... why does this state that $pK_a + pK_b = pK_w$?
 ... because $K_a K_b = K_w$... **okaaaayyyy**... but why?
 ... because $\exp(-(\Delta G_a^\circ + \Delta G_b^\circ)) = \exp(-\Delta G_w^\circ)$...
 ... **Ahhhhh!**... enough with the algebra already!
 ... but wait!... for B, BH^+ this looks like Hess's law!
 ... **so, let's add up these chemical reactions!**
 ... and that gives us water dissociation... Nice!

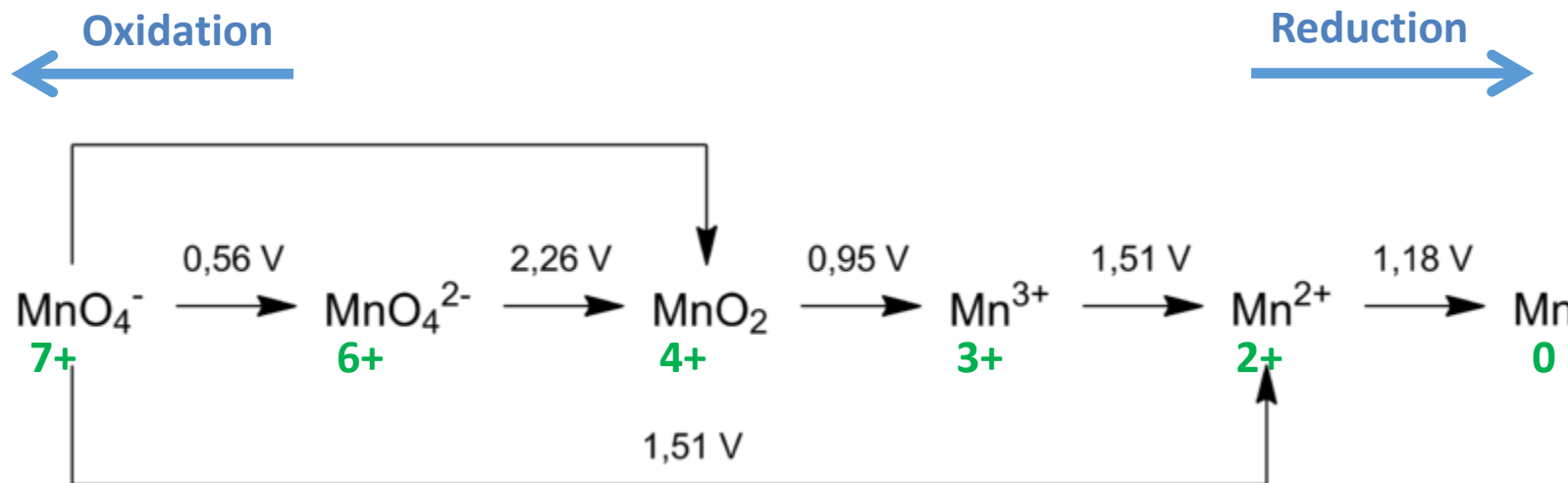
... and again, the CRC Handbook has a lot of chemical information... including tables of values...

... also those in the **Acidity/Basicity Series**...

... Do you know what the reference acidity is for this list of standard(-state) equilibrium acid dissociation constants?

Mol. form.	Name	Step	t/°C	pK _a	Mol. form.	Name	Step	t/°C	pK _a
CHNO	Cyanic acid		25	3.7	C ₂ H ₅ NO	Acetamide		25	15.1
CH ₂ N ₂	Cyanamide		29	1.1	C ₂ H ₅ NO ₂	Acetohydroxamic acid			8.70
CH ₂ O	Formaldehyde		25	13.27	C ₂ H ₅ NO ₂	Nitroethane		25	8.46
CH ₂ O ₂	Formic acid		25	3.75	C ₂ H ₅ NO ₂	Glycine	1	25	2.35
CH ₃ NO ₂	Nitromethane		25	10.21			2	25	9.78
CH ₃ NS ₂	Carbamodithioic acid		25	2.95	C ₂ H ₆ N ₂	Ethanimidamide		25	12.1
CH ₄ N ₂ O	Urea		25	0.10	C ₂ H ₆ O	Ethanol		25	15.5
CH ₄ N ₂ S	Thiourea		25	-1	C ₂ H ₆ OS	2-Mercaptoethanol		25	9.72
CH ₅ O	Methanol		25	15.5	C ₂ H ₆ O ₂	Ethylene glycol		25	15.1
CH ₅ S	Methanethiol		25	10.33	C ₂ H ₇ AsO ₂	Dimethylarsinic acid	1	25	1.57
CH ₅ N	Methylamine		25	10.66			2	25	6.27
CH ₅ NO	O-Methylhydroxylamine			12.5	C ₂ H ₇ N	Ethylamine		25	10.65
CH ₅ N ₃	Guanidine		25	13.6	C ₂ H ₇ N	Dimethylamine		25	10.73
C ₂ HCl ₃ O	Trichloroacetaldehyde		25	10.04	C ₂ H ₇ NO	Ethanolamine		25	9.50
C ₂ HCl ₃ O ₂	Trichloroacetic acid		20	0.66	C ₂ H ₇ NO ₃ S	2-Aminoethanesulfonic acid	1	25	1.5
C ₂ HF ₃ O ₂	Trifluoroacetic acid		25	0.52			2	25	9.06
C ₂ H ₂ Cl ₂ O ₂	Dichloroacetic acid		25	1.35	C ₂ H ₇ NS	Cysteamine	1	25	8.27
C ₂ H ₂ O ₃	Glyoxylic acid		25	3.18			2	25	10.53
C ₂ H ₂ O ₄	Oxalic acid	1	25	1.25	C ₂ H ₇ N ₅	Biguanide	1		11.52
		2	25	3.81			2		2.93
C ₂ H ₃ BrO ₂	Bromoacetic acid		25	2.90	C ₂ H ₈ N ₂	1,2-Ethanediamine	1	25	9.92
C ₂ H ₃ ClO ₂	Chloroacetic acid		25	2.87			2	25	6.86
C ₂ H ₃ Cl ₃ O	2,2,2-Trichloroethanol		25	12.24	C ₂ H ₈ O ₇ P ₂	1-Hydroxy-1,1-diphosphonoethane	1		1.35
C ₂ H ₃ FO ₂	Fluoroacetic acid		25	2.59			2		2.87
C ₂ H ₃ FO ₂	2,2,2-Trifluoroethanol		25	12.37			3		7.03
C ₂ H ₃ IO ₂	Iodoacetic acid		25	3.18			4		11.3
C ₂ H ₃ NO ₄	Nitroacetic acid		24	1.48	C ₃ H ₂ O ₂	2-Propynoic acid		25	1.84
C ₂ H ₃ N ₃	1H-1,2,3-Triazole		20	1.17	C ₃ H ₃ NO	Oxazole		33	0.8
C ₂ H ₃ N ₃	1H-1,2,4-Triazole		20	2.27	C ₃ H ₃ NO	Isoxazole		25	-2.0
C ₂ H ₃ N ₂	Aminoacetoneitrile		25	5.34	C ₃ H ₃ NO ₂	Cyanoacetic acid		25	2.47
C ₂ H ₄ O	Acetaldehyde		25	13.57	C ₃ H ₃ NS	Thiazole		25	2.52
C ₂ H ₄ OS	Thioacetic acid		25	3.33	C ₃ H ₃ N ₃ O ₃	Cyanuric acid	1		6.88
C ₂ H ₄ O ₂	Acetic acid		25	4.756			2		11.40
C ₂ H ₄ O ₂ S	Thioglycolic acid		25	3.68			3		13.5
C ₂ H ₄ O ₃	Glycolic acid		25	3.83	C ₃ H ₄ N ₂	1H-Pyrazole		25	2.49
C ₂ H ₄ N	Ethyleneimine		25	8.04	C ₃ H ₄ N ₂	Imidazole		25	6.99

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

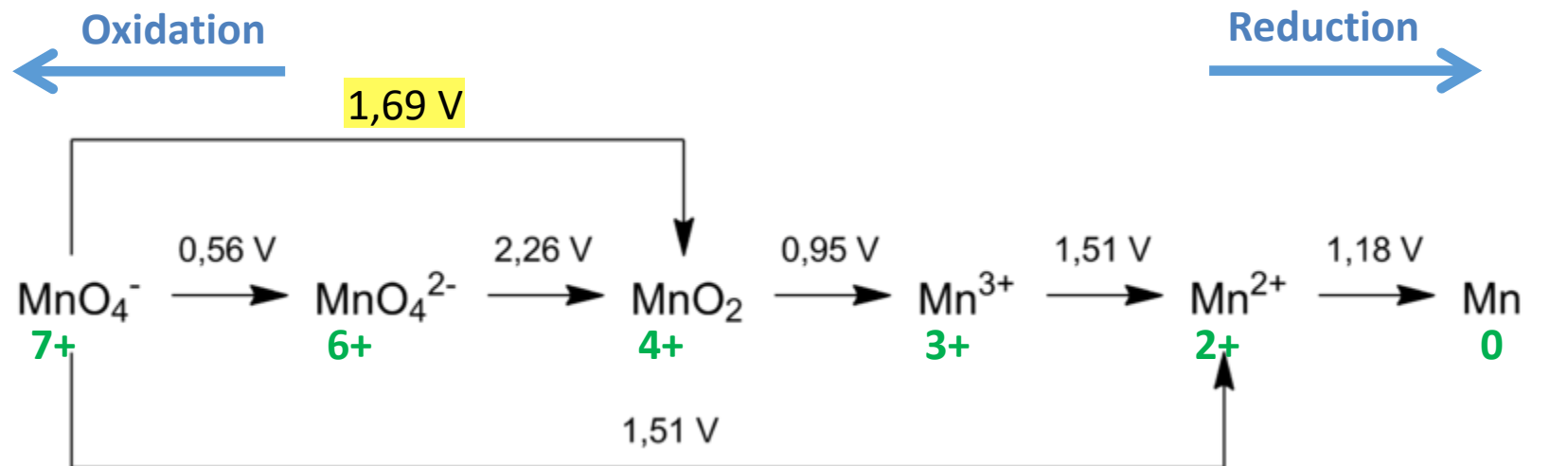
Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule (*the opposite is comproportionation (AKA: symproportionation)*)

(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 ?



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$$\Delta G^0 = -nFE^0 = -3FE^0$$

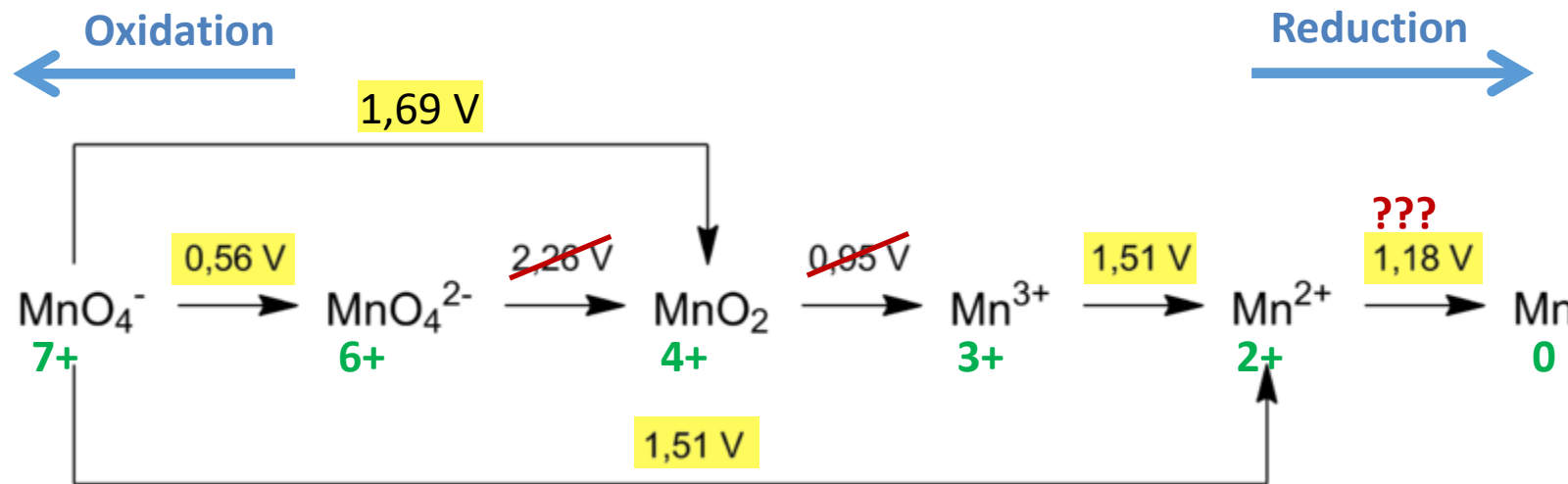
$$\Delta G^0 = -nFE^0_1 + -nFE^0_2 = -F((1 \times 0.56 \text{ V}) + (2 \times 2.26 \text{ V})) = -F(5.08 \text{ V})$$

Set them equal to each other, and thus, $3E^0 = 5.08$ and $E^0 = 1.69 \text{ V}$

... for #1, you can work with E^0 only (do not need ΔG^0), because the reaction is always balanced/equal in the number of electrons

Two diagrams of empirical standard potentials...

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

Recall from before...

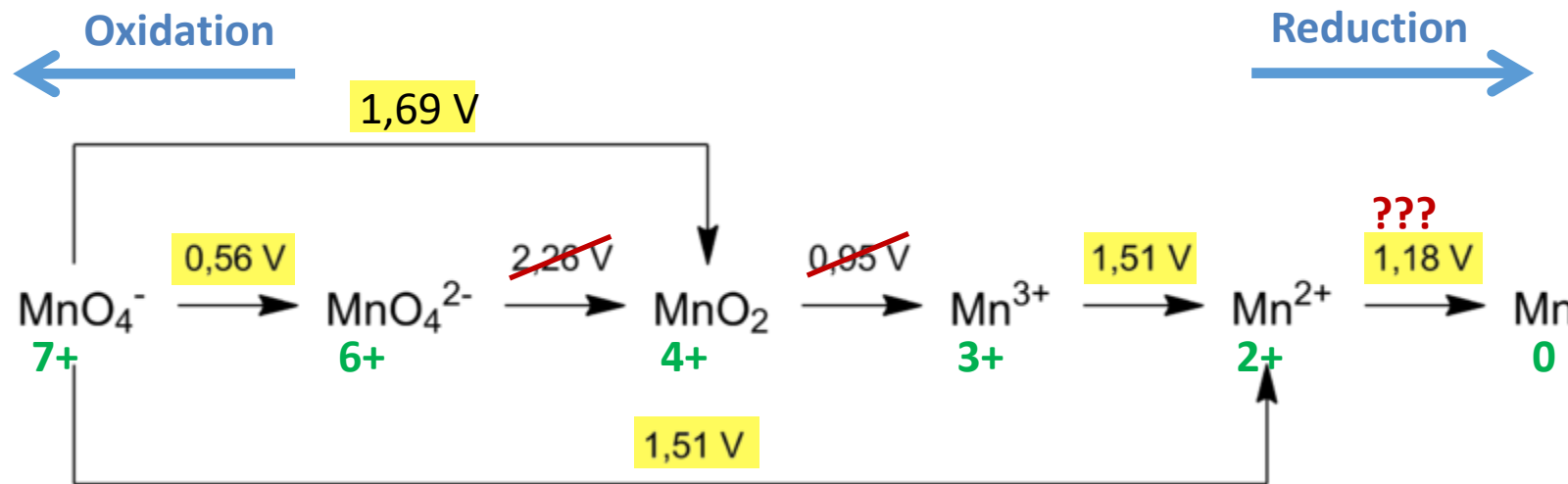
$Mn^{2+} + 2 e \rightleftharpoons Mn$???	-1.185
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$		1.5415
$MnO_2 + 4 H^+ + 2 e \rightleftharpoons Mn^{2+} + 2 H_2O$		1.224
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$		0.558
$MnO_4^- + 4 H^+ + 3 e \rightleftharpoons MnO_2 + 2 H_2O$		1.679
$MnO_4^- + 8 H^+ + 5 e \rightleftharpoons Mn^{2+} + 4 H_2O$		1.507
$MnO_4^- + 2 H_2O + 3 e \rightleftharpoons MnO_2 + 4 OH^-$		0.595
$MnO_4^{2-} + 2 H_2O + 2 e \rightleftharpoons MnO_2 + 4 OH^-$		0.60
$Mn(OH)_2 + 2 e \rightleftharpoons Mn + 2 OH^-$		-1.56
$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$		0.15
$Mn_2O_3 + 6 H^+ + e \rightleftharpoons 2 Mn^{2+} + 3 H_2O$		1.485

... anyway, why are these bottom E^0 values not on the Latimer diagram?

... because they are at basic/alkaline standard state with ~1 M OH^- !

Two diagrams of empirical standard potentials...

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



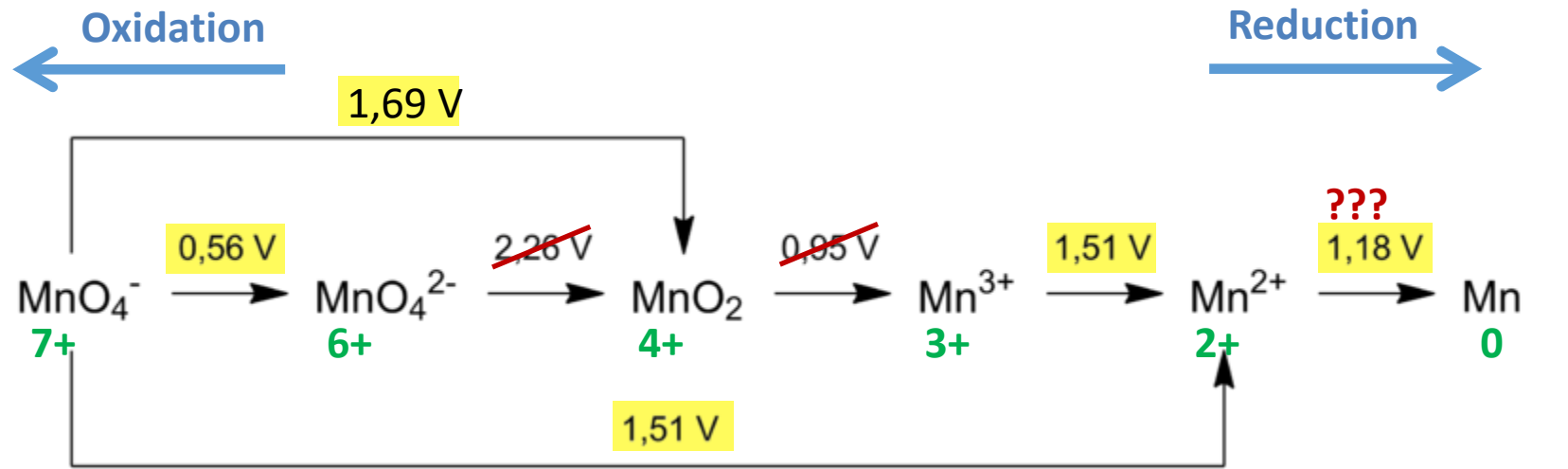
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Recall from before...

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$\text{Mn}(\text{OH})_2 + 2 e \rightleftharpoons \text{Mn} + 2 \text{OH}^-$		-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

What would this E^0 value be when at acidic standard state?

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

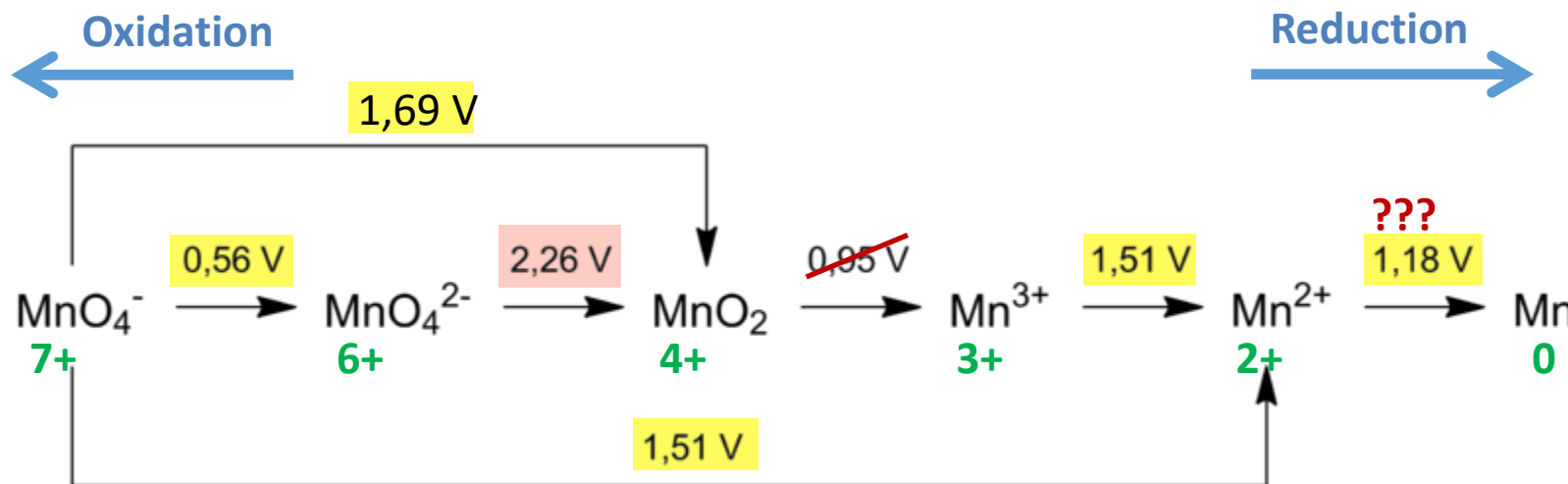
$$E = E_{\text{acid}}^{\circ} - \frac{0.05916 \text{ V}}{n} \log \left(\frac{[\text{MnO}_2]^1 [\text{H}_2\text{O}]^2}{[\text{MnO}_4^{2-}]^1 [\text{H}^+]^4} \right) = E_{\text{acid}}^{\circ} - \frac{0.05916 \text{ V}}{2} \log \left(\frac{(1)^1}{(1)^1 (10^{-14})^4} \right) = E_{\text{acid}}^{\circ} - 0.02958 \text{ V} \quad (56)$$

$$E = E_{\text{acid}}^{\circ} - 1.65648 \text{ V} = 0.60 \text{ V}$$

What would this E° value be when at acidic standard state?

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from Wiki

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$\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + \text{e} \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}$	1.485

$$E_{\text{SHE}}^{\circ} = 2,25648 \text{ V}$$

SWEET!

... but then why didn't the CRC Handbook list this? ...

... a second diagram of (not truly) empirical standard potentials...

A Pourbaix diagram is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable

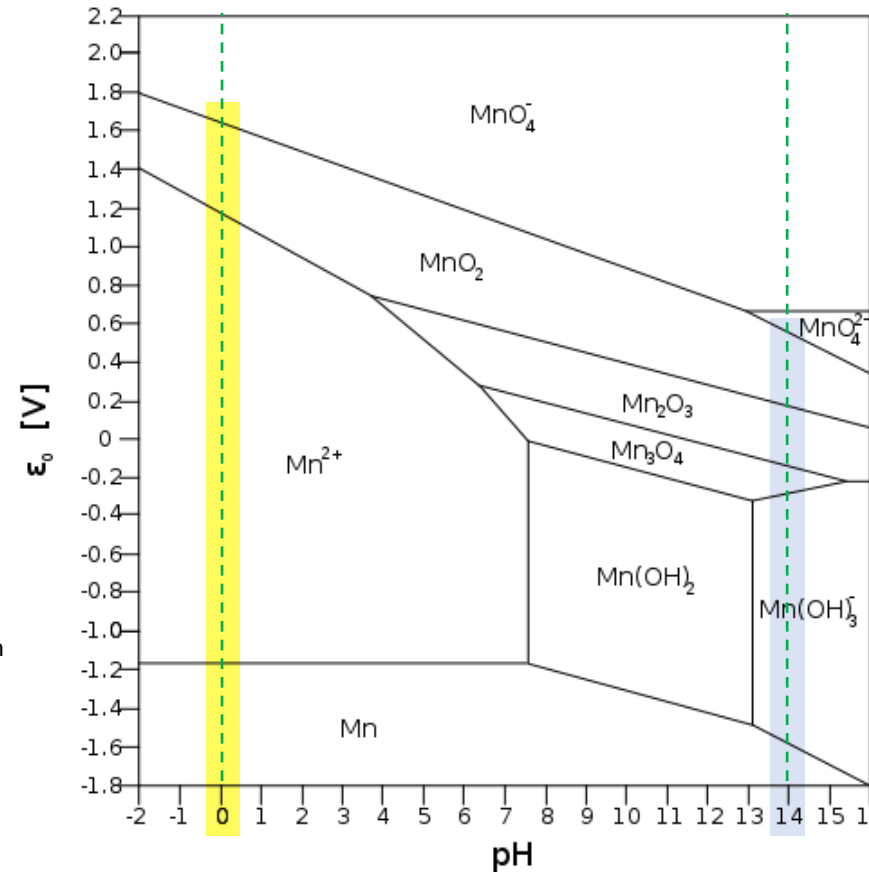
... mostly based on thermochemical data

Chemist

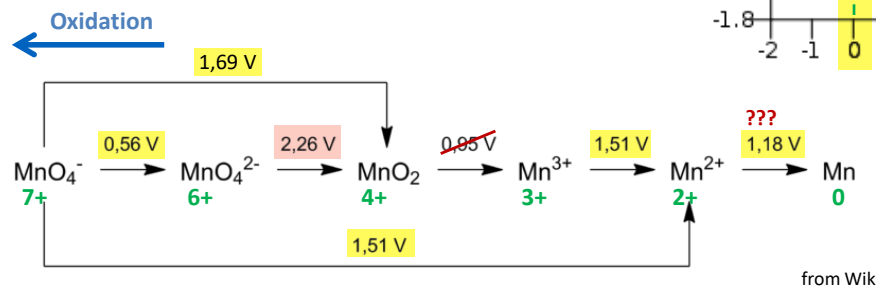


Marcel Pourbaix
(1904–1998)

<http://corrosion-doctors.org/Biographies/PourbaixBio.htm>



from Wiki



... because in acid, the reaction does not occur!

... but then why didn't the CRC Handbook list this? ...

... a second diagram of (not truly) empirical standard potentials...

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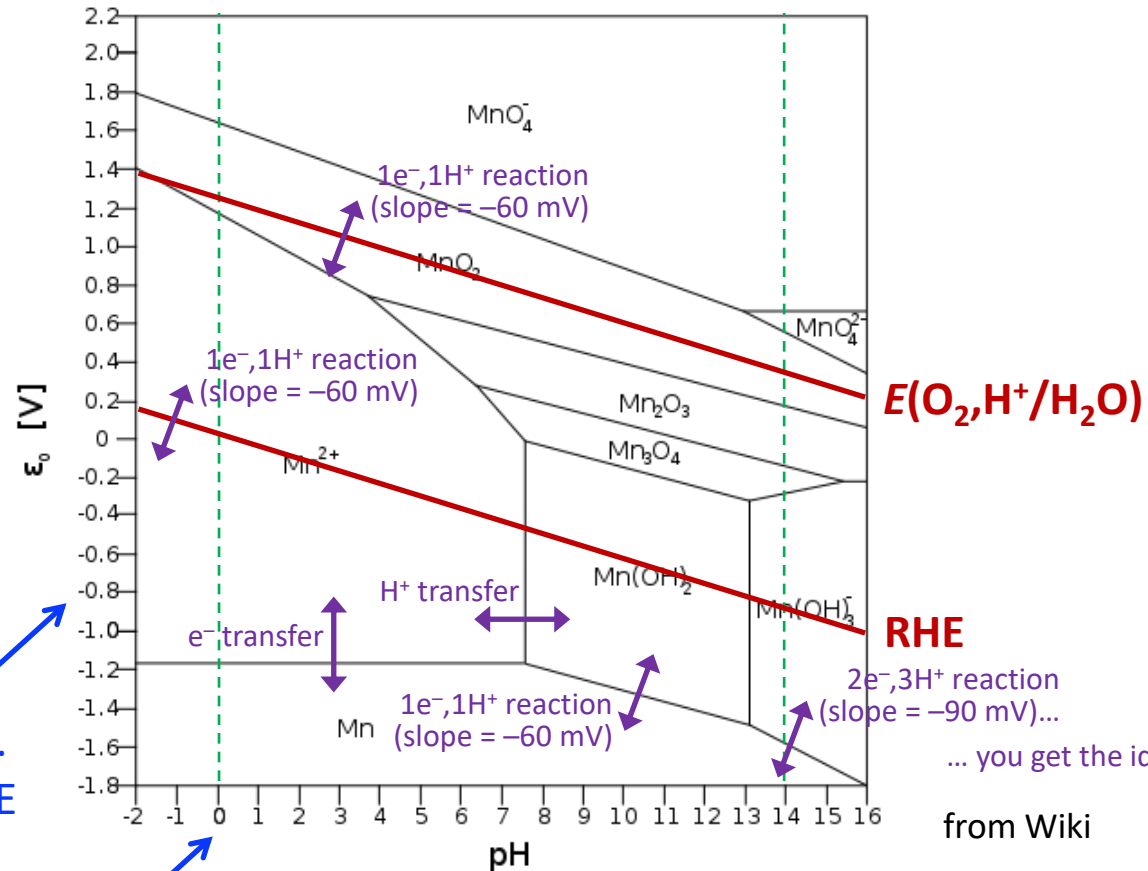


Marcel Pourbaix
(1904–1998)

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Why don't I like this? ...
Even though EVERYONE
plots it this way

Anyway, ... standard state is here, at ~1 M H⁺ (pH = 0) → SHE
... but if written under alkaline conditions, ~1 M OH⁻ is standard state (pH 14)



from Wiki

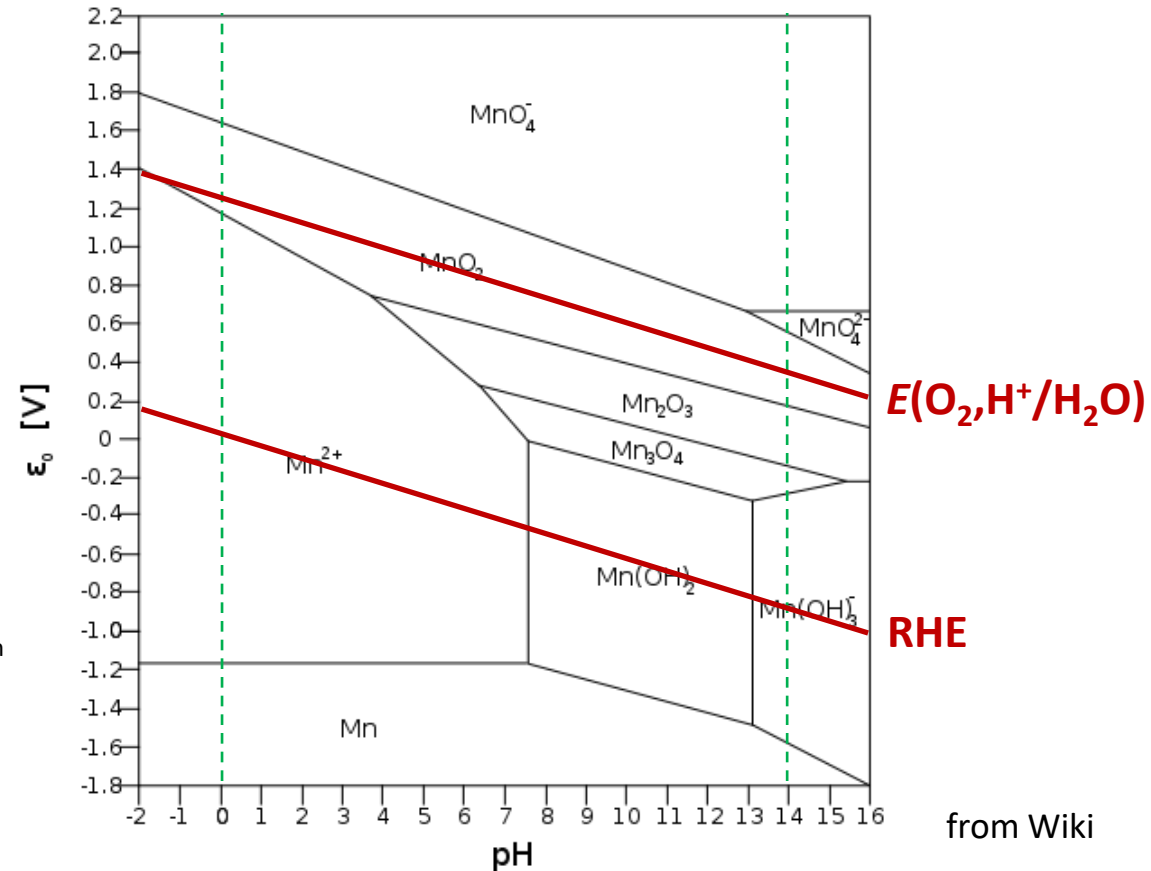
A Pourbaix diagram is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable ... mostly based on thermochemical data

Chemist



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(1904–1998)

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- (1) What is the electrocatalyst for O_2 evolution through water oxidation? MnO_2
- (2) At what pH values is a solid electrocatalyst for H_2 evolution stable? pH 7.5 – 13



Chemical Kinetics

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

Straight into Groups!

**Quiz Time!
... Paper Time!**

Chemical Kinetics

- **Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer**
- **Mass action, Microscopic reversibility, Förster cube, Square schemes, Rate constants, Activation energies, Transition-state theory, Marcus–Hush theory, Transition-state character, Reorganization energies (outer and inner)**
- Linear free energy relationships, Charge transfer across electrified interfaces, Butler–Volmer equation, Fermi’s golden rule, Solid-state physics, Marcus–Gerischer theory
- Rate-determining step, Steady-state & Pre-equilibrium approximations, Langmuir/Frumkin isotherms

... mass transfer in chemical systems is concerned with the movement of material = mass (even species as small as electrons) from one location (in solution) to another, and arises from spatial differences in electric potential, chemical potential, or from volume movement (of solution)...

... ***We need to understand mass transfer! ...***

... *but first, because it relates directly to mass transfer, I need to introduce the governing equation for the continuity of mass, which is even more stringent than the law of the conservation of mass!*

... and later, let's step our game up and do a more rigorous PChem / Physics derivation!

Thermodynamics *versus* Kinetics

Thermodynamics are only as important as their influence on **kinetics**...

... energetics from thermodynamics dictate **equilibrium concentrations**...

... but it is the **kinetic (and transport) properties** that influence how those conditions change upon perturbation...

$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

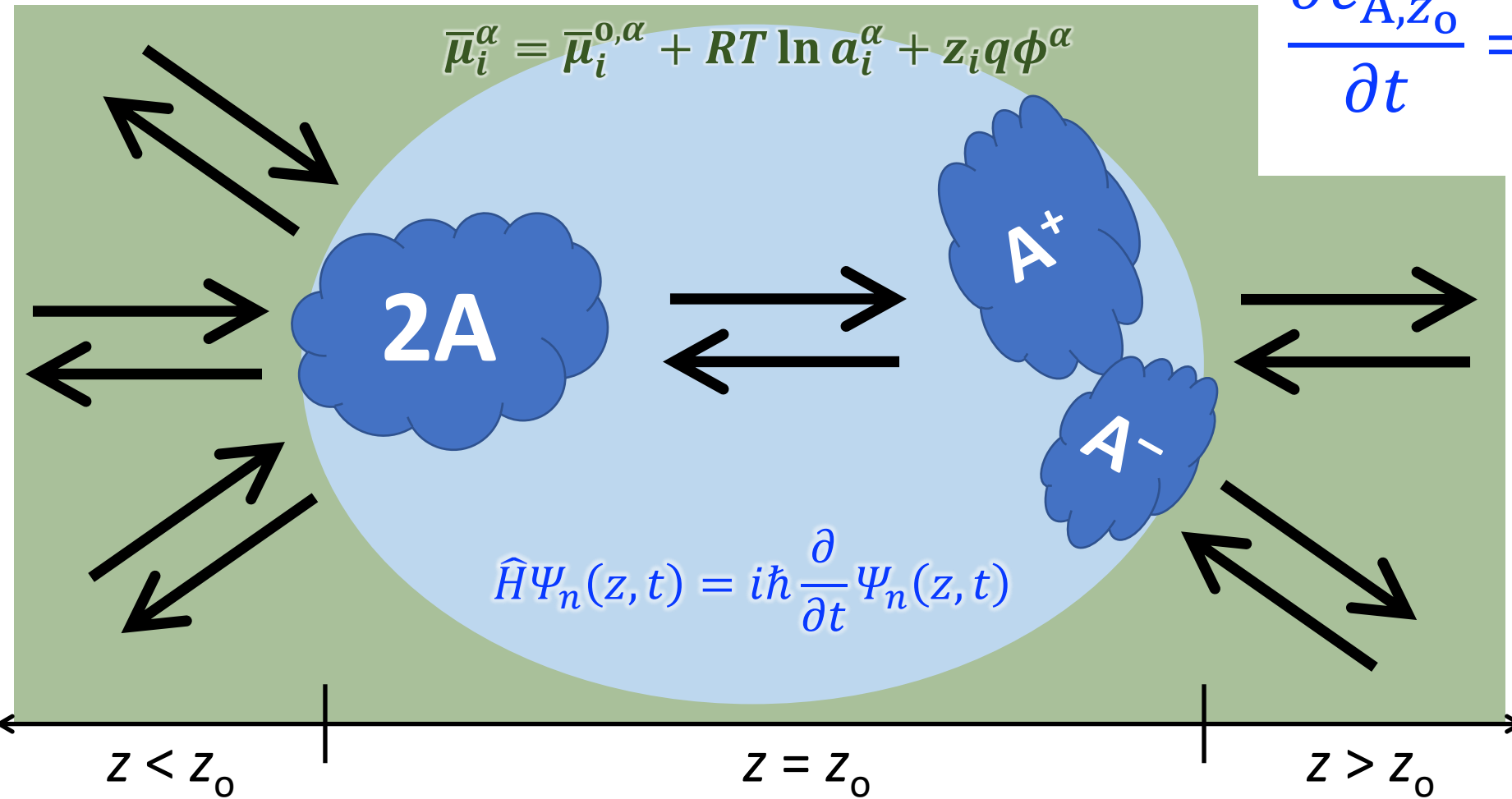
rate of change of the (c)oncentration of species A with respect to (t)ime, in units of $M s^{-1}$ ($mol dm^{-3} s^{-1}$)

mass action (R)ate laws that effect species A, e.g. $R_A = k_3 a_B a_D^2 \approx k_3 [B][D]^2$ (to a first order, this is driven by differences in chemical potential of various species, μ_j)

rate of change of the molar flux (N) of species A with respect to position (z), e.g. $N_A = -D \frac{\partial a_A}{\partial z}$ (to a first order, this is driven by differences in electrochemical potential of a single species, $\bar{\mu}_i$)

... this master equation describes all kinetic and transport processes for mass... more on this later...

Continuity of Mass



$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

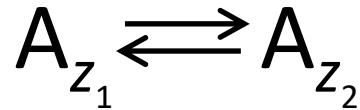
Note: Adjusting just one variable is difficult... but people, like us, can try



“Jean Piaget, the Swiss psychologist who first studied object permanence in infants, argued that it is one of an infant's most important accomplishments, as, without this concept, objects would have no separate, permanent existence.”

– Wiki, Object permanence

1D Transport in Liquids (solids are simpler)



$$\frac{\partial c_{A,z_0}}{\partial t} = \frac{\partial N_A}{\partial z}$$

$$N_A = - \left(\frac{D_A c_A}{RT} \right) \frac{\partial \bar{\mu}_A}{\partial z} + v c_A$$

(MechEs should be yawning)

... there are many driving forces for flux of species...
... convection (vc) is just one (e.g., dT/dx)

Group terms... then mass transfer resembles mass action (assume $v = 0$ for simplicity)...

$$N_A = -D_A \frac{\partial \left(\bar{\mu}_A / RT \right)}{\partial z} c_A$$

What are the directions for the dimensions of D_A ?

BOLD $((\text{cm}^2/\text{s}) / \text{cm}) = \text{cm}/\text{s}$... a velocity!

... and with $\frac{\partial}{\partial z}$, units are s^{-1} ... an inverse time constant!

... and that equals zero at **steady state**

(Note that... $R_{A,\text{total}} = -k'_f c_A + k'_b c_B$... with k'_j (s^{-1}), an inverse time constant!)

mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: *diffusion*, *migration/drift*, and *convection*

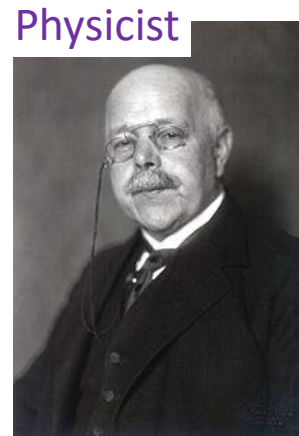
the *Nernst–Planck Equation*:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

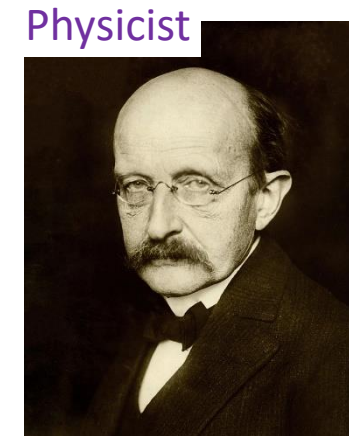
B&F, 1.4.2
& 4.1.8



This is the typical equation that is given to someone who wants to consider mass transfer of charged species... the total **flux** of reactant i to a flat electrode (this is $N_i(x)$ in many textbooks – not B&F – especially engineering ones; it has units of $\text{mol cm}^{-2} \text{s}^{-1}$)



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



Max Karl Ernst Ludwig Planck
(1858–1947)
Nobel Prize (Physics, 1918)

from Wiki

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B&F, 1.4.2
& 4.1.8



the diffusive flux of reactant i to a flat electrode where D_i is the diffusion coefficient for species, i (D has units of $\text{cm}^2 \text{s}^{-1}$)

Diffusion Coefficient

mean square displacement
(variance)

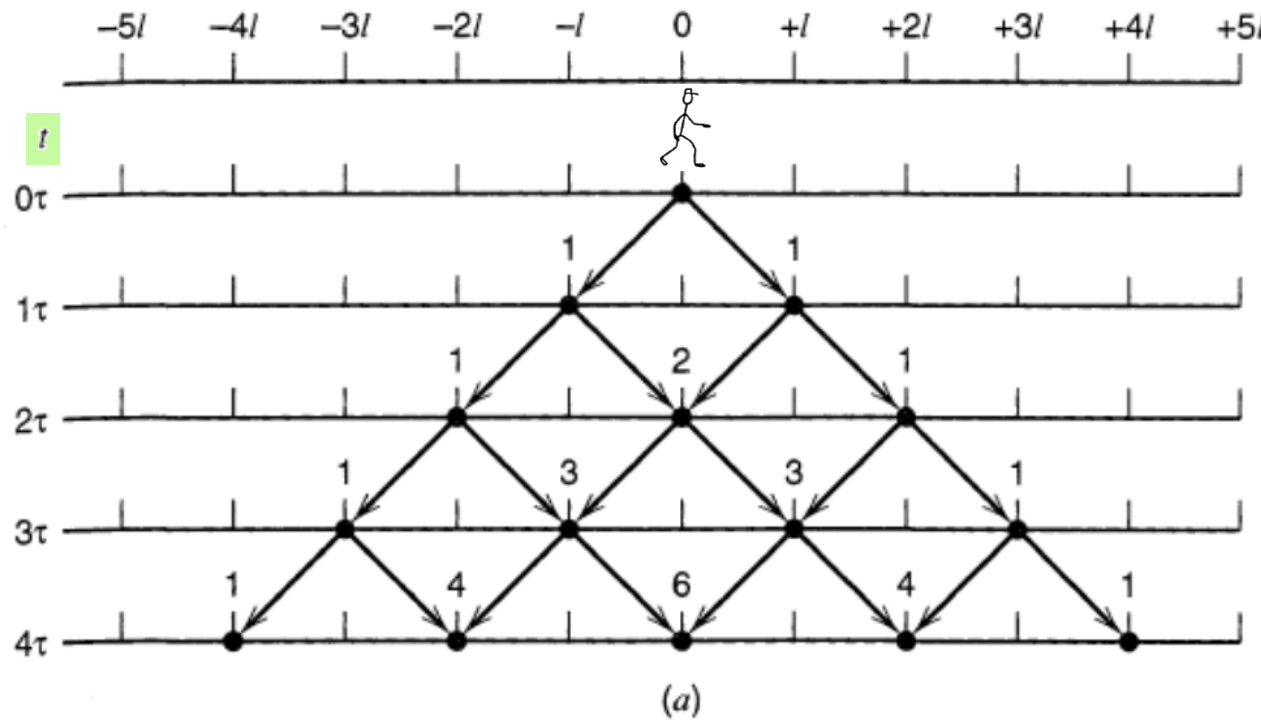
$$\overline{\Delta^2} = m l^2 = \frac{t}{\tau} l^2 = 2Dt$$

$$\dots D = \frac{l^2}{2\tau}$$

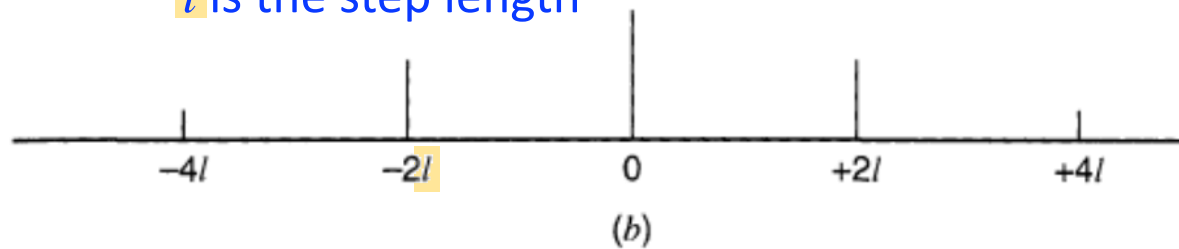
(Recall: D_z is has units of $\text{cm}^2 \text{s}^{-1}$... as zz)

... and why do we care?

Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is $6/16$, at $x = \pm 2l$ is $4/16$, and at $x = \pm 4l$ is $1/16$.



l is the step length



m is just the number
 τ is the step time

root mean square (rms)
displacement
(standard deviation)

$$\overline{\Delta} = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension}$$

... and the "2" is for positive and negative directions

mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: *diffusion*, *migration/drift*, and *convection*

the *Nernst–Planck Equation*:

$$J_i(\mathbf{x}) = -D_i \frac{\partial C_i(\mathbf{x})}{\partial \mathbf{x}} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(\mathbf{x})}{\partial \mathbf{x}} + C_i \mathbf{v}(\mathbf{x})$$

B&F, 1.4.2
& 4.1.8

... **migration/drift** relies on the electric-field-driven variant of the random walk diffusion coefficient... obviously the ability for a species to random walk is still important, but on top of that an electric field will drive the species directionally... this is called the mobility, μ_i

$$\mu_i = \frac{|z_i| F D_i}{RT}$$

↑
the flux due to migration/drift of reactant i where z_i is the charge on species i , and $\partial\phi/\partial\mathbf{x}$ is the gradient in electric potential (which is equal to the negative of the electric field, E)

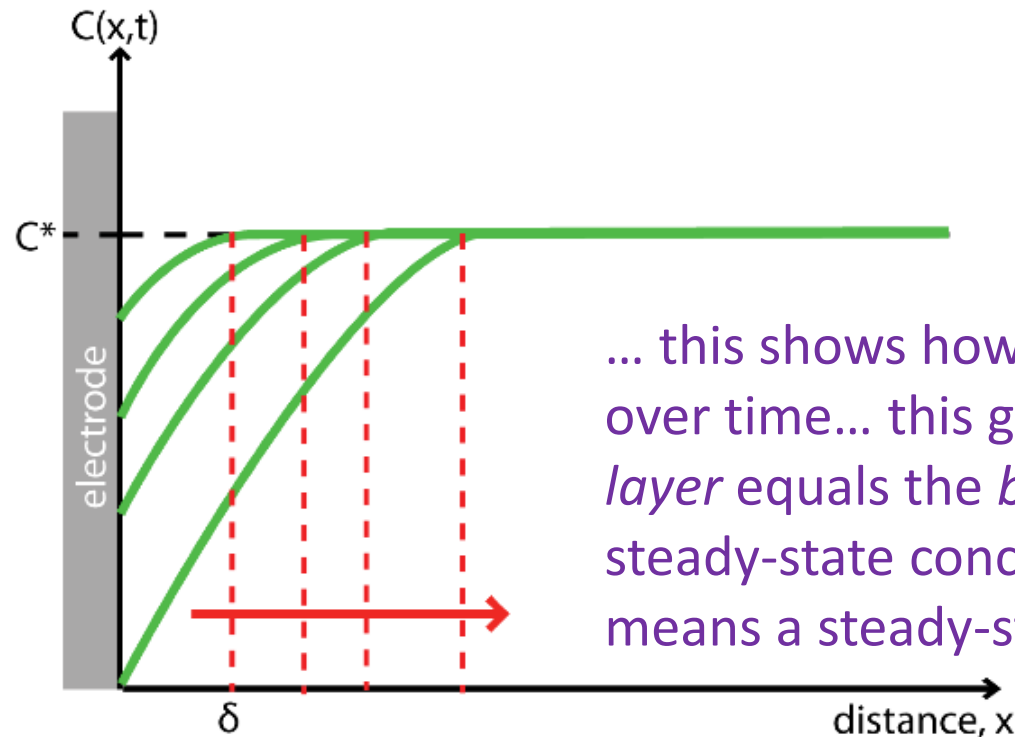
... this is the Einstein–Smoluchowski equation...
... sorry that *mobility* and *chemical potential* have the same symbol... ugh!

mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: *diffusion*, *migration/drift*, and *convection*

the *Nernst–Planck Equation*:

$$J_i(\mathbf{x}) = -D_i \frac{\partial C_i(\mathbf{x})}{\partial \mathbf{x}} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(\mathbf{x})}{\partial \mathbf{x}} + \overset{\text{B\&F, 1.4.2 \& 4.1.8}}{C_i \mathbf{v}(\mathbf{x})}$$

... **convection** forms a boundary layer that to a first approximation is fixed for a given stir rate... which sets a slope for the concentration gradient to dictate maximum diffusive flux... stirring faster shrinks this boundary layer, which increases the limiting mass transfer flux

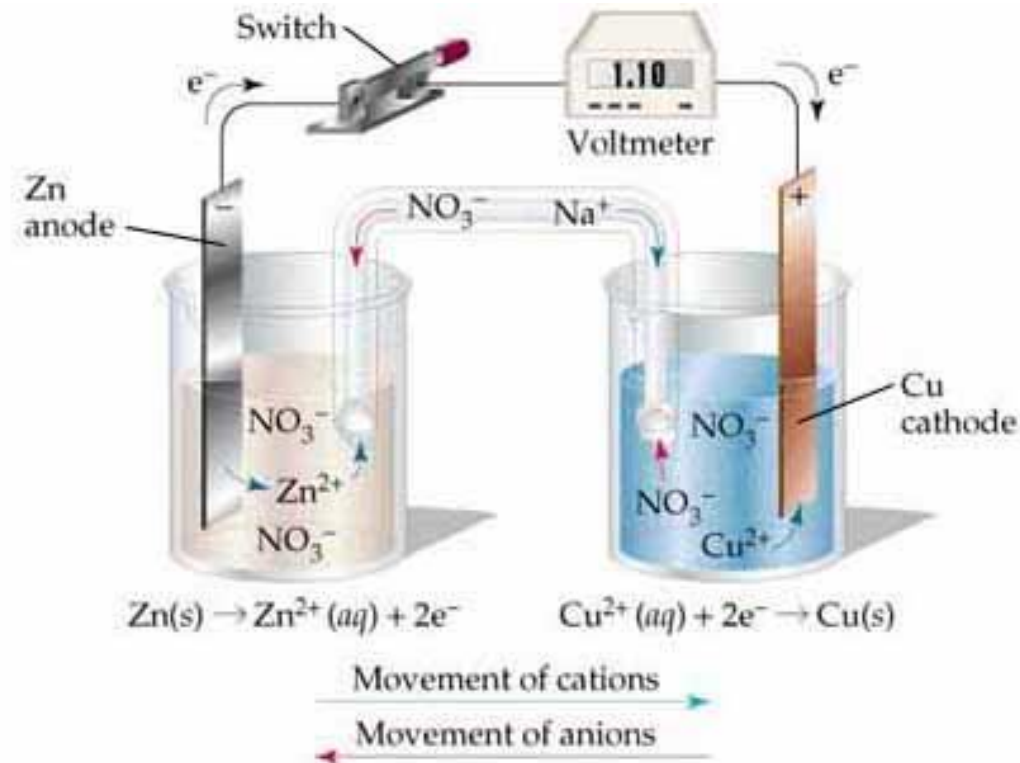


the flux due to convection of reactant i where $\mathbf{v}(\mathbf{x})$ is the velocity profile of the solution

... this shows how the *diffusion layer* grows over time... this growth stops once the *diffusion layer* equals the *boundary layer*... it results in a steady-state concentration gradient... which means a steady-state diffusive flux

(1) Migration / Drift (*no analogous term for heat, as heat is not charged*)

Flux ($\text{mol cm}^{-2} \text{s}^{-1}$) of **charged species** due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions



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(2) Diffusion *(analogous heat transfer is down a temperature gradient)*

Net flux of **species** due to a spatial gradient in their concentration and random thermal motion (no real “force”)



Diffusion

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Flux ($\text{mol cm}^{-2} \text{ s}^{-1}$) of **charged species** due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions

(2) Diffusion *(analogous heat transfer is down a temperature gradient)*

Net flux of **species** due to a spatial gradient in their concentration and random thermal motion (no real “force”)

(3) Convection *(analogous heat transfer is fluid/gas motion)*

Hydrodynamic movement (e.g. forced convection (stirring)) of **species**, where charged species still remain near each other (Coulombic attraction)

... FYI: even without intentional forced convection, unintentional forced convection (e.g. vibrations) influences an electrochemical experiment after ~ 30 seconds

1D Transport in Solids... the heavy lift

$$\bar{\mu}_i^\alpha = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}}$$

$$\text{Flux}_{z,e} = \mathbf{N}_e = - \frac{\sigma_e}{F^2} \frac{d\bar{\mu}_e}{dz}$$

(z is a direction; e means $z_e = -1$)

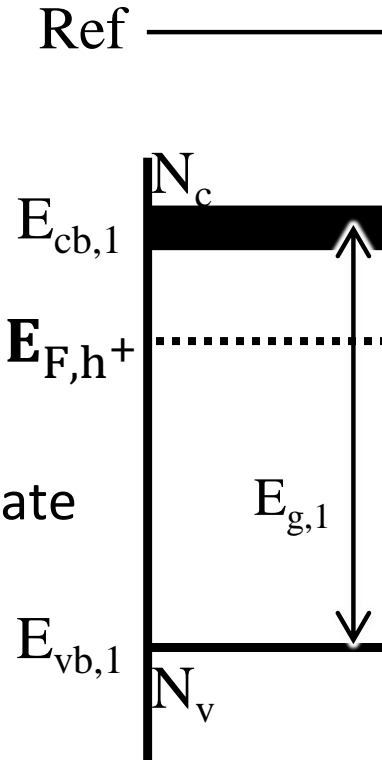
$\frac{d\bar{\mu}_e}{dz}$ dictates directionality

... multiply by $\sigma_e = \frac{F^2 D_e c_e}{RT}$ to get relative rate

... multiply $\text{Flux}_{z,e}$ by " $z_e F$ " to get $J_{z,e}$

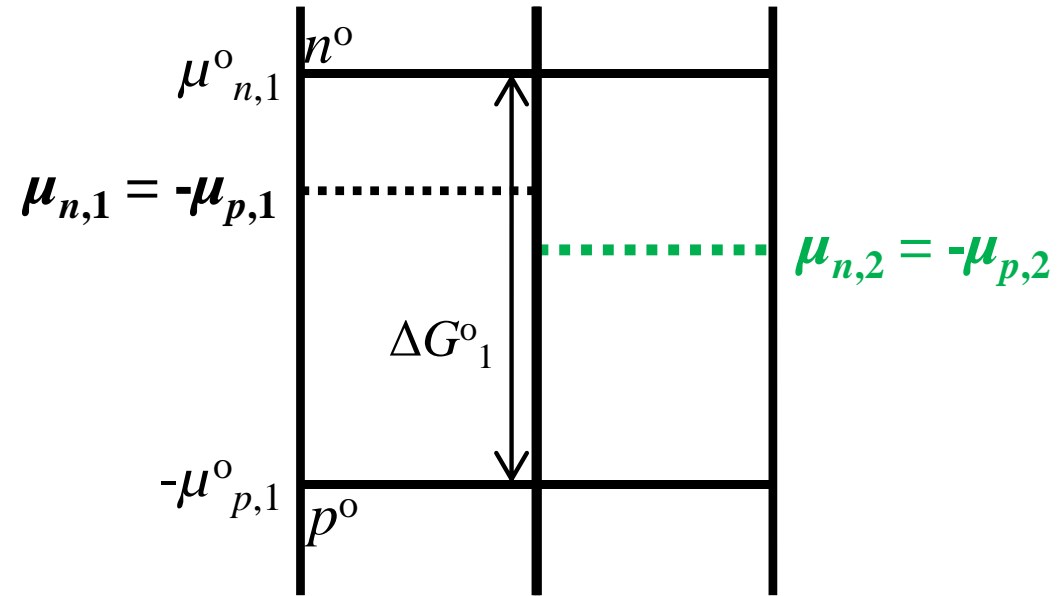
Solar cell experts say colloquial phrases like "band bending for charge separation" and "selective contacts"... I'm not a fan

$$\mathbf{E}_{F,e^-} = \mathbf{E}_{F,h^+}$$



Band diagram

$$-q\phi_1$$



"Ardo" diagram

A hybrid internal energy / free energy diagram shows several useful things at once, but (possibly usefully) glosses over details of other transport processes

1D Transport in Solids (liquids are "harder")

Let's expand the total differential...

... assuming a species, e , with valency, z_e , equal to -1

... other species may have different values for every term, except ϕ

$$\text{Flux}_{z,e} = -\frac{\sigma_e}{F^2} \frac{d\bar{\mu}_e}{dz} - S_{e,T_e} \frac{dT_e}{dz} \quad \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \bar{\mu}_i = \mu_i + z_i q \phi$$

$$\text{Flux}_{z,e} = -\frac{D_e n_e}{kT_e} \left(\frac{d\mu_e}{dz} - q \frac{d\phi}{dz} \right) - S_{e,T_e} \frac{dT_e}{dz} \quad \mu_i = \mu_i^0 + kT_i \ln a_i = \mu_i^0 + kT_i \ln \left(\frac{\gamma_i n_i}{n_i^0} \right)$$

$$\text{Flux}_{z,e} = -\frac{D_e n_e}{kT_e} \left(\frac{d\mu_e^0}{dz} + \frac{kT_e}{\gamma_e} \frac{d\gamma_e}{dz} + \frac{kT_e}{n_e} \frac{dn_e}{dz} - \frac{kT_e}{n_e^0} \frac{dn_e^0}{dz} + k \left(\ln \frac{\gamma_e n_e}{n_e^0} \right) \frac{dT_e}{dz} - q \frac{d\phi}{dz} \right) - S_{e,T_e} \frac{dT_e}{dz}$$

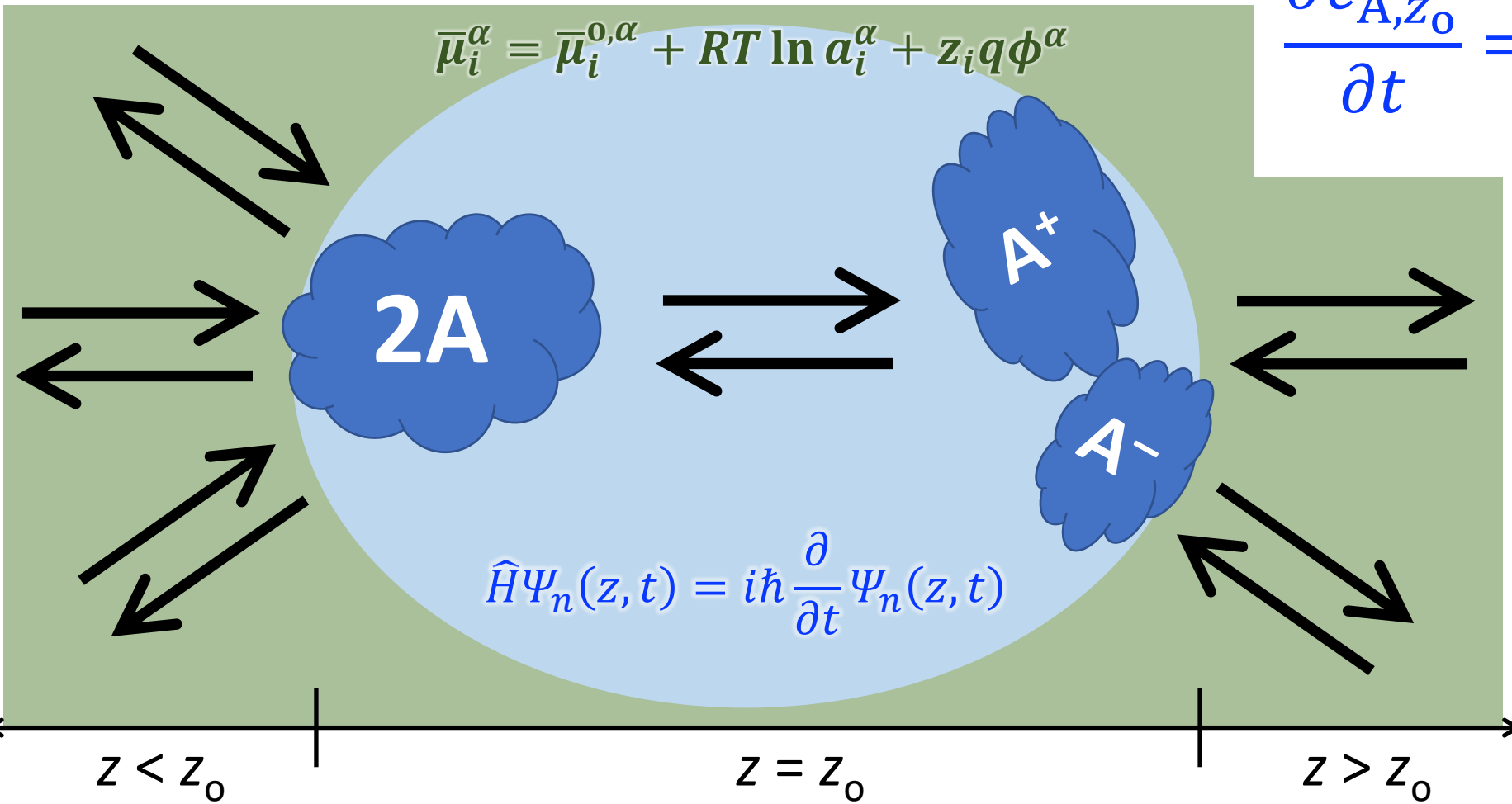
$$\text{Flux}_{z,e} = -D_e \left(\frac{n_e}{kT_e} \frac{d\mu_e^0}{dz} + \frac{n_e}{\gamma_e} \frac{d\gamma_e}{dz} + \frac{dn_e}{dz} - \frac{n_e}{n_e^0} \frac{dn_e^0}{dz} + \frac{n_e}{T_e} \left(\ln \frac{\gamma_e n_e}{n_e^0} \right) \frac{dT_e}{dz} - \frac{q n_e}{kT_e} \frac{d\phi}{dz} \right) - S_{e,T_e} \frac{dT_e}{dz}$$

$$\text{Flux}_{z,e} = -D_e \frac{dn_e}{dz} + \frac{q D_e n_e}{kT_e} \frac{d\phi}{dz} \quad \dots \text{ assuming spatially invariant } \mu_e^0, \gamma_e, n_e^0, T_e$$

Drift-Diffusion equation

$$\text{Flux}_{z,e} = -D_e n_e \left(\frac{d\mu_e^0}{kT_e dz} + \frac{d(\ln \gamma_e)}{dz} + \frac{d(\ln n_e)}{dz} - \frac{d(\ln n_e^0)}{dz} - \frac{d(q\phi)}{kT_e dz} \right) - D_{n_e, \gamma_e, n_e^0, T_e} \frac{dT_e}{dz}$$

Continuity of Mass



$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

Note: Adjusting just one variable is difficult... but people, like us, can try



“Jean Piaget, the Swiss psychologist who first studied object permanence in infants, argued that it is one of an infant's most important accomplishments, as, without this concept, objects would have no separate, permanent existence.”
 – Wiki, Object permanence

Thermodynamics *versus* Kinetics

Thermodynamics are only as important as their influence on **kinetics**...

... energetics from thermodynamics dictate **equilibrium concentrations**...

... but it is the **kinetic (and transport) properties** that influence how those conditions change upon perturbation...

$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

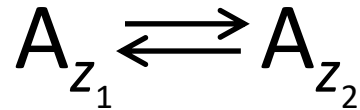
rate of change of the (c)oncentration of species A with respect to (t)ime, in units of $M s^{-1} (mol dm^{-3} s^{-1})$

mass action (R)ate laws that effect species A, e.g. $R_A = k_3 a_B a_D^2 \approx k_3 [B][D]^2$ (to a first order, this is driven by differences in chemical potential of various species, μ_j)

rate of change of the molar flux (N) of species A with respect to position (z), e.g. $N_A = -D \frac{\partial a_A}{\partial z}$ (to a first order, this is driven by differences in electrochemical potential of a single species, $\bar{\mu}_i$)

... this master equation describes all kinetic and transport processes for mass... more on this later...

1D Transport in Liquids (solids are simpler)



$$\frac{\partial c_{A,z_0}}{\partial t} = \frac{\partial N_A}{\partial z}$$

$$N_A = - \left(\frac{D_A c_A}{RT} \right) \frac{\partial \bar{\mu}_A}{\partial z} + v c_A$$

(MechEs should be yawning)

... there are many driving forces for flux of species...

... convection ($v c$) is just one (e.g., dT/dx)

Group terms... then mass transfer resembles mass action (assume $v = 0$ for simplicity)...

$$N_A = -D_A \frac{\partial \left(\bar{\mu}_A / RT \right)}{\partial z} c_A$$

What are the directions for the dimensions of D_A ?

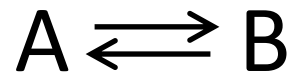
BOLD $((\text{cm}^2/\text{s}) / \text{cm}) = \text{cm}/\text{s}$... a velocity!

... and with $\frac{\partial}{\partial z}$, units are s^{-1} ... an inverse time constant!

... and that equals zero at **steady state**

(Note that... $R_{A,\text{total}} = -k'_f c_A + k'_b c_B$... with k'_j (s^{-1}), an inverse time constant!)

Mass Action / Microscopic Reversibility



$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j}$$

(Chemists should be yawning)

$$\Delta G^\alpha = \Delta G^{0,\alpha} + RT \ln Q \dots \text{ where } Q = \frac{a_B^\alpha}{a_A^\alpha} = \frac{\gamma_B^\alpha (c_B^\alpha / c_B^{0,\alpha})}{\gamma_A^\alpha (c_A^\alpha / c_A^{0,\alpha})}$$

$$R_{A,f} = -k_f a_A \quad R_{B,f} = +k_f a_A$$

$$R_{A,b} = +k_b a_B \quad R_{B,b} = -k_b a_B$$

- Law of mass action
- Principle of microscopic reversibility

... and in solid-state physics... $R_{e^-,total} = \sum_j \text{Gen}_{e^-,j} - \sum_j \text{Rec}_{e^-,j}$

k_j (M/s)... a rate!

k'_j (s^{-1})... an inverse time constant!

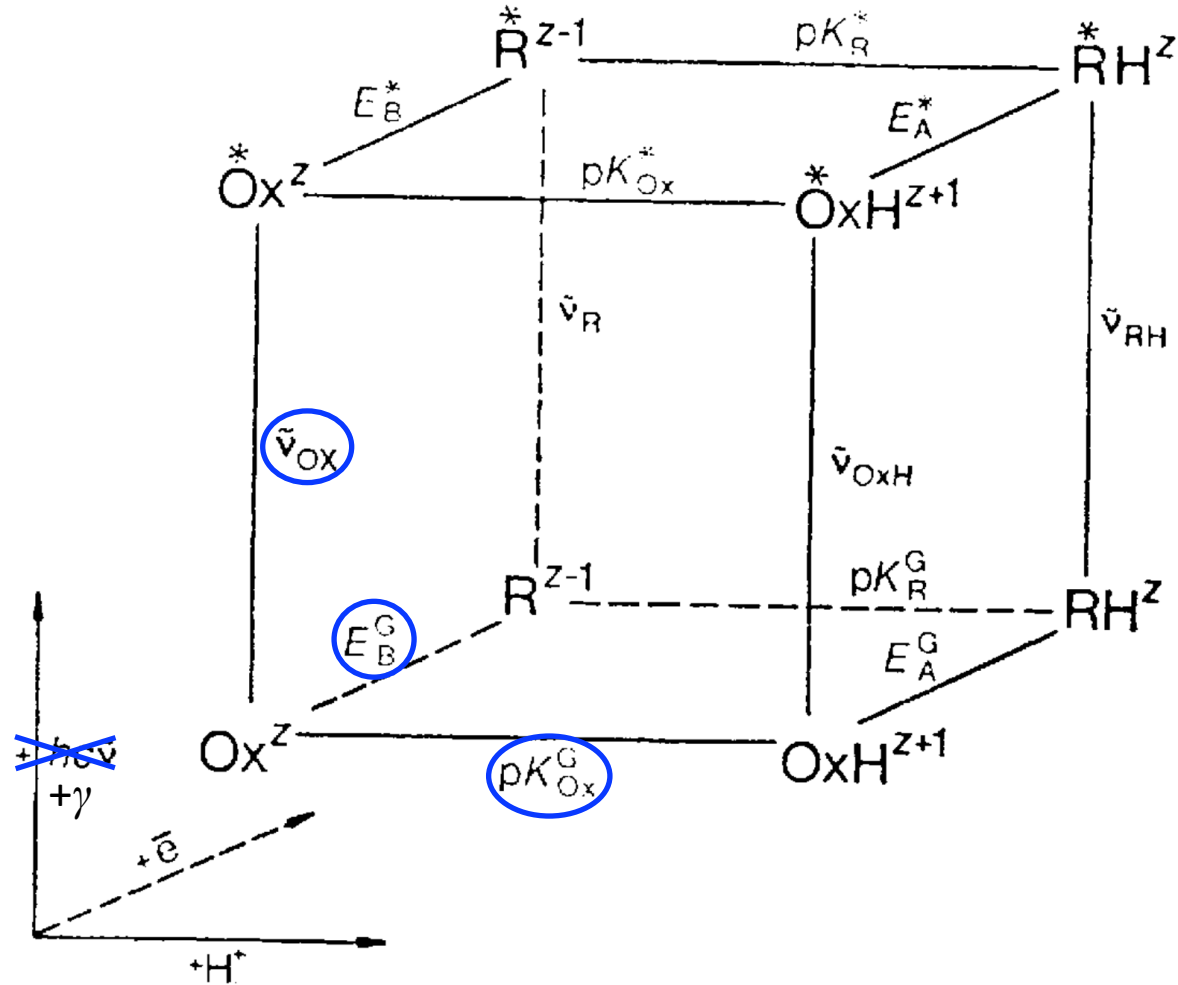
Now, consider the reaction to be at equilibrium... $\Delta G^\alpha = 0 = \Delta G^{0',\alpha} + RT \ln Q' = \bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha$

So, $\Delta G^{0',\alpha} = -RT \ln K'$, with $K' = \frac{c_{B,eq}^\alpha / c_B^{0,\alpha}}{c_{A,eq}^\alpha / c_A^{0,\alpha}} \dots$ and, of course, $K' = \exp\left(-\frac{\Delta G^{0',\alpha}}{RT}\right)$

But also, $\frac{\partial c_A}{\partial t} = 0 = -k_f a_{A,eq}^\alpha + k_b a_{B,eq}^\alpha \dots \frac{k_f}{k_b} = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = K = K' \frac{\gamma_B^\alpha}{\gamma_A^\alpha} \dots$ it can get messy

Or equivalently, $\frac{\partial c_A}{\partial t} = 0 = -k'_f c_{A,eq}^\alpha + k'_b c_{B,eq}^\alpha \dots \frac{k'_f}{k'_b} = \frac{c_{B,eq}^\alpha}{c_{A,eq}^\alpha} = K' \frac{c_B^{0,\alpha}}{c_A^{0,\alpha}} = K \frac{\gamma_A^\alpha c_B^{0,\alpha}}{\gamma_B^\alpha c_A^{0,\alpha}}$

Förster Cube and Square Schemes



Questions to ponder...

In this figure, what do the thermodynamic parameters E , pK , and $\bar{\nu}$ represent?

$E = E^0$ (standard-state reduction potential)

$pK = pK_a = -\log K_a$ (acid dissociation constant)

$\bar{\nu} = \frac{1}{\lambda}$ (wavenumber)

How are they related?

Redox: $E^0 = -\Delta G^0/nF$

Acidity: $pK_a = -\log K_a = \Delta G^0/(2.303RT)$

Light: $hc\bar{\nu} = \frac{hc}{\lambda} = h\nu = E_{\text{photon}}$

In 10

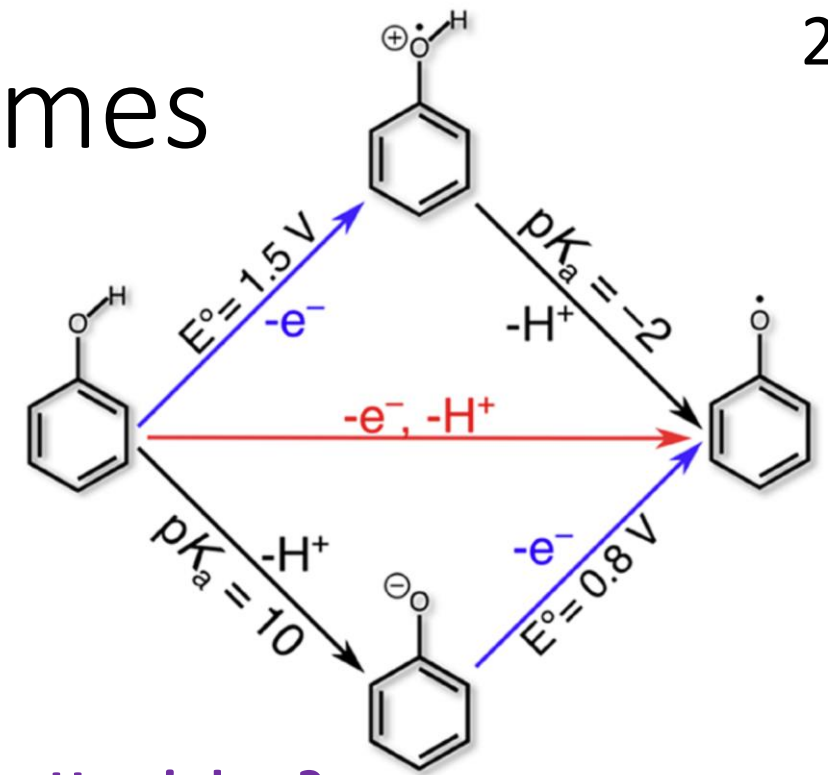
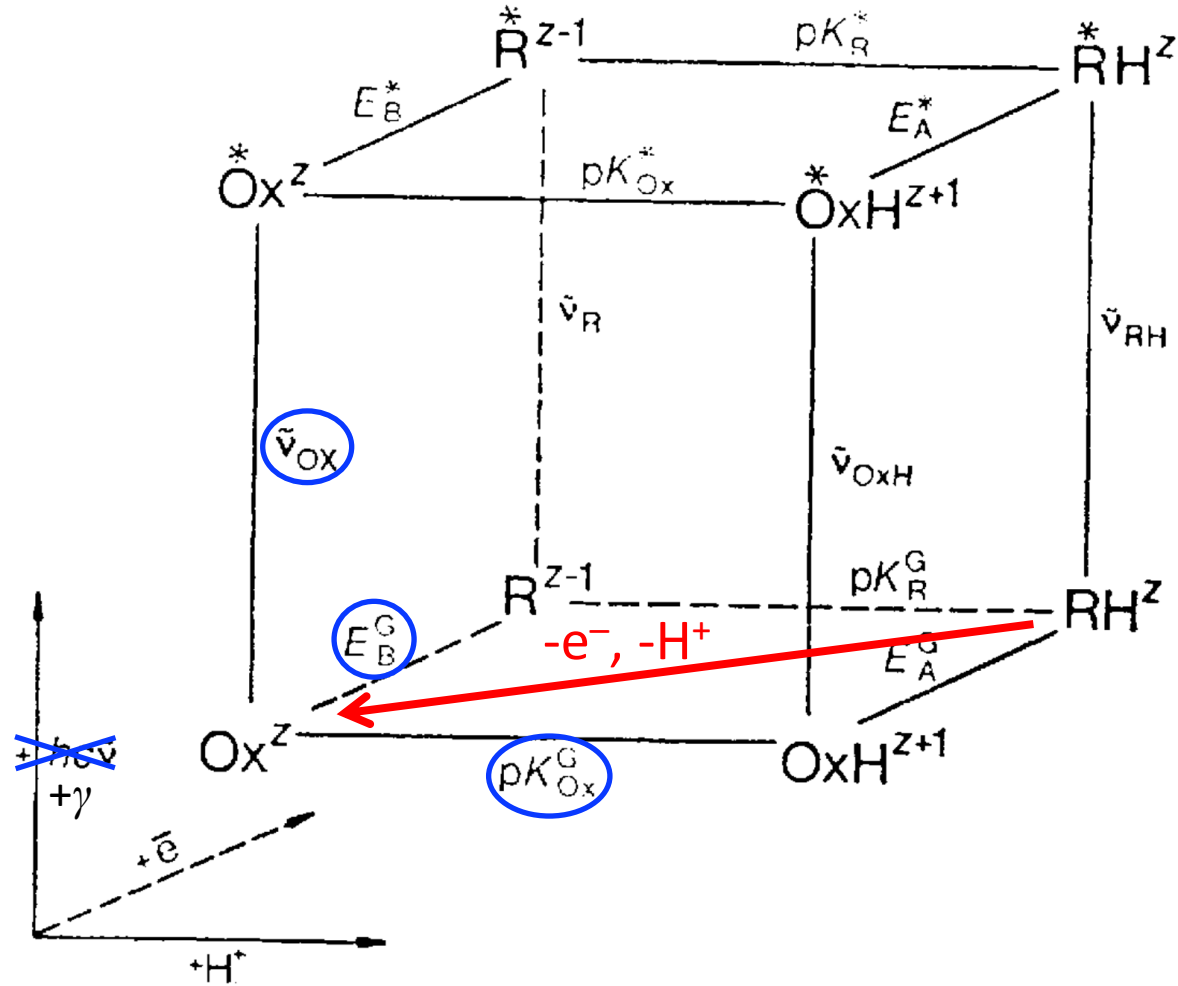
What is the reference state for each?

$E^0(\text{H}^+(\text{aq})/\text{H}_2) = 0$; $pK_a(\text{H}^+(\text{aq})) = 0$; 0

... before we add light... let's backtrack a bit...

... first we must understand dark thermal processes... Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, 73, 11–28

Förster Cube and Square Schemes



Does this obey Hess's law?

Redox: $E^\circ = -\Delta G^\circ/nF$

Acidity: $pK_a = -\log K_a = \Delta G^\circ/(2.303RT)$

Thus, $E^\circ = -pK_a \times (2.303RT/nF) = -59.2\text{mV} \times pK_a$

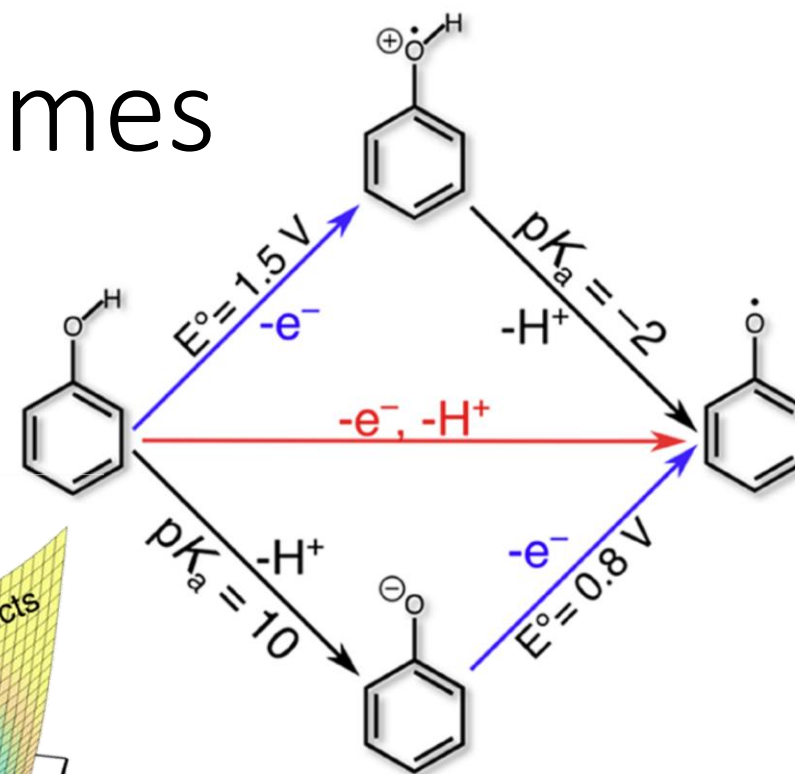
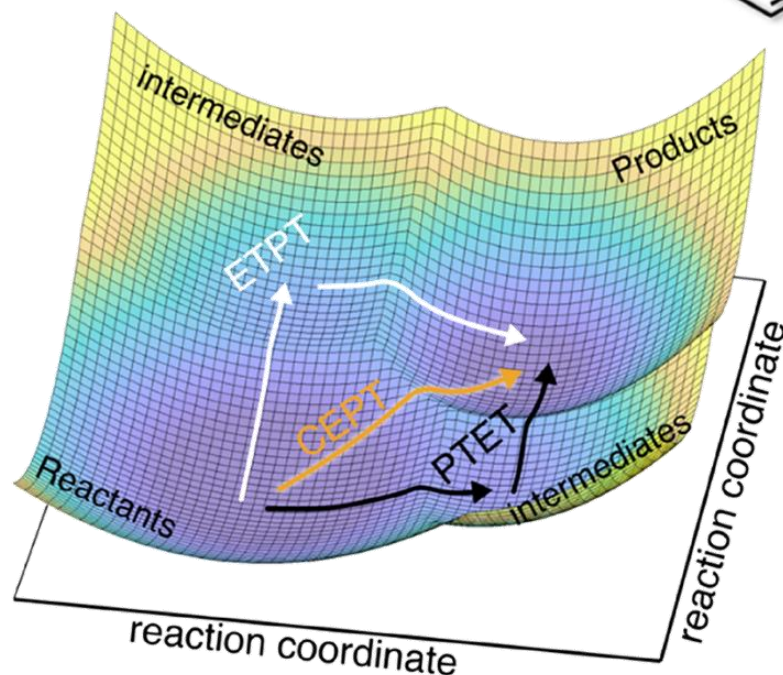
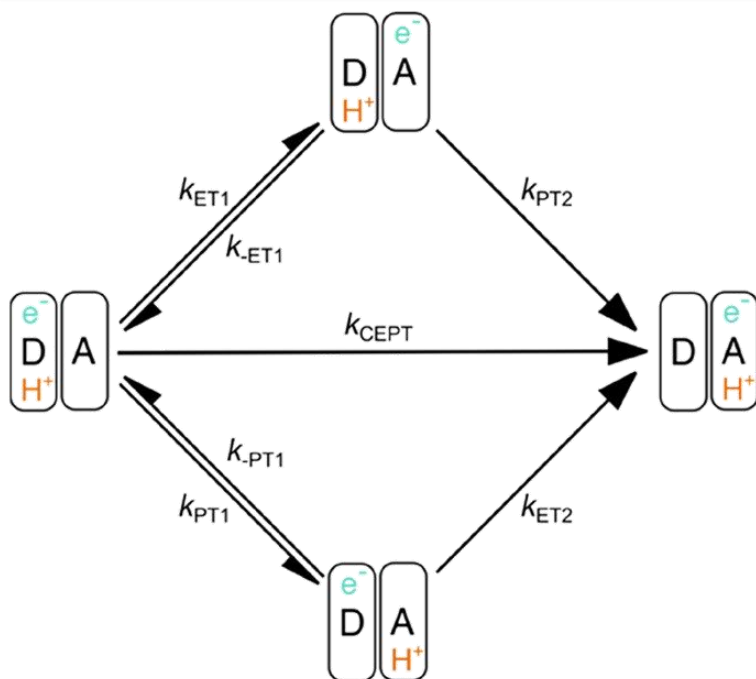
Does Bottom Route = Top Route?

$10(-0.0592V) + -0.8V = -1.5V + -2(-0.0592V)$

$-0.59V + -0.8V \approx -1.5V + 0.12V$... so, ~yes!

Förster Cube and Square Schemes

... oh, I see... by moving oppositely charged species in a concerted fashion, electrostatic (Born solvation) energy will be much smaller



... and this can constitute a ground-state, or excited-state, free energy landscape (N-dimensional potential energy surface)

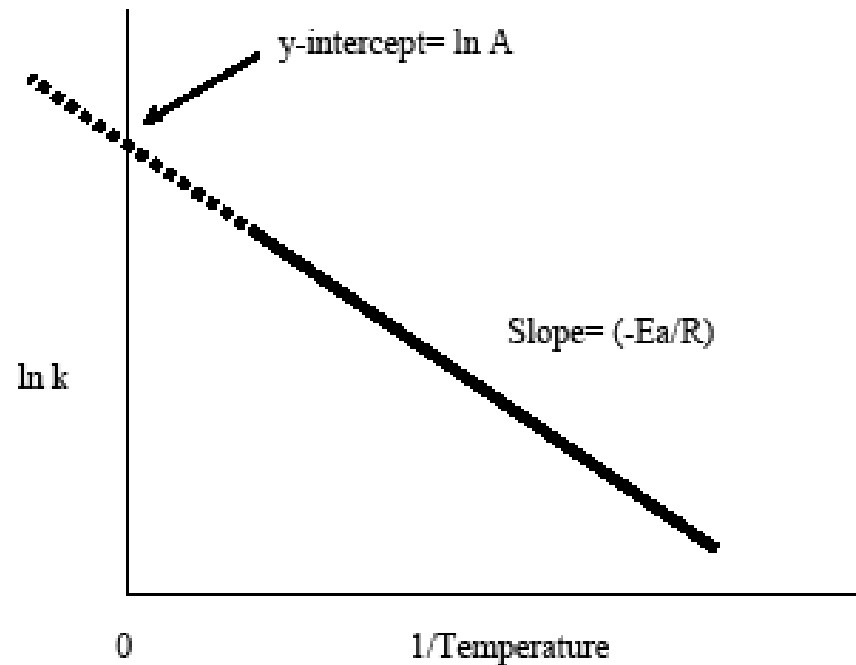
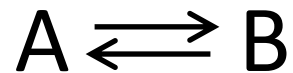
Figure 2. (Left) Square scheme that summarizes the mechanisms by which proton-coupled electron transfer can proceed. The edges of the square show the sequential mechanisms with ETPT and PTET on the top and bottom, respectively. The pathway bisecting the square is concerted, where e^- and H^+ are transferred without the formation of an intermediate species. Note that the donor and acceptor units for ET and PT can be the same or different species. (Right) Illustration of the three main mechanisms for PCET, each with a distinct transition state.

Activation Energies

Arrhenius (1889)

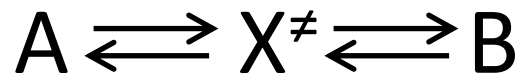
empirical rate constant equation

$$k_f = A e^{-\frac{E_a}{RT}} \dots \text{pre-exponential factor, } A, \text{ has units of } s^{-1} \quad \ln k$$



Eyring–Polanyi–Evans (1930s)

theoretical rate constant equation (from **transition-state theory / activated complex theory**)



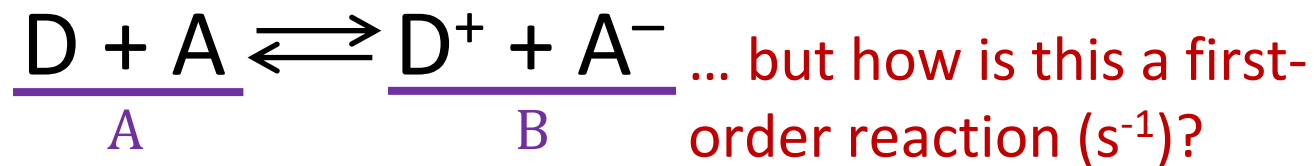
$$k_f = \kappa \nu K^\ddagger = \frac{\kappa k_B T}{h} K^\ddagger \dots \text{with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu \text{ (s}^{-1}\text{)}$$

... and $R = N_A k_B \dots$ and $\frac{\kappa k_B T}{h}$ has units of s^{-1}

$$k_f = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{\kappa k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \dots \text{and so } A \text{ contains } \Delta S^\ddagger$$

... what is the largest predicted pre-exponential factor at 25 °C? $(161 \text{ fs})^{-1} = (1.61 \times 10^{-13} \text{ s})^{-1}$

Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^\ddagger}{kT}\right) \dots \frac{2\pi|H_{\text{DA}}|^2}{\hbar\sqrt{4\pi\lambda kT}} \text{ has units of s}^{-1}$$



Eyring–Polanyi–Evans (1930s)

theoretical rate constant equation (from **transition-state theory / activated complex theory**)

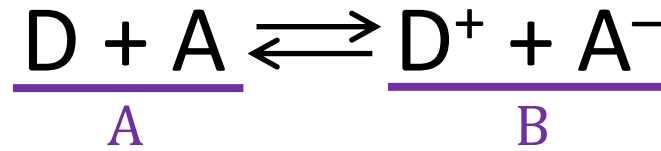
$$k_f = \kappa \nu K^\ddagger = \frac{\kappa k_{\text{B}}T}{h} K^\ddagger \dots \text{ with } \mathbf{transmission\ coefficient, } \kappa, \text{ and } \mathbf{vibrational\ frequency, } \nu \text{ (s}^{-1}\text{)}$$

... and $R = N_A k_{\text{B}} \dots$ and $\frac{\kappa k_{\text{B}}T}{h}$ has units of s^{-1}

$$k_f = \frac{\kappa k_{\text{B}}T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{\kappa k_{\text{B}}T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \dots \text{ and so } A \text{ contains } \Delta S^\ddagger$$

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quantum adiabatic
electronic coupling

classical nuclear free-
energy dependence

$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

proportional to $\frac{d\bar{\mu}_A}{dz}$

proportional to $\exp\left((\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2\right)$

... which term shall we discuss first?

... I don't know about you, but when given a choice between classical and quantum mechanical

... I go with classical... OK?

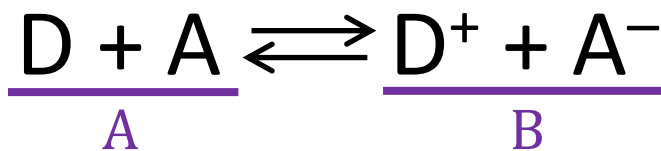
$$\Delta G_{\text{AB}}^\ddagger = \frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}}$$

... wait... there is a direct relation between thermodynamics (ΔG_{AB}^0) and kinetics ($\Delta G_{\text{AB}}^\ddagger$)?

... this makes sense since $\frac{d\bar{\mu}_A}{dz}$ drives transport... *which can be written as a chemical reaction*

... but that key relationship is quadratic... meaning a parabola? Huh?!?!?!?

Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^\ddagger}{kT}\right)$$

quantum adiabatic
electronic coupling

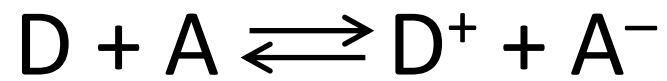
classical nuclear free-
energy dependence

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right) \dots \text{what kind of function is this?}$$

$$\Delta G_{\text{AB}}^\ddagger = \frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}}$$

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{\text{AB}}kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{\text{AB}}^0 - (-\lambda_{\text{AB}})}{\sqrt{2\lambda_{\text{AB}}kT}}\right)^2\right) \dots \text{does this help at all?}$$

Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

Standard Normal Distribution

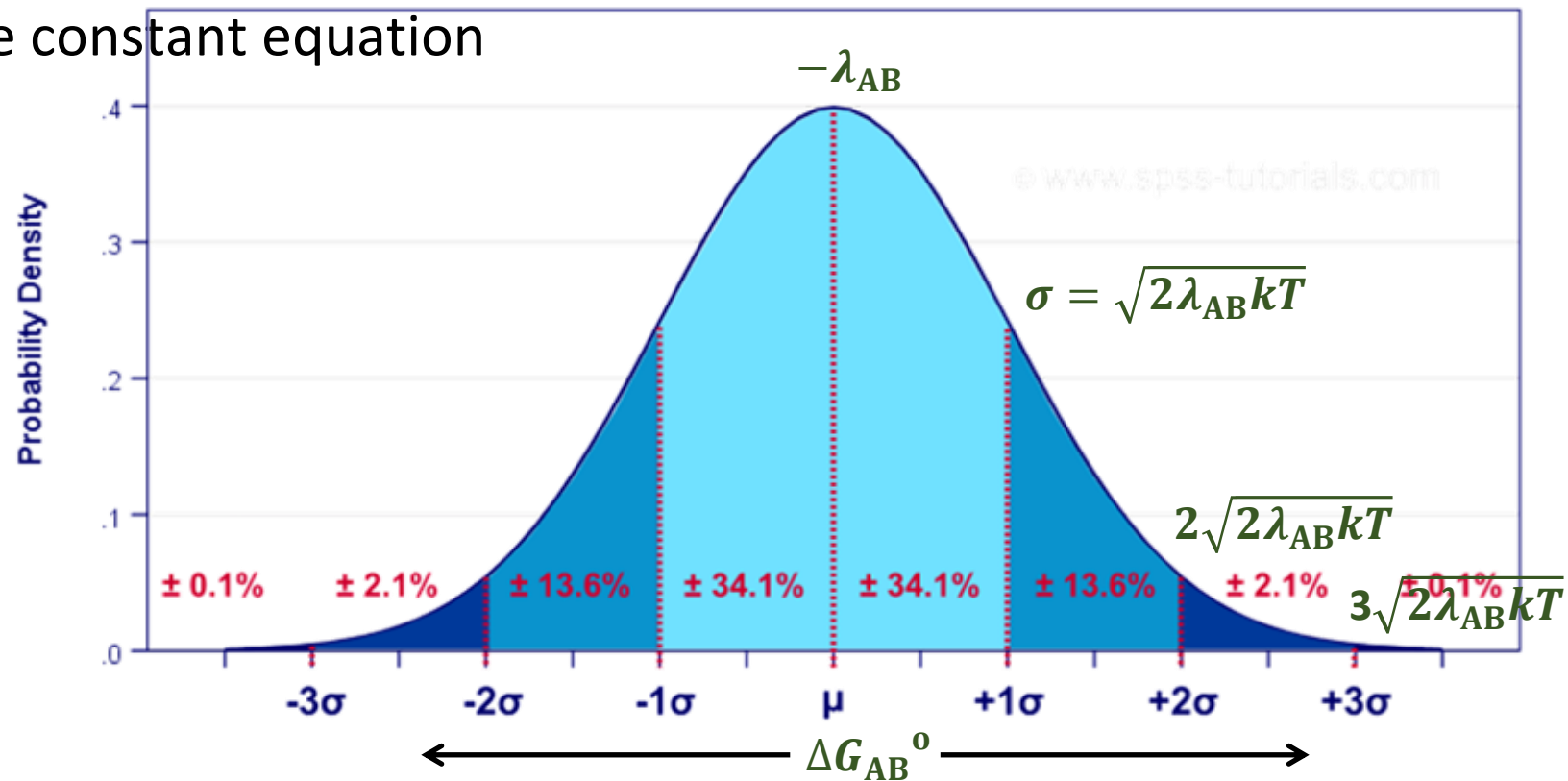
A

B

$\mu = 0 | \sigma = 1$

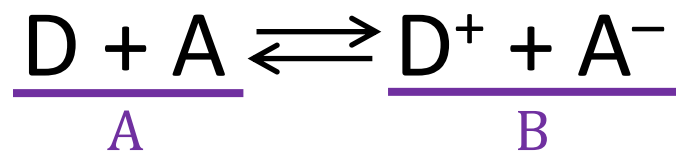
theoretical (semiclassical) rate constant equation

... wait... the classical component in Marcus electron-transfer theory is a **normal distribution** as a function of standard-state thermodynamic driving force (ΔG_{AB}^0)?... **Yep!**



$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{2\pi} \sqrt{2\lambda_{\text{AB}} kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{\text{AB}}^0 - (-\lambda_{\text{AB}})}{\sqrt{2\lambda_{\text{AB}} kT}}\right)^2\right) \dots \text{does this help at all?}$$

Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

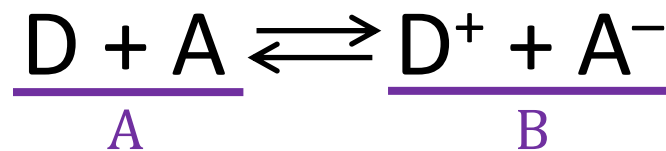
$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

$\ln k_{\text{ET}}$

0 $-\Delta G_{\text{AB}}^0$



Marcus–Hush Theory



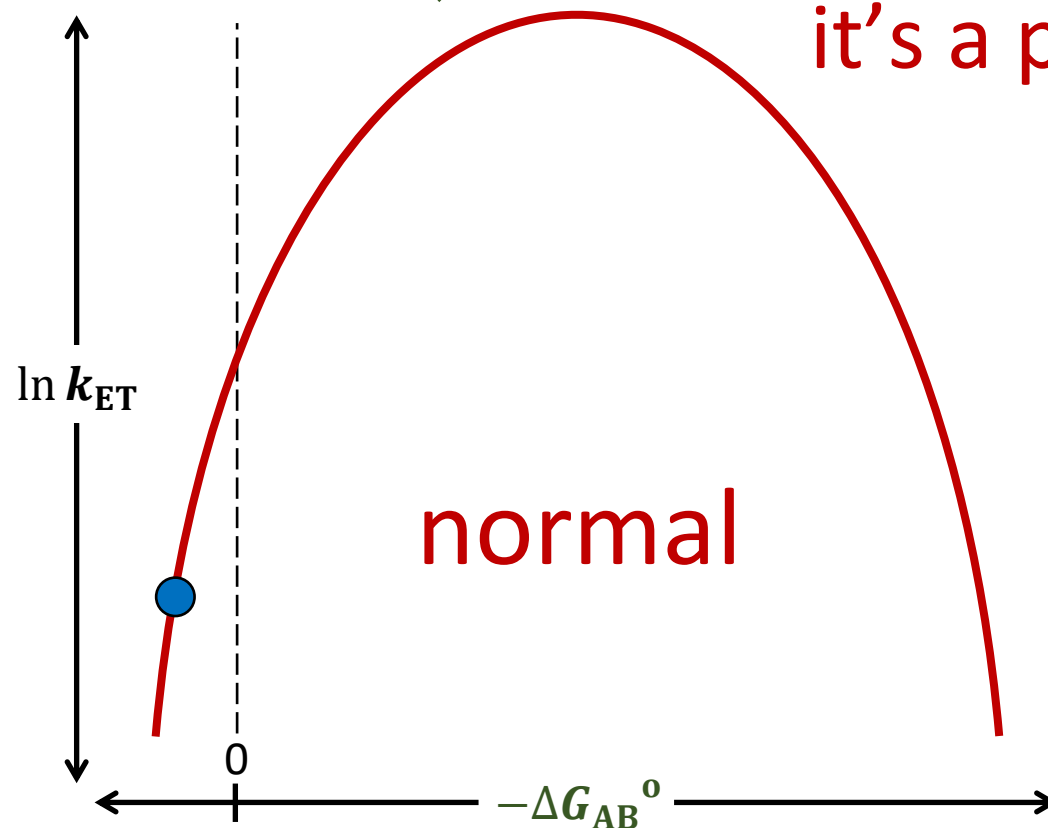
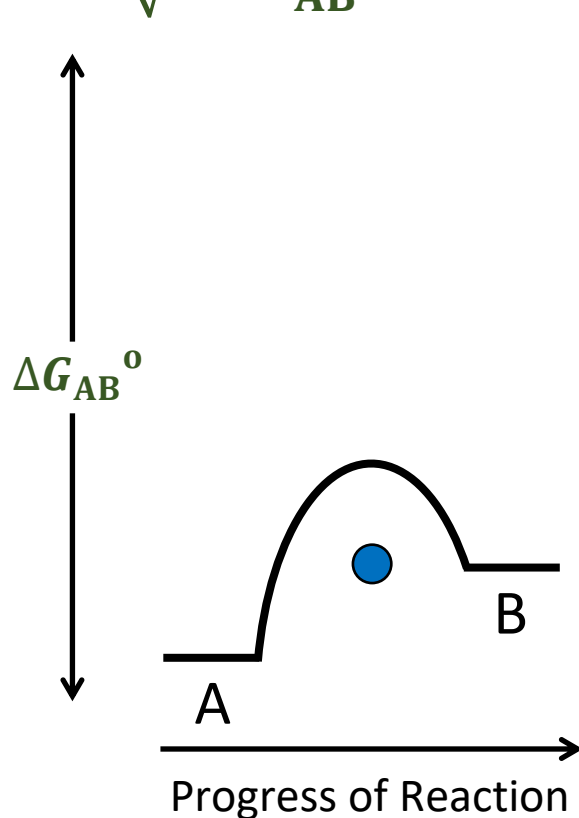
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

How can a thermodynamically unfavorable reaction proceed?

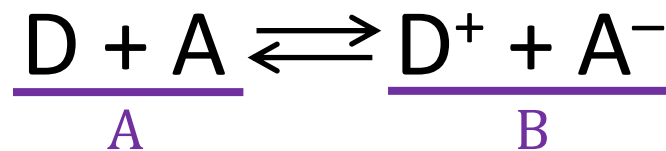
Mass Action!



it's a parabola

normal

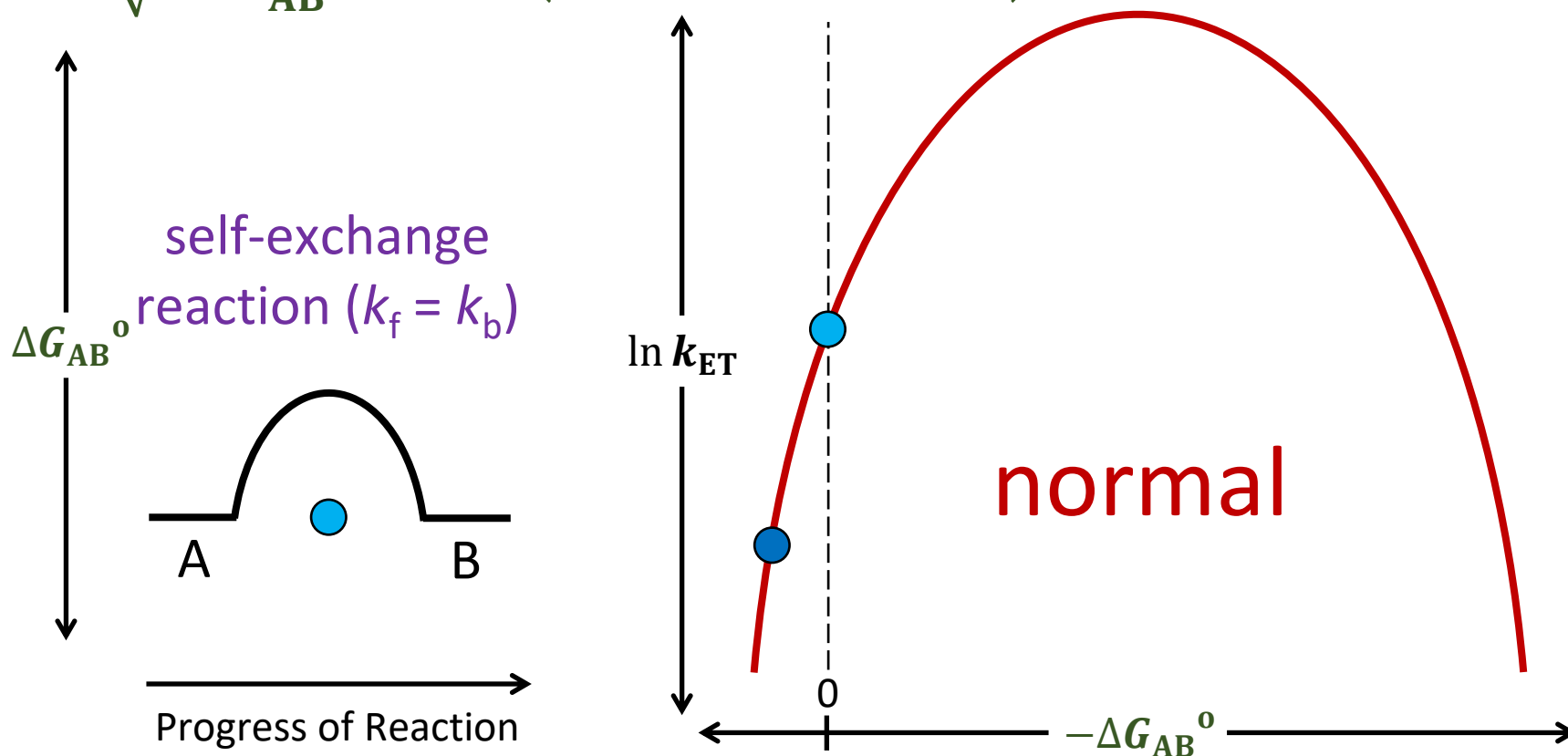
Marcus–Hush Theory



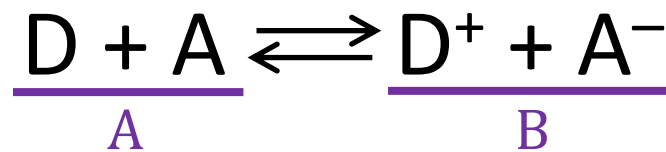
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$



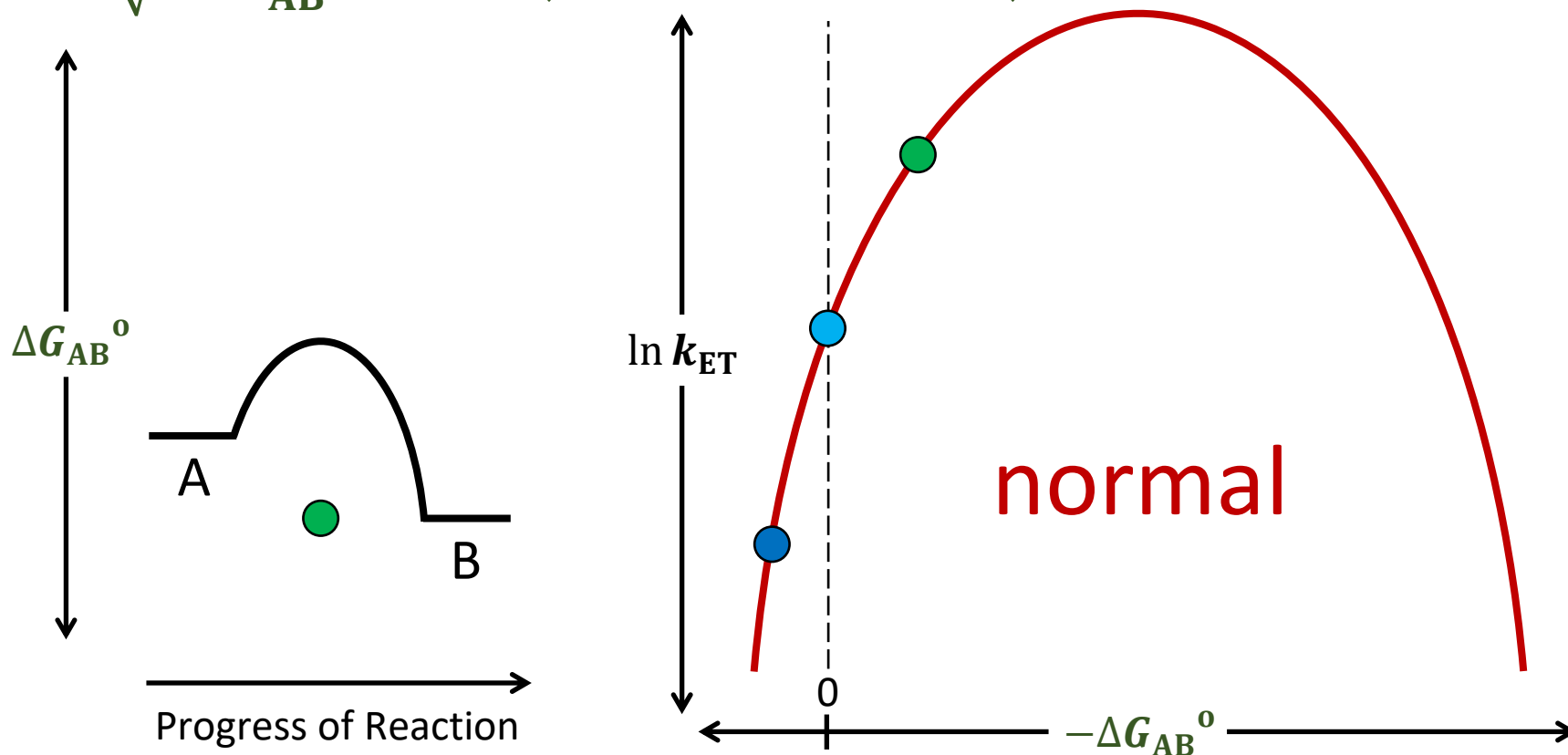
Marcus–Hush Theory



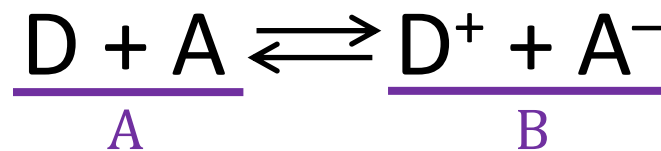
Marcus–Hush (1950s–1960s)

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$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$



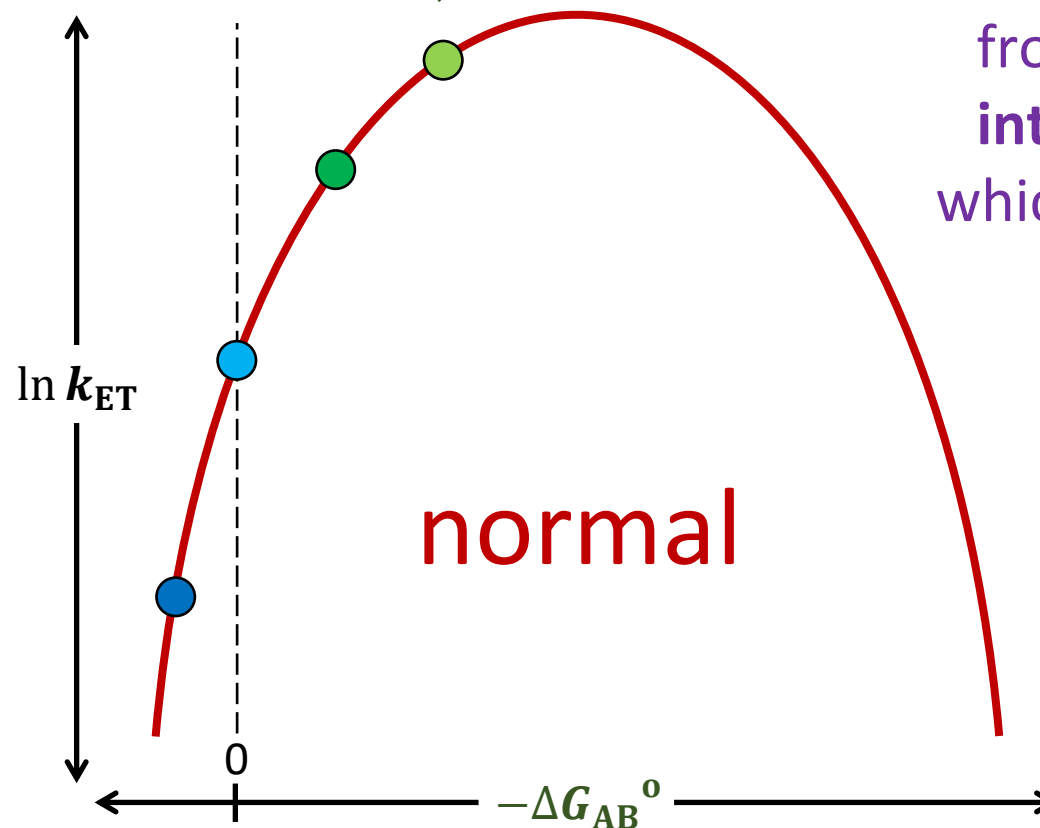
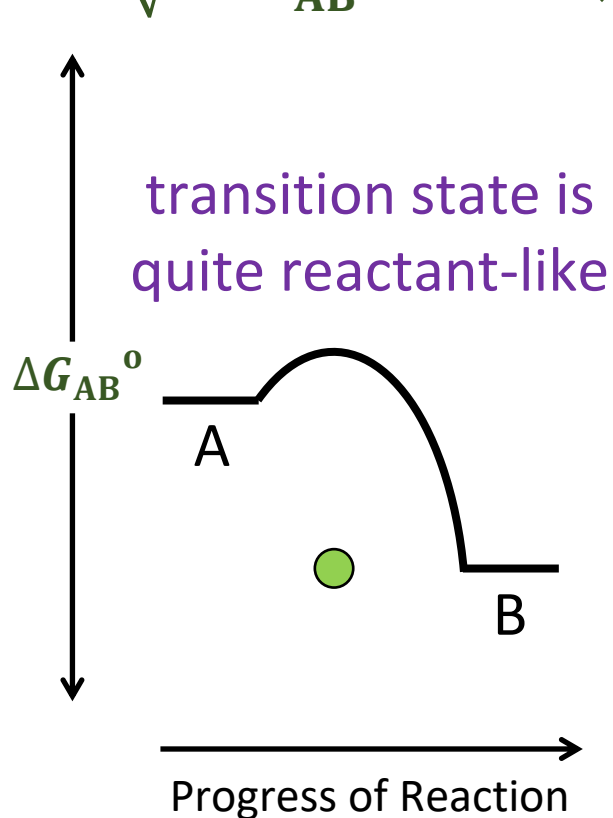
Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

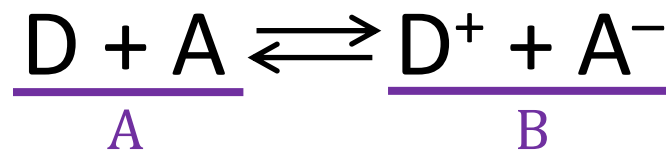
theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$



Note that a **transition state** only lasts on the order of a bond vibration ($h/k_{\text{B}}T \approx 160$ fs) and differs from a proper **intermediate**, which lasts much longer

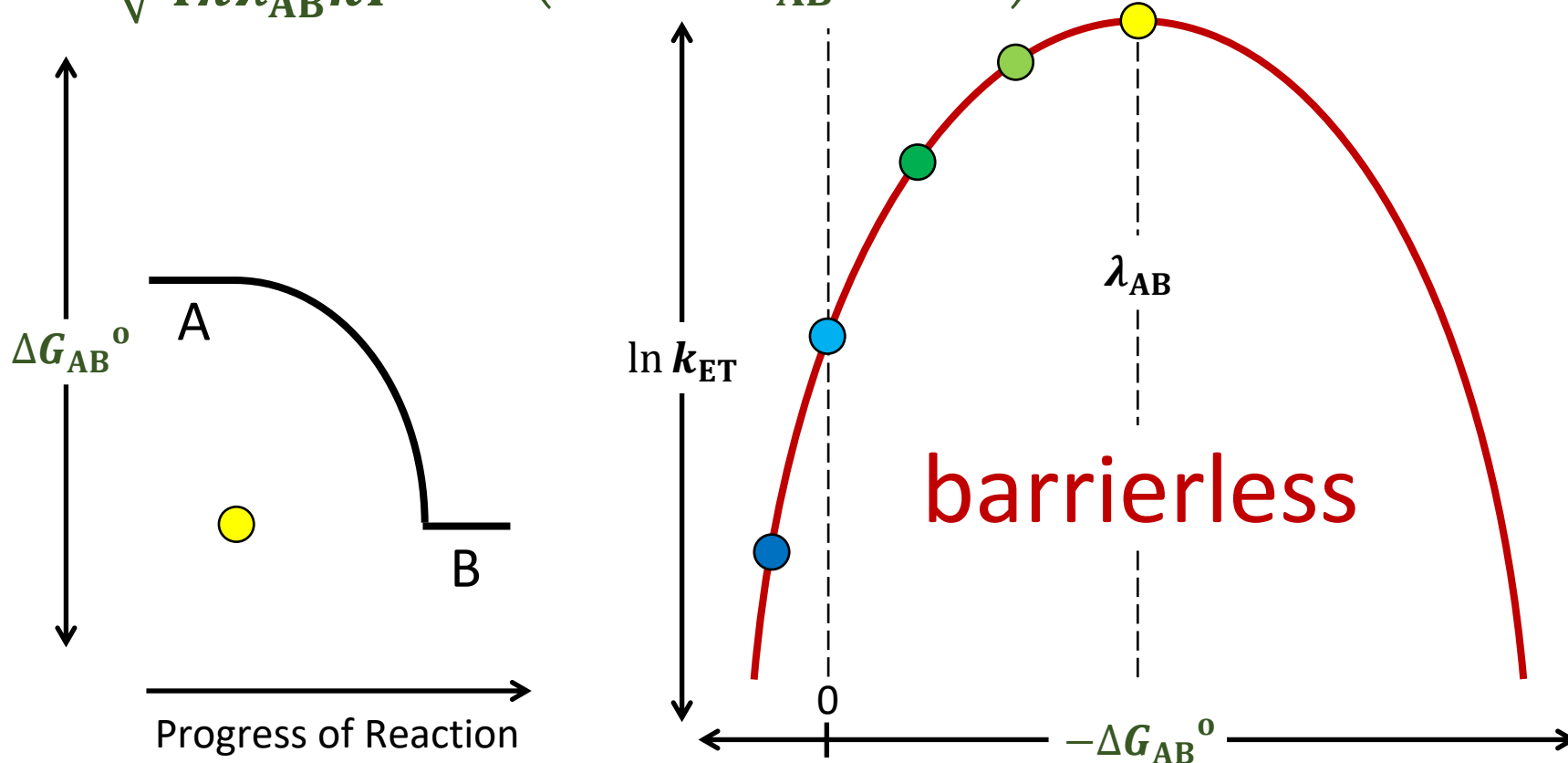
Marcus–Hush Theory



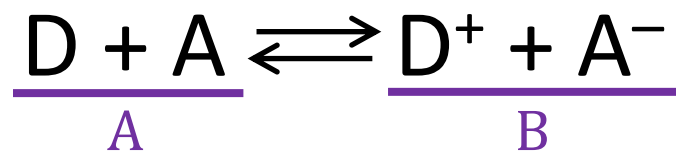
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$



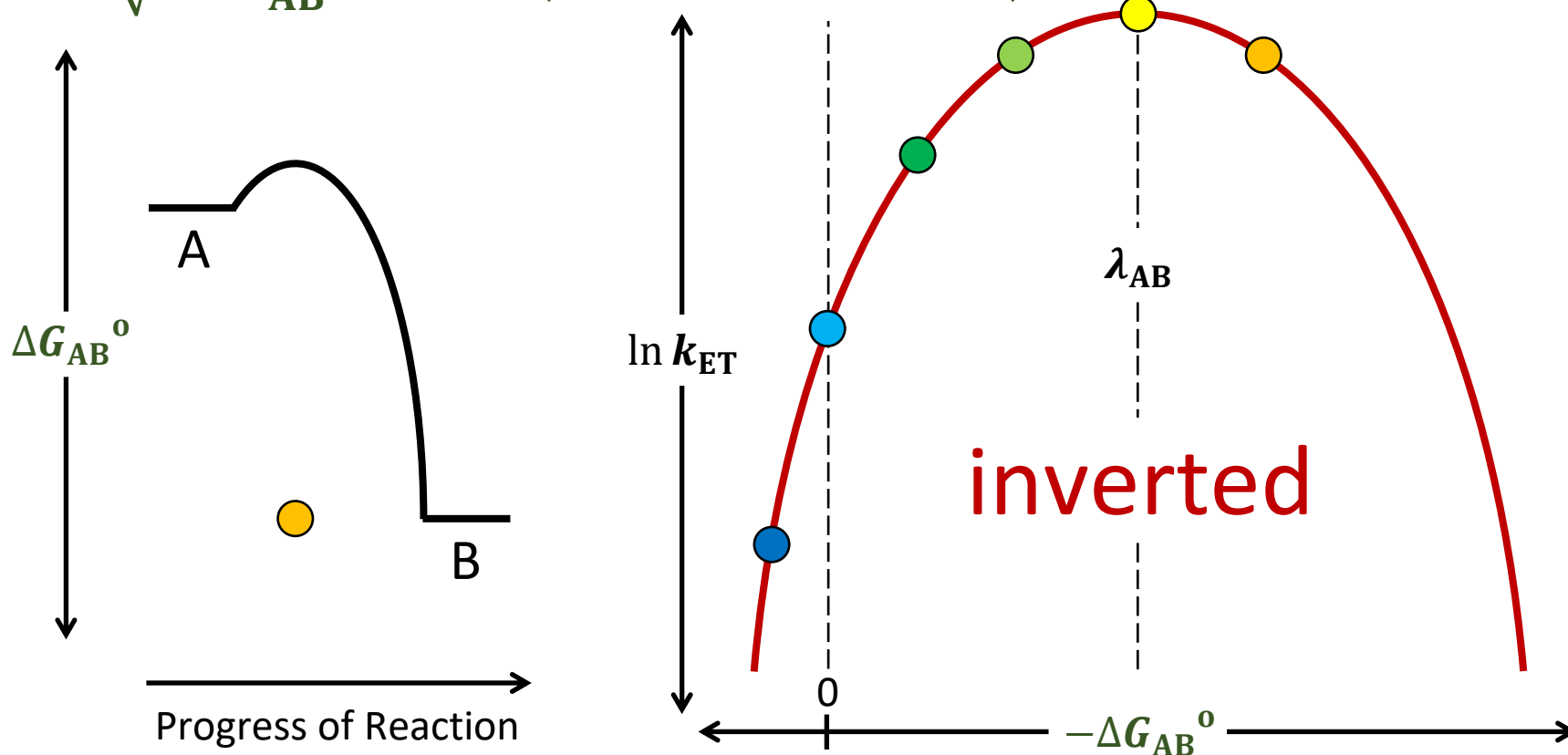
Marcus–Hush Theory



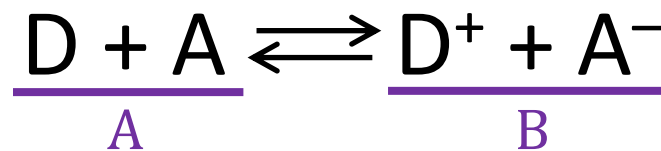
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Marcus–Hush Theory



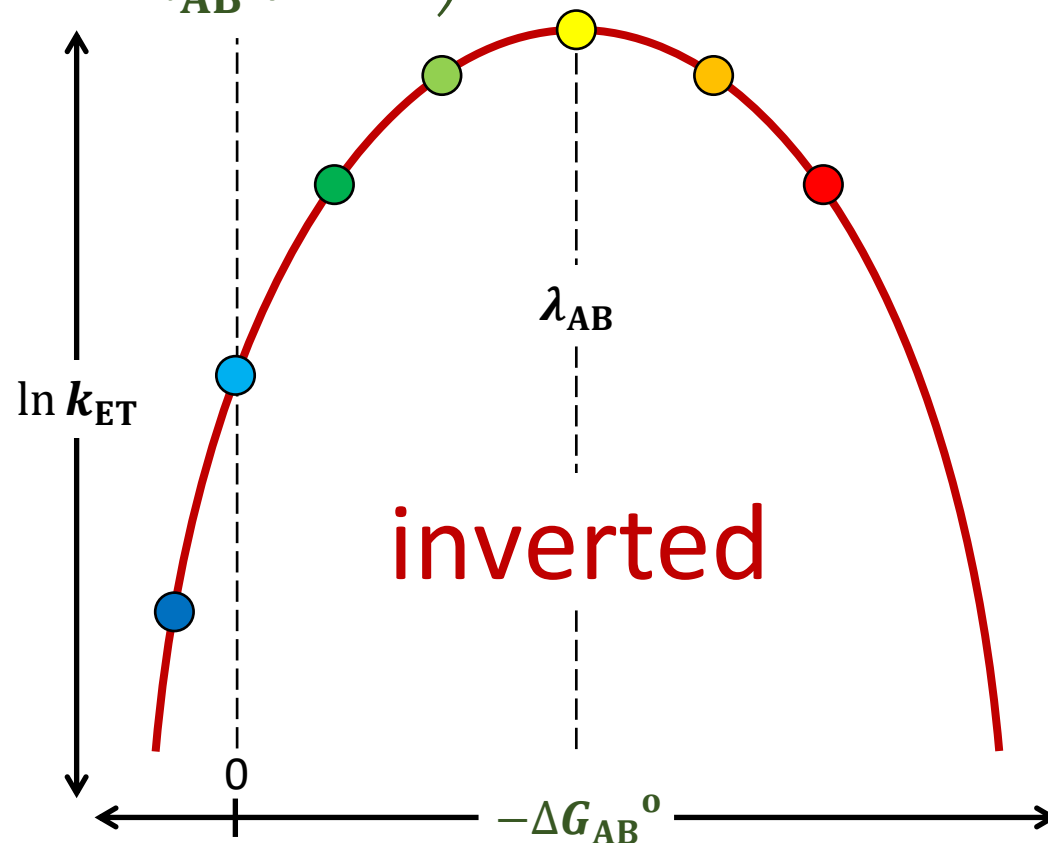
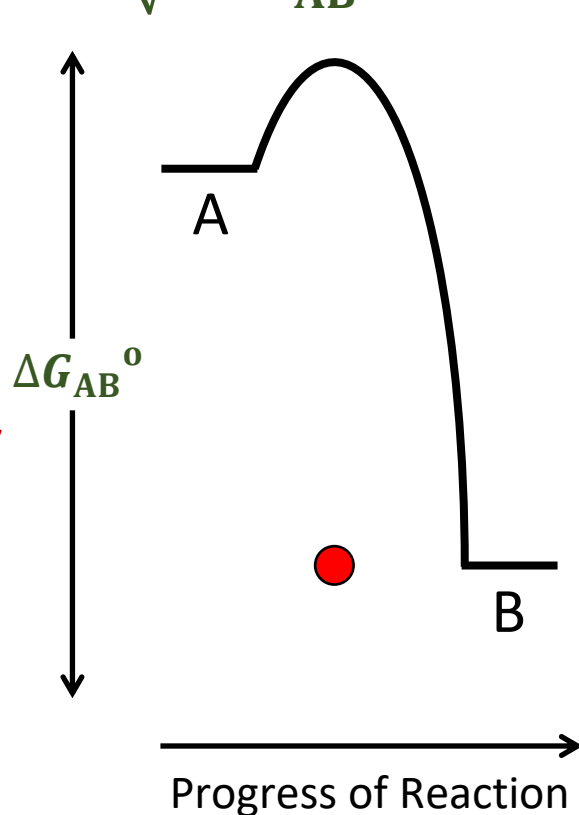
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

... this looks odd...

... but what did we expect from a General Chemistry cartoon



Outer Reorganization Energy

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theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{kT}\right)$$

$$\Delta G_{\text{AB}}^{\ddagger} = \frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}}$$

... but what causes this parabolic relationship?...

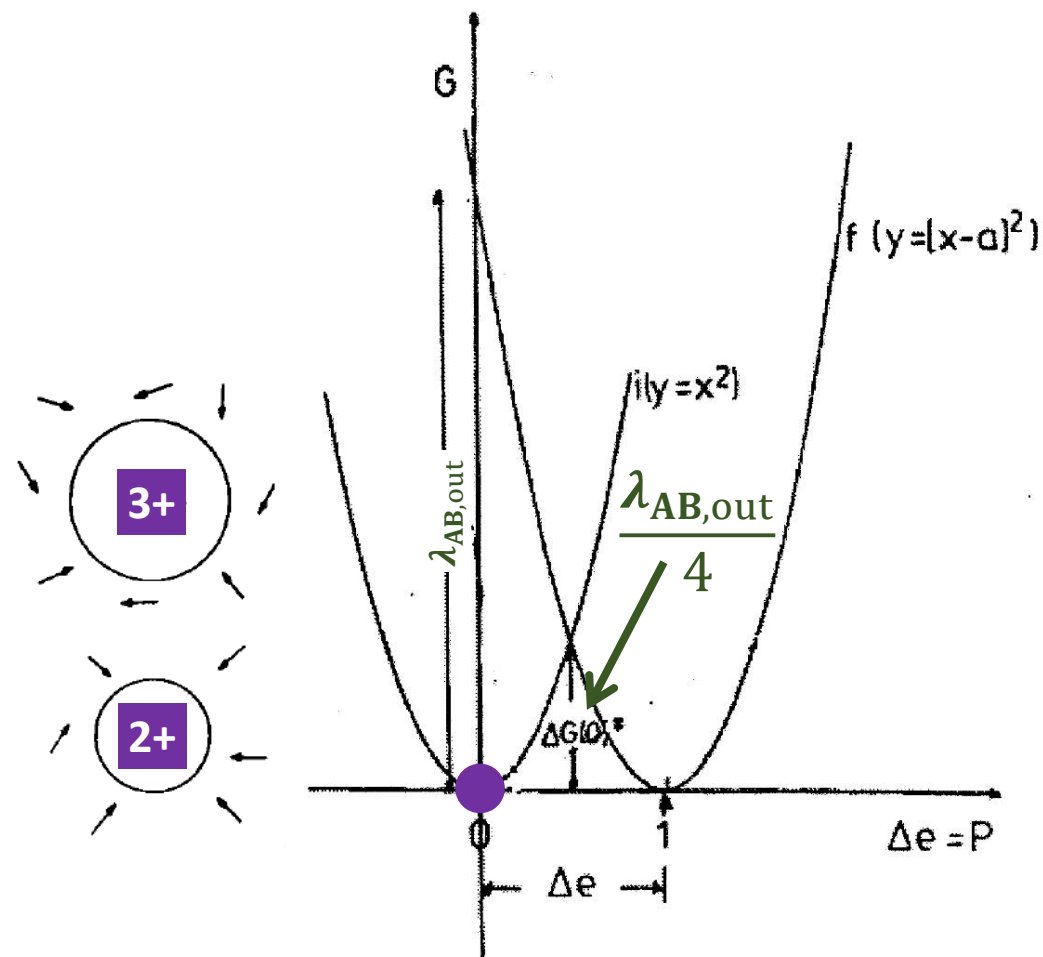
... what physical expression results in a quadratic dependence on **charge**?

... **classical electrostatics... of the solvent!**

... dielectric continuum model...

... $G_{\text{out}} \approx 1$ eV in water

... G_{out} decreases as permittivity decreases



$$\lambda_{\text{out}} = \left(\frac{1}{2r_{\text{D}}} + \frac{1}{2r_{\text{A}}} - \frac{1}{R_{\text{DA}}} \right) \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_{\text{s}}} \right) (\Delta e)^2$$

Outer + Inner Reorganization Energy

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

This theory came about by answering the following question: For an electron-transfer event, how does one satisfy the Franck–Condon principle and the conservation of energy?

- Franck–Condon principle: Nuclei are fixed during electron-transfer between orbitals... Born–Oppenheimer approximation is relevant

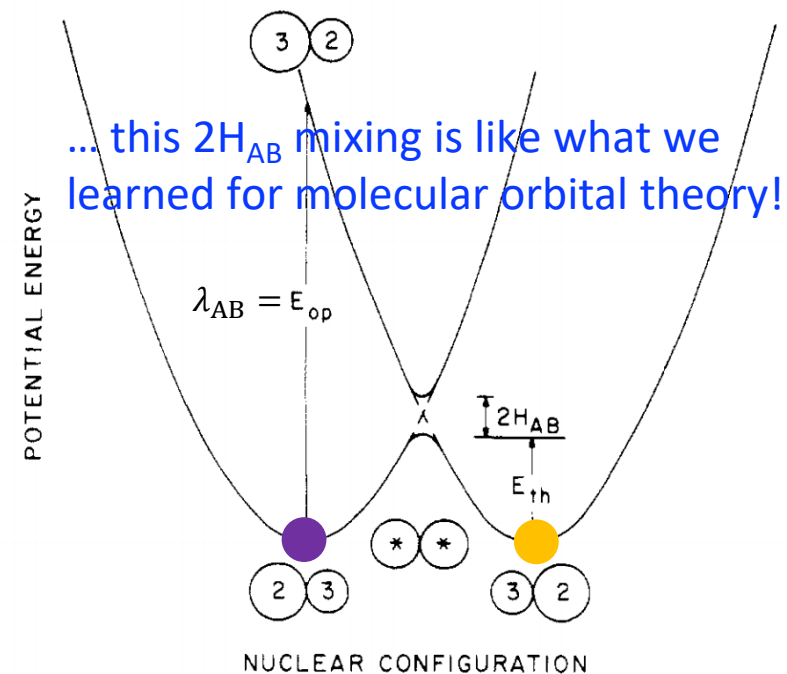
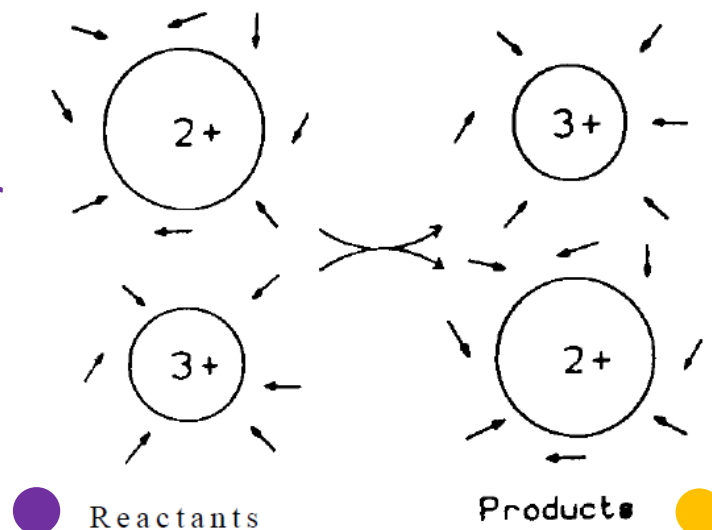
$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2} \sum_l f_l (\Delta q_{e,l})^2$$

... this is for a harmonic oscillator
... with force constants, f_l ...

... and yes, it's another parabola!

Electron Transfer in Solution

$$\lambda_{AB} = \lambda_{in} + \lambda_{out}$$



More Quantum Mechanics

But you still didn't tell us why we need to recall this equation

$$\hat{H}\psi_n(x) = (\hat{T} + \hat{V})\psi_n(x) = E_n\psi(x)$$

... we need to fill **internal energies**, E_n , with particles... okay.

Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\epsilon} \quad \mathbf{E} = -\frac{\partial \phi(x)}{\partial x}$$

$$\phi(r) = \frac{q}{4\pi\epsilon r}$$

for a point charge...
look familiar?

... and that under most chemical conditions, potential energy, $\hat{V}(x)$, is **electrostatic**, $\phi(x)$

... which is actually not so limiting because there are only 4-ish forces of Nature

... and while we're at it, let's (re)learn **overlap integral** (S_{nm}), **expectation value** ($\langle p_n \rangle$), **bra-ket notation** ($\langle \psi_n | \psi_m \rangle$), and exponential **tunneling probability**...

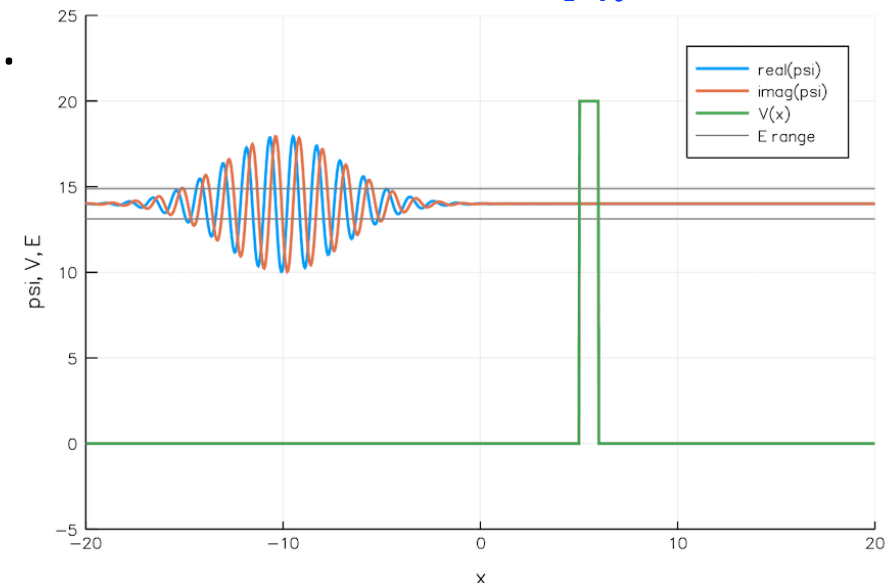
$$\text{Probability Density}(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$$

... with $\psi_n^*(x)$ (complex conjugate)

$$\text{Overlap integral, } S_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x) dx = \langle \psi_n | \psi_m \rangle$$

... with $\langle \Psi_n |$ ("bra") and $|\Psi_m \rangle$ ("ket")

$$\text{Mean Energy, } \langle E_n \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\hat{H}\Psi_n(x,t)dx}{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_n(x,t)dx} = \langle \Psi_n | \hat{H} | \Psi_n \rangle = \langle \hat{H} \rangle$$



Molecular Orbital Theory

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{\Delta G_{\text{AB}}^{\ddagger}}{kT}\right)$$

quantum adiabatic
electronic coupling

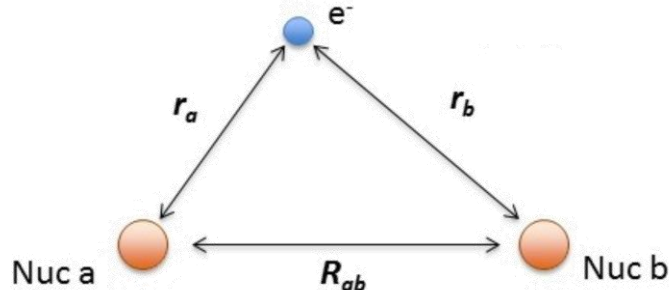
classical nuclear free-
energy dependence

... remember the simplicity of H_2^+ ... which resembles λ_{out} math

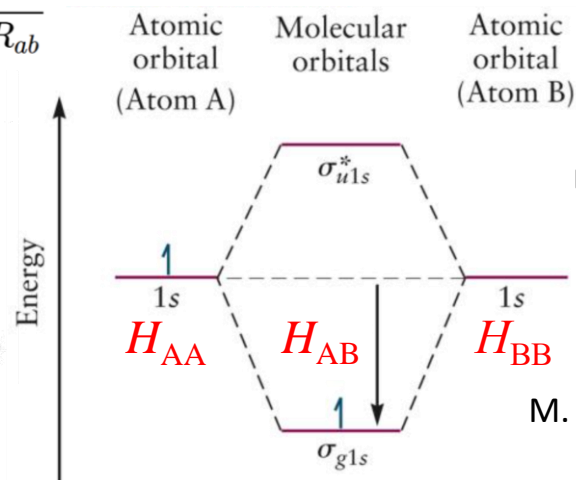
$$\hat{H}(r, R_{ab}) = -\frac{\hbar^2}{2m} \nabla_a^2 - \frac{\hbar^2}{2m} \nabla_b^2 - \frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

matrix

$$\hat{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$



$$E_{\pm}(R) = \frac{1}{1 \pm S(R)} (H_{AA}(R) \pm H_{AB}(R))$$

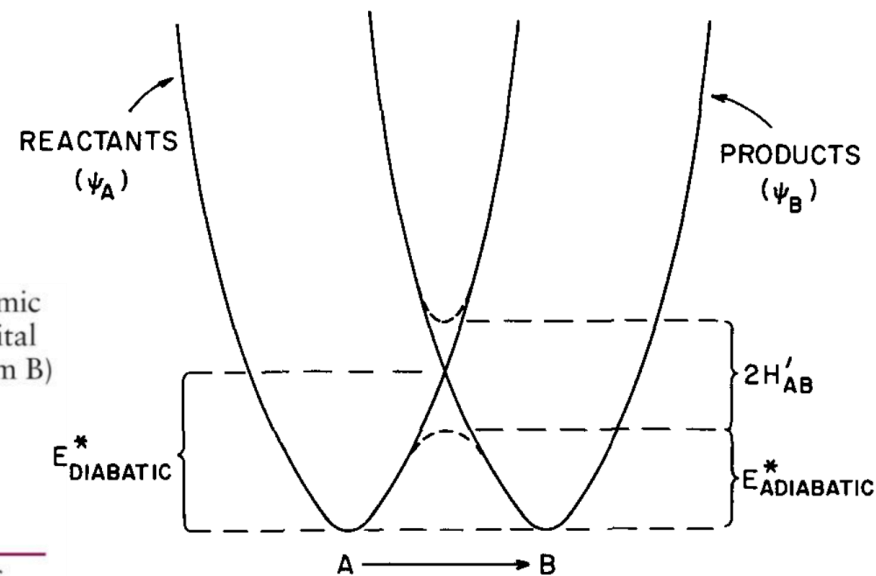


Molecular Orbital Theory

linear combination of atomic orbitals

(50) The splitting at the intersection is only equal to $2H_{\text{AB}}$ when the overlap of the electronic wave functions can be neglected. More generally it is equal to $2(H_{\text{AB}} - S_{\text{AB}}H_{\text{AA}})/(1 - S_{\text{AB}}^2)$ where $S_{\text{AB}} = \langle \psi_A | \psi_B \rangle$.

... which equals $(E_+ - E_-)$ from MO Theory



M. D. Newton, *Int. J. Quantum. Chem.*, **1980**, *18*, 363–391
N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

Chemical Kinetics (*summary for today*)

- Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer
- Mass action, Microscopic reversibility, Förster cube, Square schemes, Rate constants, Activation energies, Transition-state theory, Marcus–Hush theory, Transition-state character, Reorganization energies (outer and inner)
- Linear free energy relationships, Charge transfer across electrified interfaces, Butler–Volmer equation, Fermi’s golden rule, Solid-state physics, Marcus–Gerischer theory
- Rate-determining step, Steady-state & Pre-equilibrium approximations, Langmuir/Frumkin isotherms