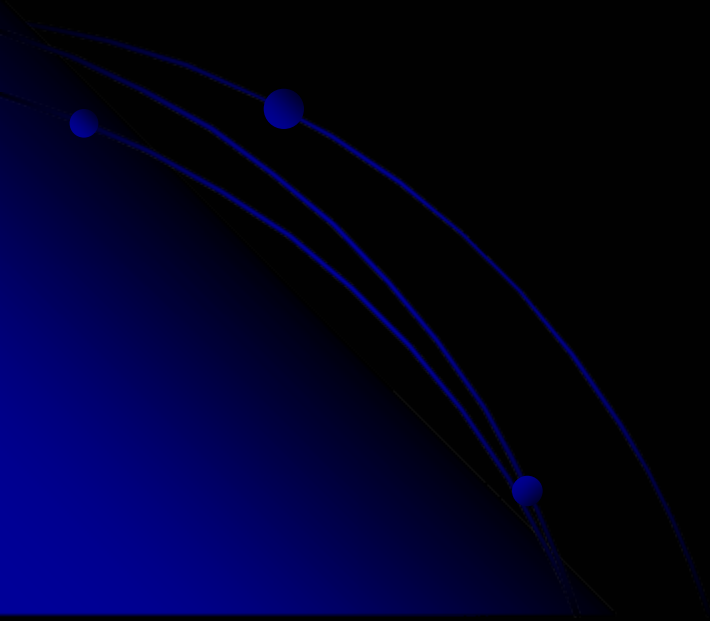


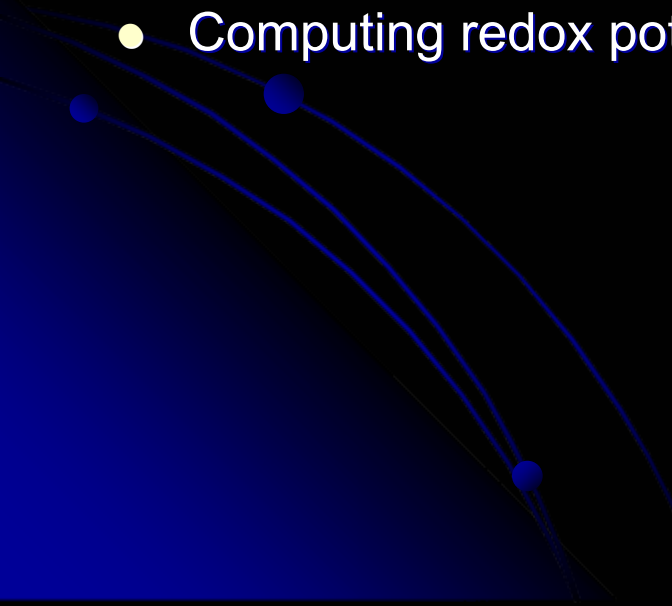
Gherman Group Meeting

Thermodynamics and Kinetics and Applications

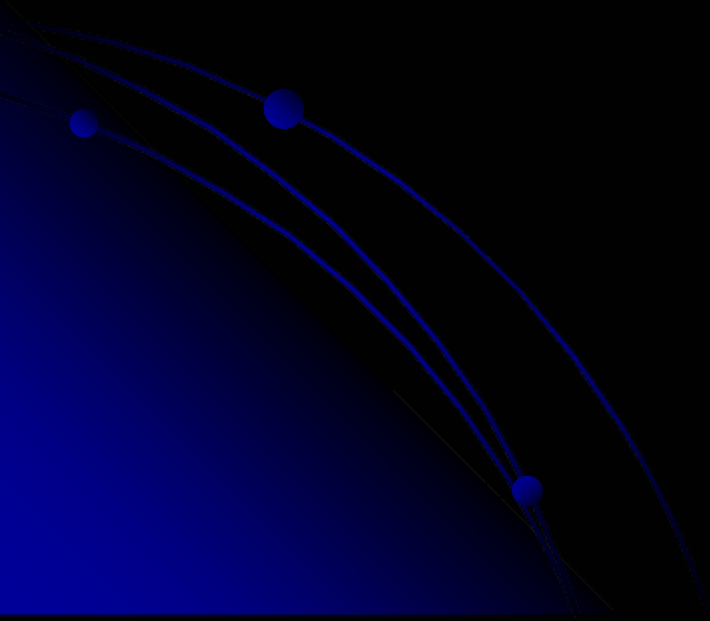
June 25, 2009



Outline

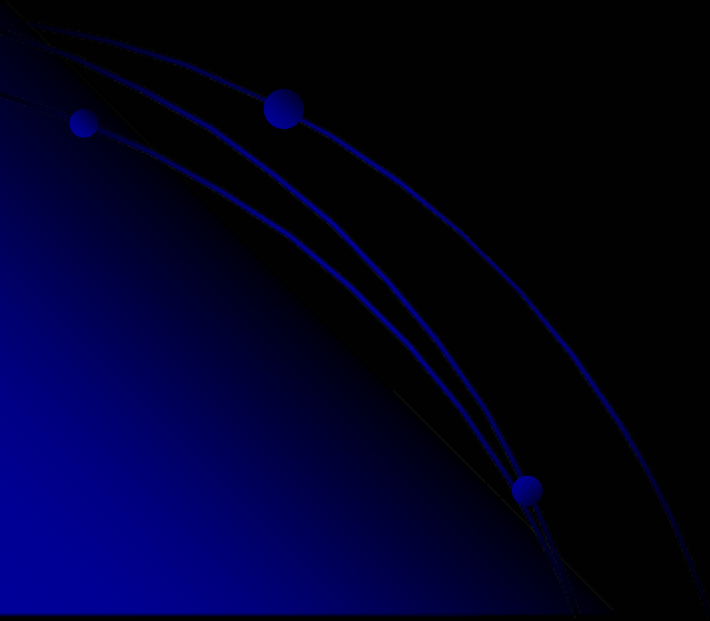
- Calculating H_f , S , G_f
 - Components which contribute to H_f , S , G_f
 - Calculating ΔH° , ΔS° , ΔG°
 - Calculating rate constants for chemical reactions
-
- Computing pK_a values
 - Computing electron affinities
 - Computing redox potentials
- 

Part 1: Thermodynamics



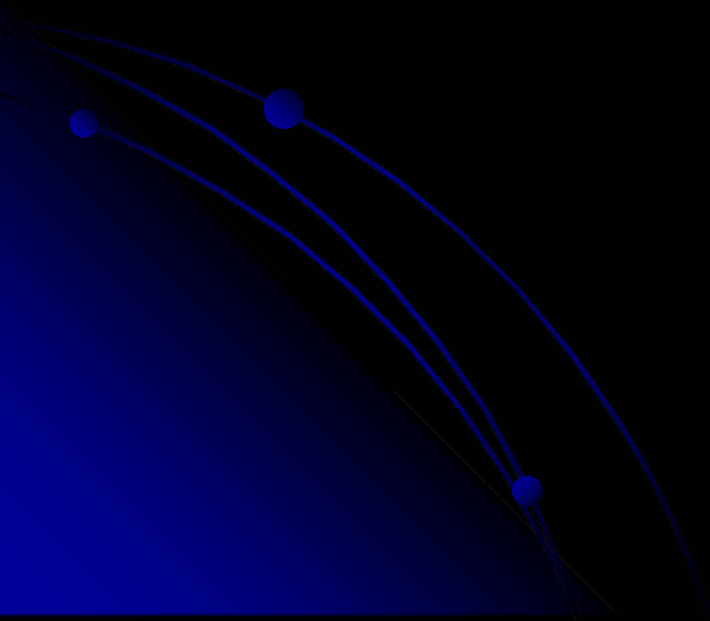
Calculating H_f , S , G_f

- $H_f^\circ = E_{\text{SCF}} + \text{ZPE} + E_{\text{solvation}} + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + H_{\text{elec}}$



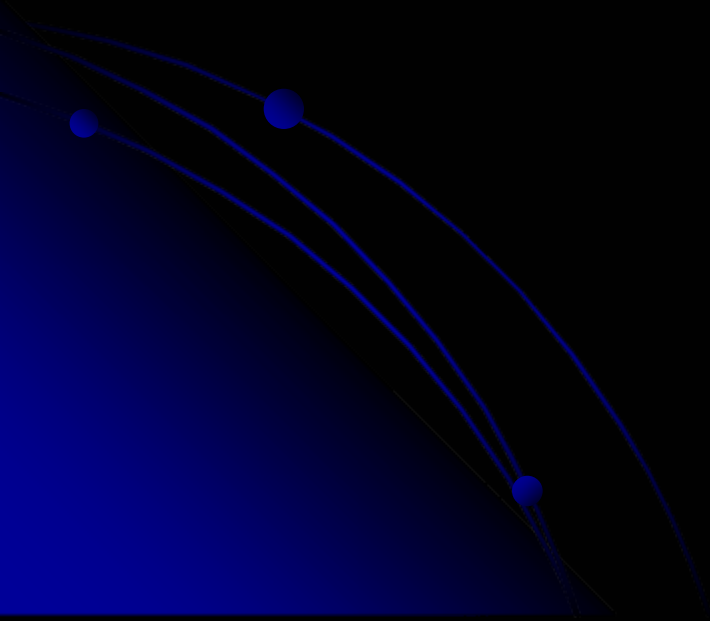
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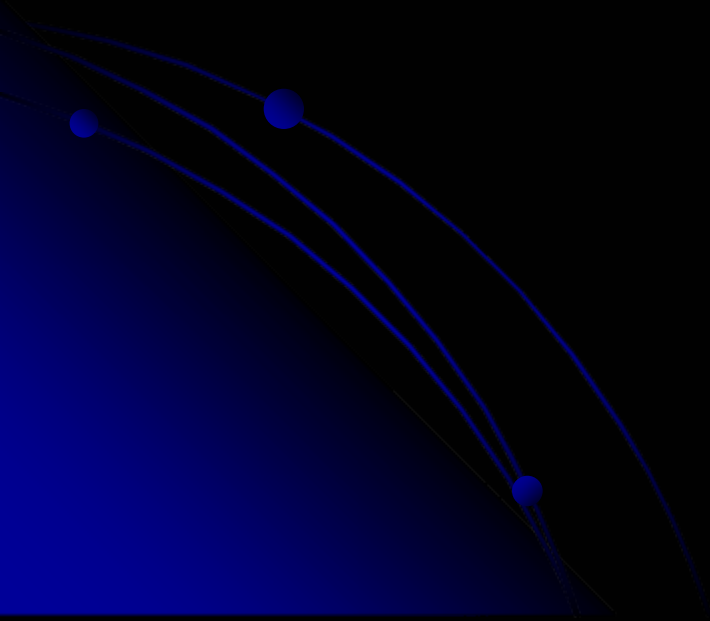
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Calculating H_f , S , G_f

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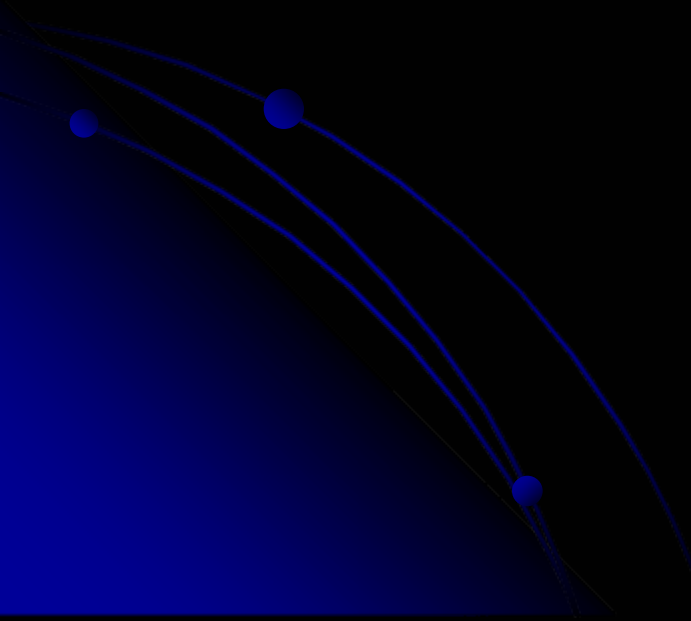
- Components of enthalpy / entropy...
 - SCF energy
 - Zero-point energy
 - molecular translation
 - molecular rotation
 - molecular vibration
 - electronics

Energy Components (1)

- Zero-point energy

$$ZPE = \sum_i^{\text{modes}} \frac{1}{2} h \omega_i$$

- sum of energies for lowest vibrational level for each vibration
- harmonic oscillator approximation



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- Translation

- $U_{\text{trans}} = 3/2 RT$ $H_{\text{trans}} = U_{\text{trans}} + PV = U_{\text{trans}} + RT = 5/2 RT$

- $$S_{\text{trans}}^{\circ} = R \left\{ \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{V^{\circ}}{N_A} \right] + 5/2 \right\}$$

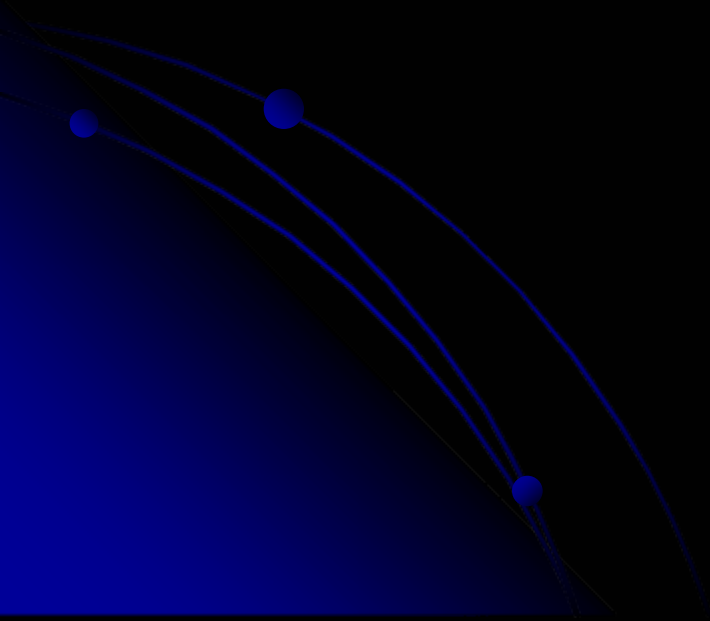
- particle in a 3-dimensional box
- V in formula \rightarrow standard state must be defined
 - standard state $P^{\circ} = 1 \text{ atm}$ ($V^{\circ} = 24.5 \text{ L}$ at 298 K)

Energy Components (2)

- Rotation
 - linear molecules

$$H_{rot}^{linear} = U_{rot}^{linear} = RT$$

$$S_{rot}^{linear} = R \left[\ln \left(\frac{8\pi^2 I k_B T}{\sigma h^2} \right) + 1 \right]$$



Energy Components (2)

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$$S_{rot}^{linear} = R \left[\ln \left(\frac{8\pi^2 I k_B T}{\sigma h^2} \right) + 1 \right]$$

- non-linear molecules

$$H_{rot}^{linear} = U_{rot}^{linear} = \frac{3}{2} RT$$

$$S_{rot}^{linear} = R \left[\ln \left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} \right]$$

- rigid-rotor approximation

- I, I_A, I_B, I_C – moments of inertia

- σ – symmetry number

- # of rotations that carry molecule into itself

- depends on point group (e.g. $C_1=1, C_{2v}=2, T_d=12$)

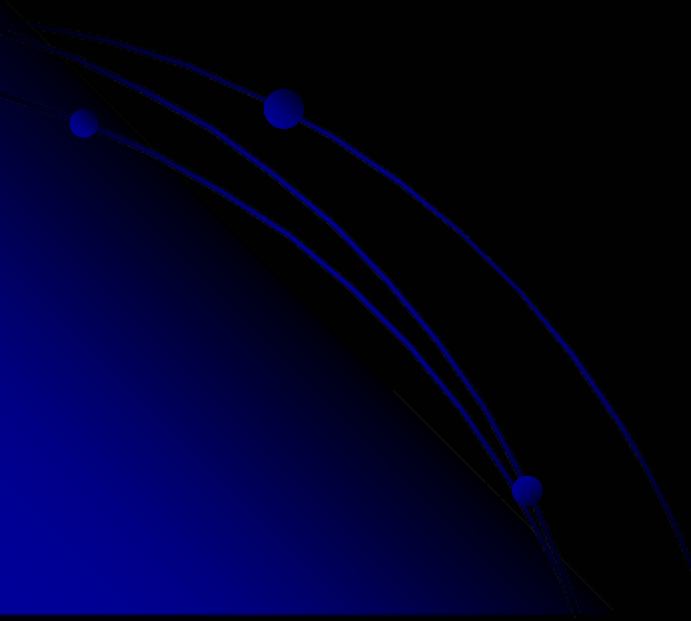
Energy Components (3)

- Vibration

$$H_{vib} = U_{vib} = R \sum_{i=1}^{3N-6(5)} \frac{h\omega_i}{k_B (e^{h\omega_i/k_B T} - 1)}$$

$$S_{vib} = R \sum_{i=1}^{3N-6(5)} \left[\frac{h\omega_i}{k_B T (e^{h\omega_i/k_B T} - 1)} - \ln(1 - e^{-h\omega_i/k_B T}) \right]$$

- harmonic oscillators



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- harmonic oscillators

- Electronic

- $H_{elec} = U_{elec} = 0$

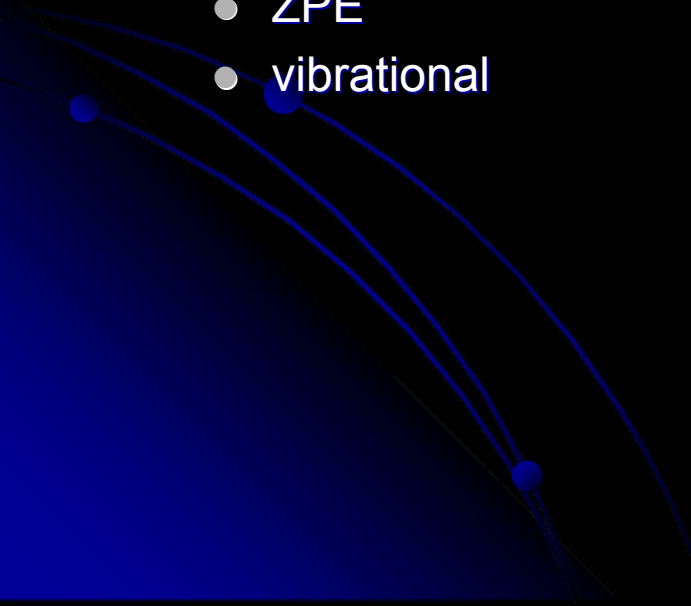
- $S_{elec} = R \ln(2S+1)$

- where $2S+1$ is the spin multiplicity

- $S = \frac{1}{2} * \#$ of unpaired e^-

Energy Components - Notes

- Independent of any QM calculation
 - translational, electronic
- Depend on geometry only:
 - rotational (provided an accurate geometry)
- Requiring an electronic structure calculation
 - E_{SCF}
 - ZPE
 - vibrational



Calculating ΔH , ΔS , ΔG

- $H_f^\circ = E_{\text{SCF}} + \text{ZPE} + E_{\text{solvation}} + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + H_{\text{elec}}$

$$H_f^\circ (0 \text{ K}) = E_{\text{SCF}} + \text{ZPE}$$

- $S^\circ = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}}$

- $G_f^\circ = H_f^\circ - TS^\circ$

- For a chemical reaction: $A + B \rightarrow C + D$

- $\Delta H^\circ = H_f^\circ(\text{C}) + H_f^\circ(\text{D}) - H_f^\circ(\text{A}) - H_f^\circ(\text{B})$

- $\Delta S^\circ = S^\circ(\text{C}) + S^\circ(\text{D}) - S^\circ(\text{A}) - S^\circ(\text{B})$

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Rate Constants

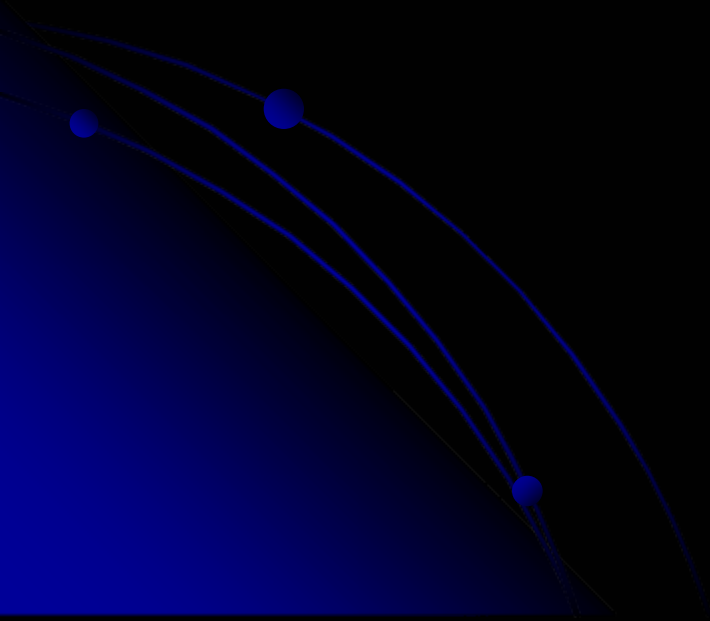
- Transition State Theory

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

- compare to Arrhenius expression

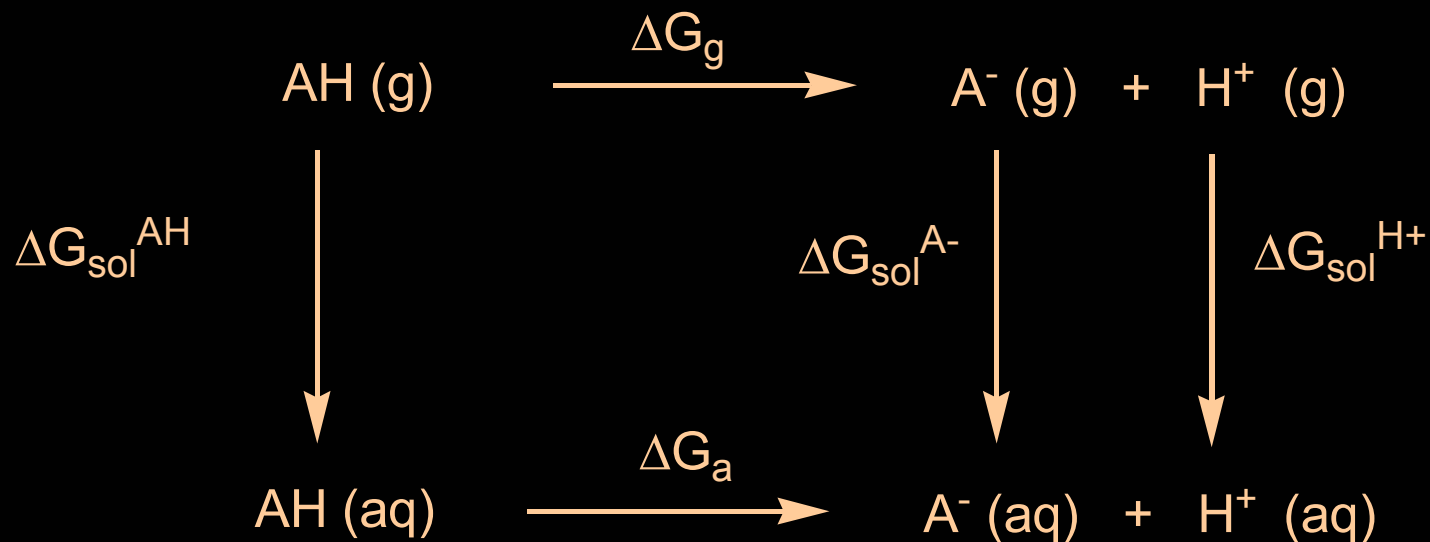
$$k = A e^{-\frac{E_a}{RT}}$$


Part 2: Applications of Thermodynamics



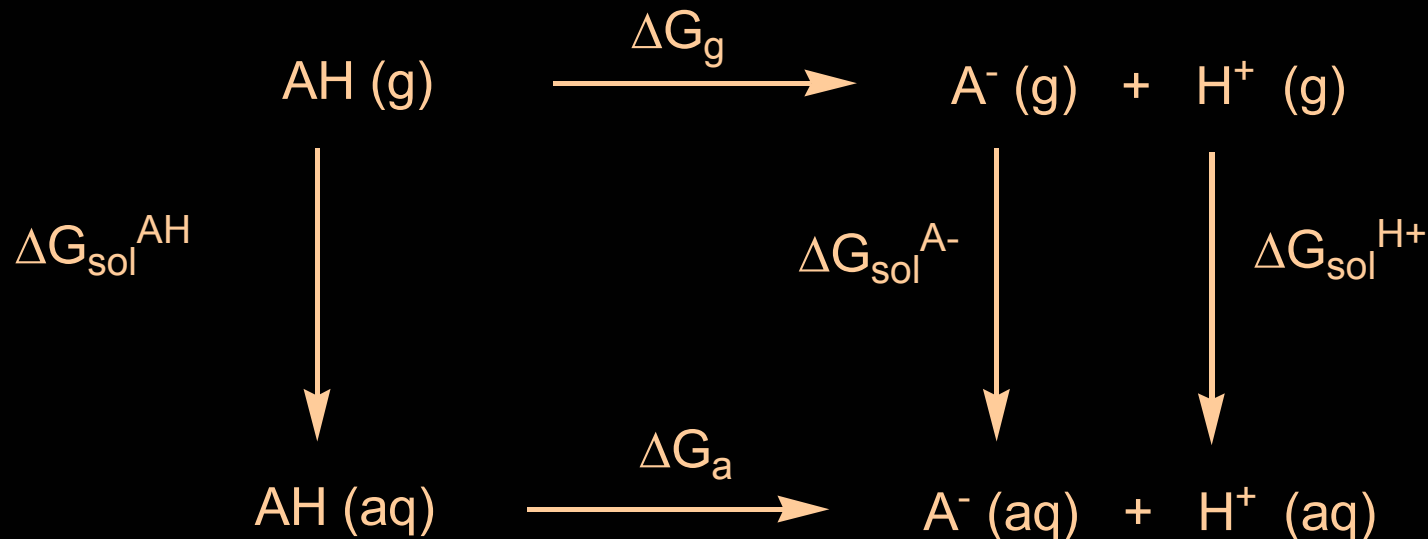
pK_a Calculations (1)

- Calculate pK_a values using a free energy cycle (Born-Haber cycle):



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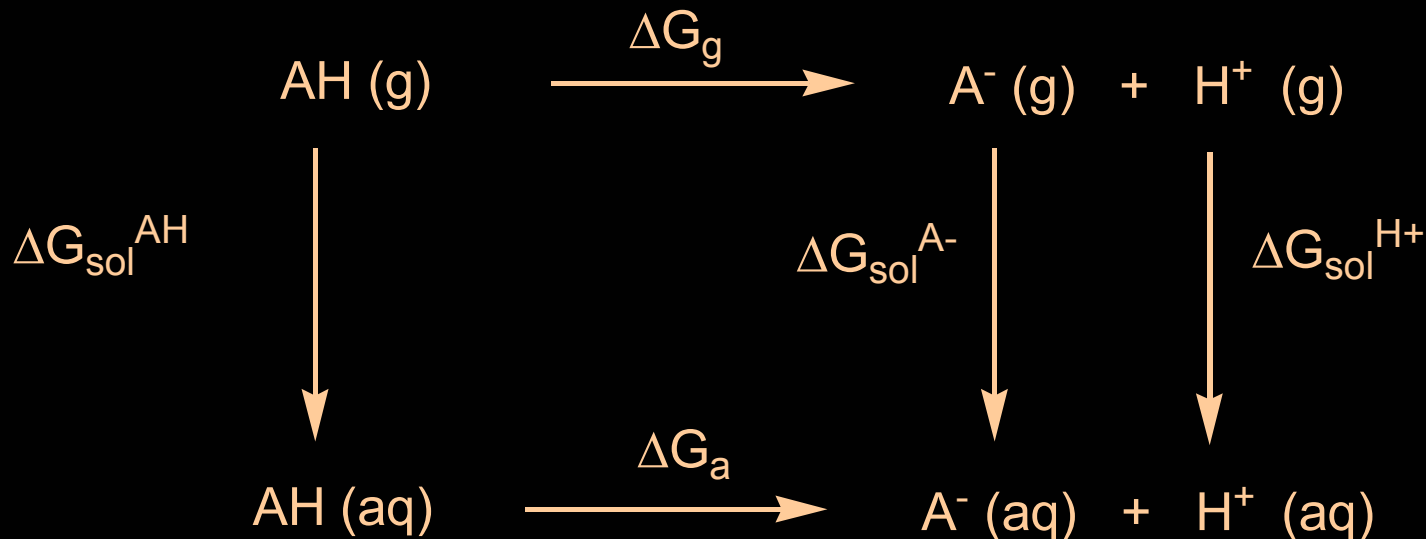


$$\Delta G_g = \Delta G_g^{A^-} + \Delta G_g^{H^+} - \Delta G_g^{AH}$$

$$\Delta G_g^{H^+} = -0.00999 \text{ hartrees} \quad (@ P = 1 \text{ atm} \ \& \ T = 298 \text{ K})$$

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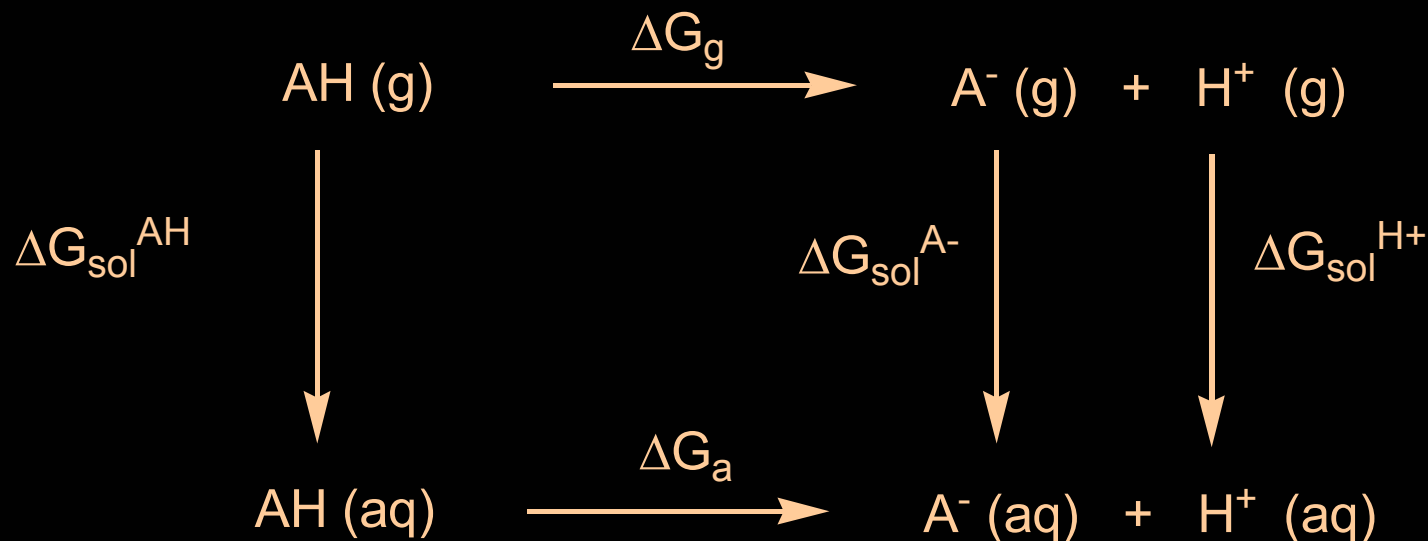
$$\Delta G_g^{H^+} = -0.00999 \text{ hartrees} \quad (@ P = 1 \text{ atm} \ \& \ T = 298 \text{ K})$$

$$\Delta G_a = \Delta G_g + \Delta G_{sol}^{A^-} + \Delta G_{sol}^{H^+} - \Delta G_{sol}^{AH}$$

$$\Delta G_{sol}^{H^+} = -264.0 \text{ kcal/mol} \quad (\text{experimental value})$$

pK_a Calculations (2)

- Calculate pK_a values using a free energy cycle (Born-Haber cycle):

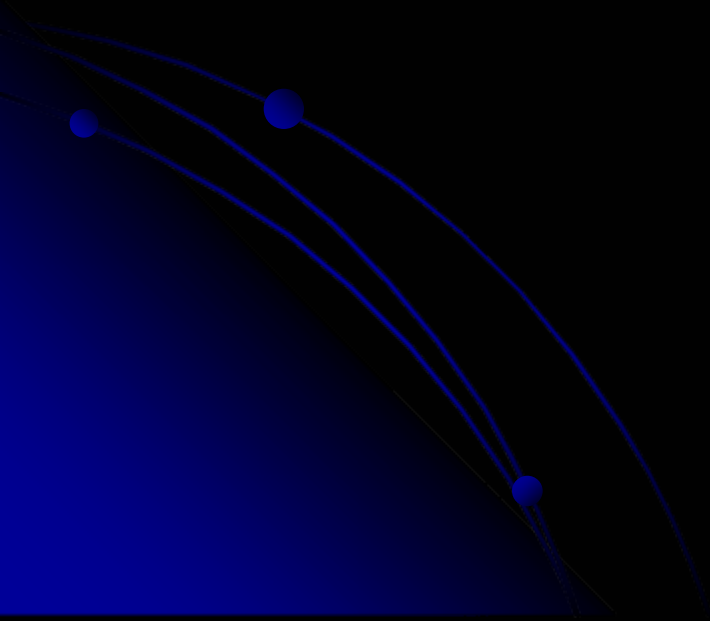


$$K_a = e^{-\Delta G_a / RT}$$

$$pK_a = -\log(K_a) = -\log\left(e^{-\Delta G_a / RT}\right)$$

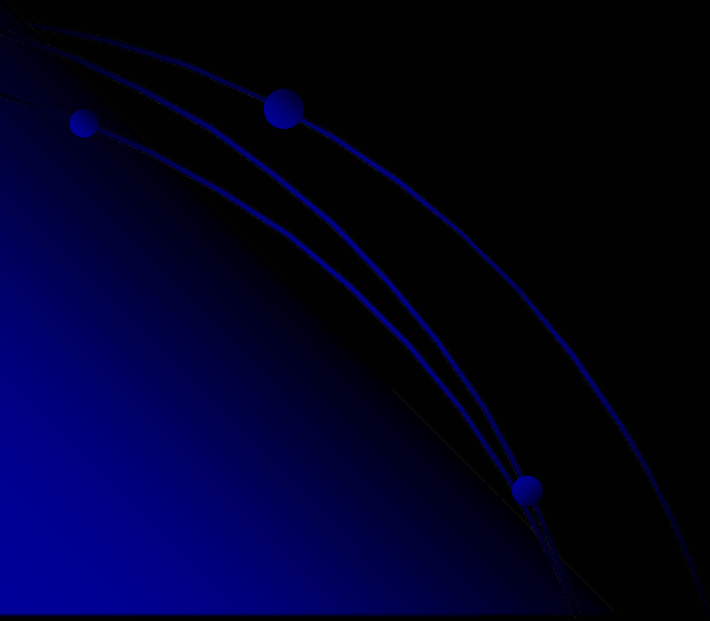
pK_a Calculations (3)

- Accuracy...
 - depends mostly upon accuracy of the solvation energy of the ions
 - and upon the accuracy of ΔG_g



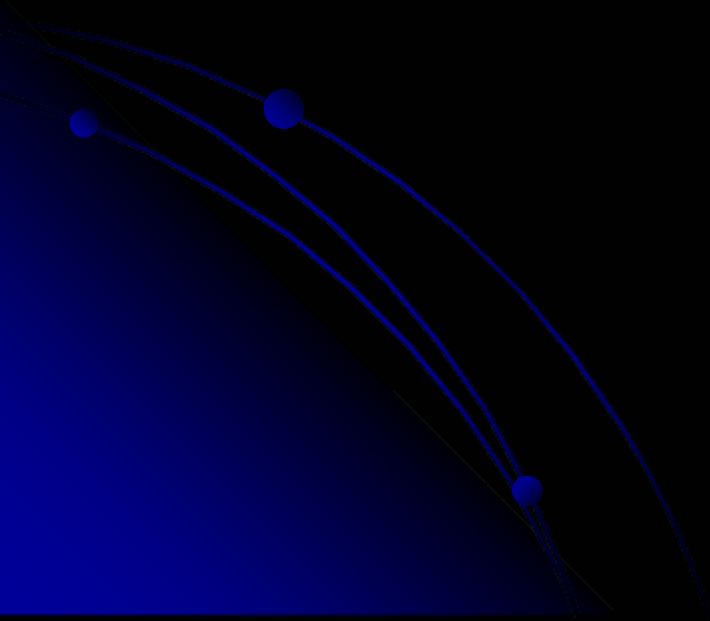
pK_a Calculations (3)

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 - depends mostly upon accuracy of the solvation energy of the ions
 - approximately ±5 kcal/mol
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 - approximately ±5 kcal/mol
 - expected accuracy of pK_a values approximately ±5 units



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- Accuracy...
 - depends mostly upon accuracy of the solvation energy of the ions
 - approximately ± 5 kcal/mol
 - and upon the accuracy of ΔG_g
 - approximately ± 5 kcal/mol
 - expected accuracy of pK_a values approximately ± 5 units
- prediction of relative pK_a values can be more chemically meaningful

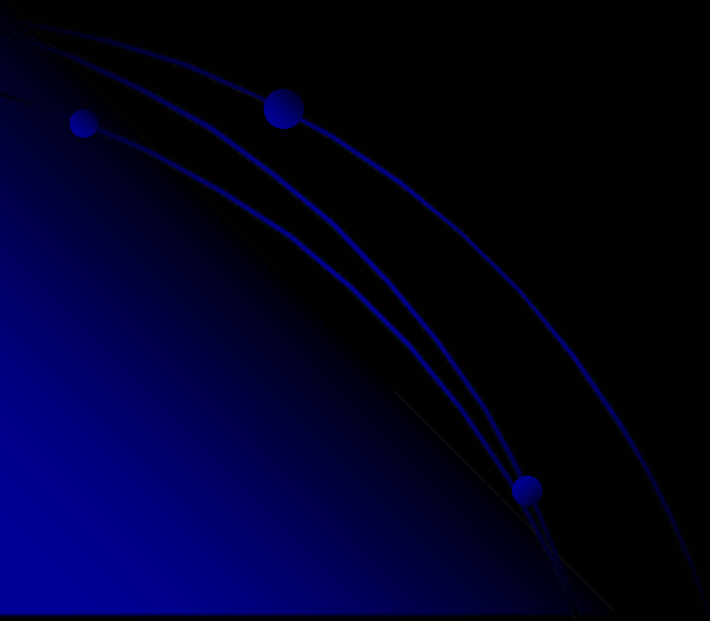


Electron Affinities



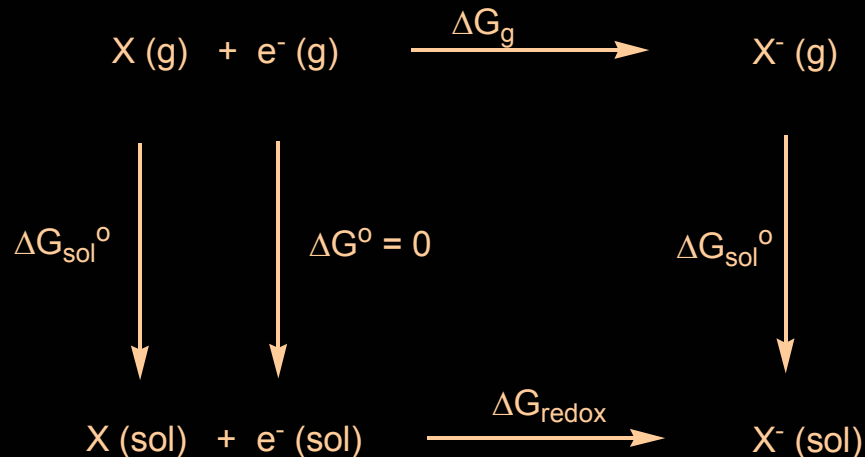
one-electron reduction in the gas phase

$$\text{Electron Affinity} = EA = -\Delta G_g = \Delta G_g^{X} - \Delta G_g^{X^{-}}$$

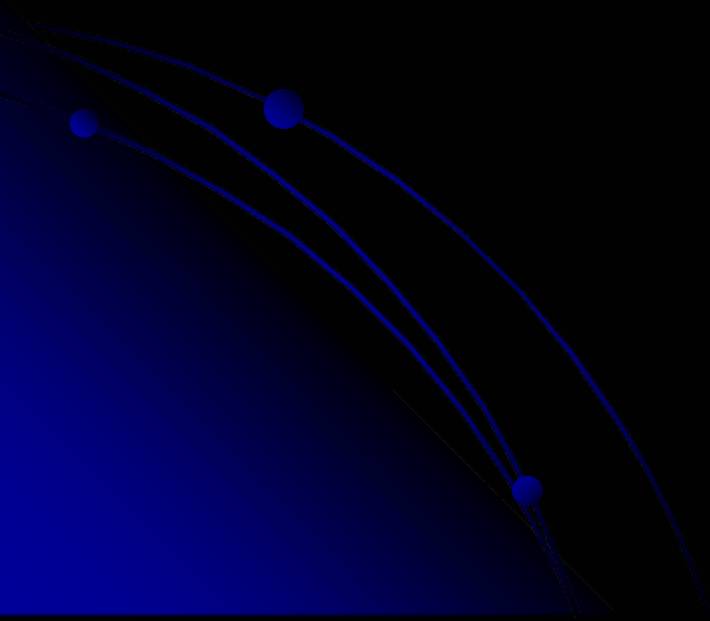


Redox Potential Calculations (1)

- Calculate redox potentials using free energy cycles...

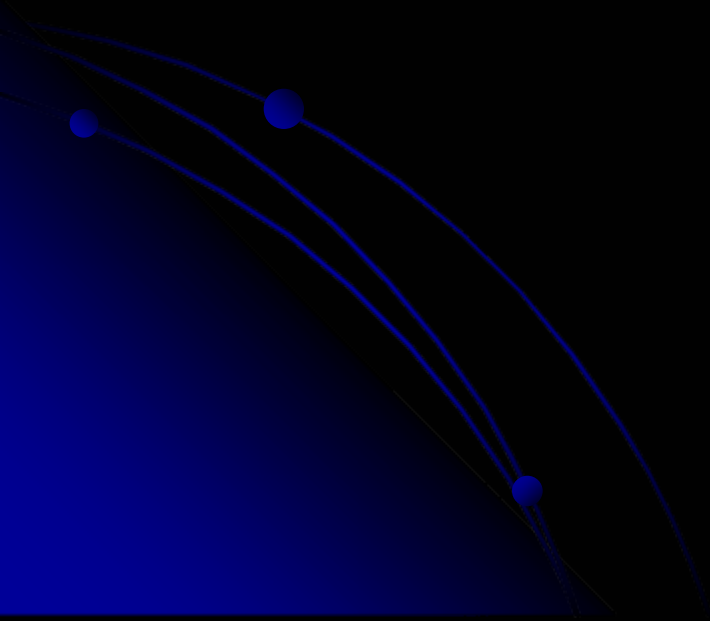
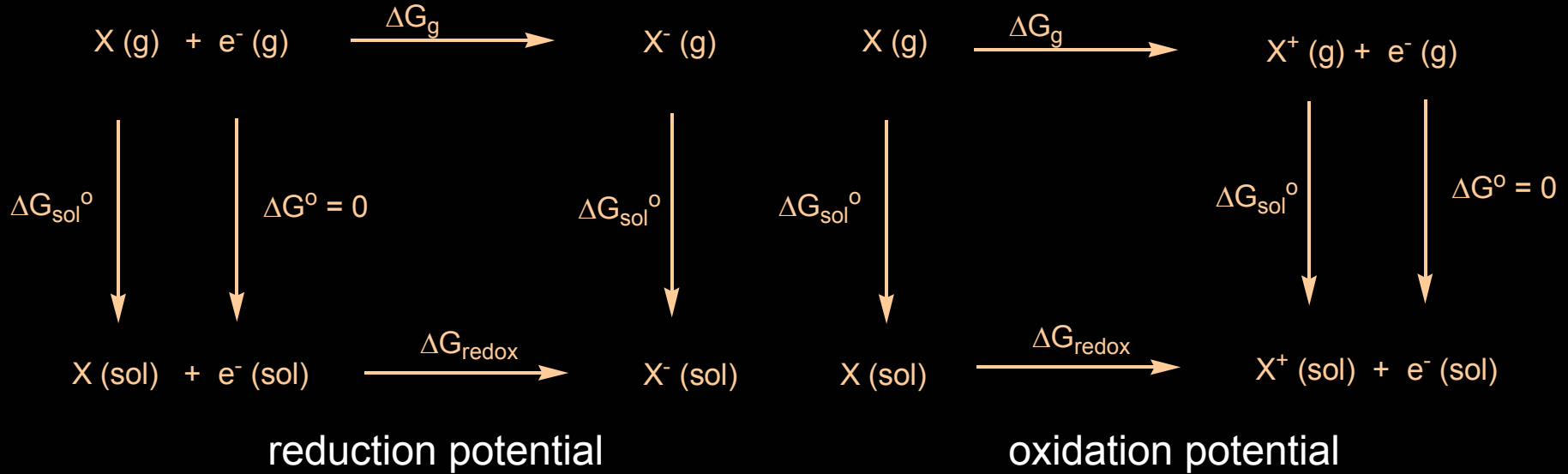


reduction potential



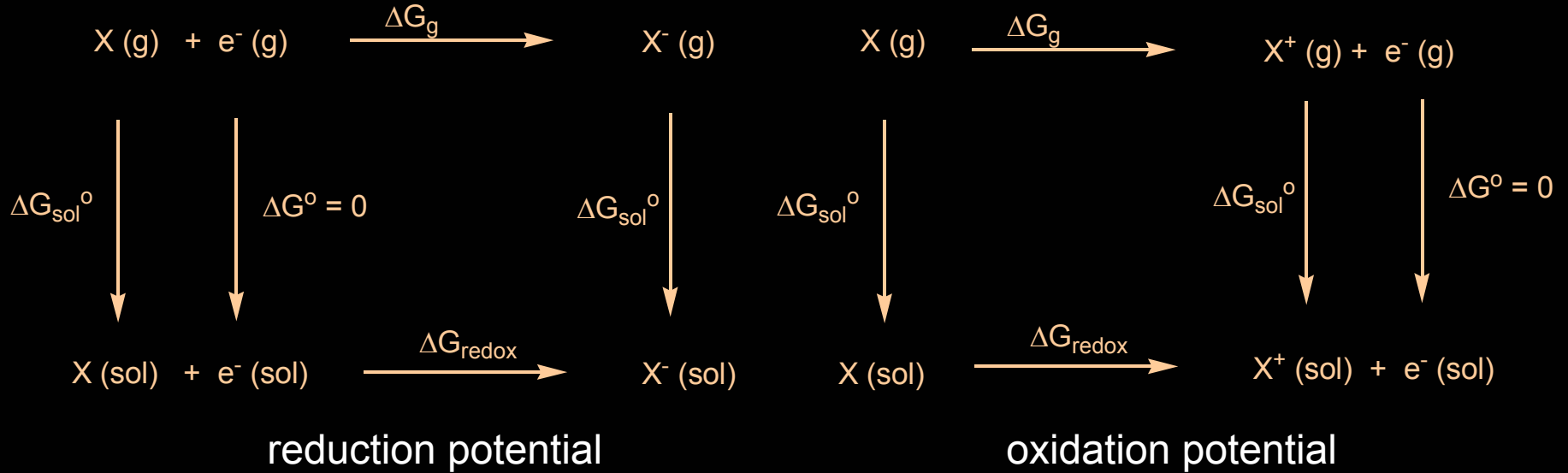
Redox Potential Calculations (1)

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- Calculate redox potentials using free energy cycles...



$$\Delta G_g = \Delta G_g^{X^-} - \Delta G_g^X$$

$$\Delta G_{redox} = \Delta G_g + \Delta G_{sol}^{X^-} - \Delta G_{sol}^X$$

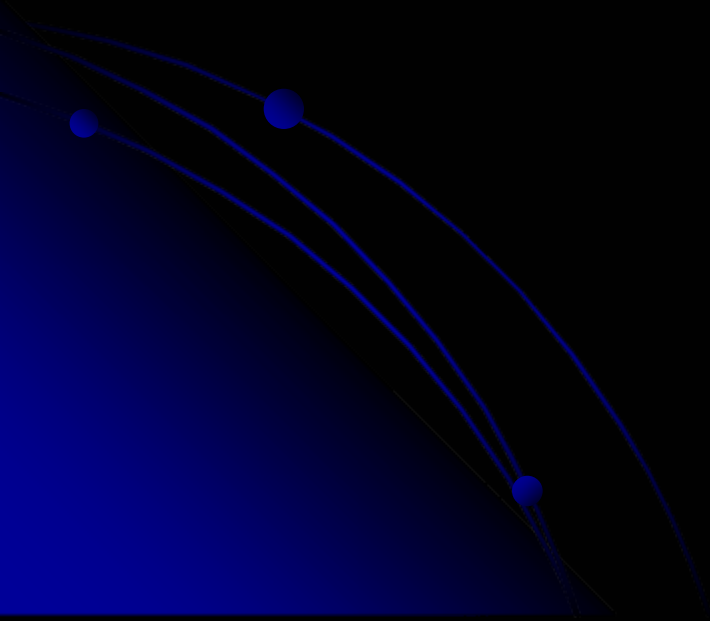
$$E^\circ = -\frac{\Delta G_{redox}}{nF}$$

n=number of electrons F=Faraday constant=23.060kcal/V*mol

e.g. reduction potential case

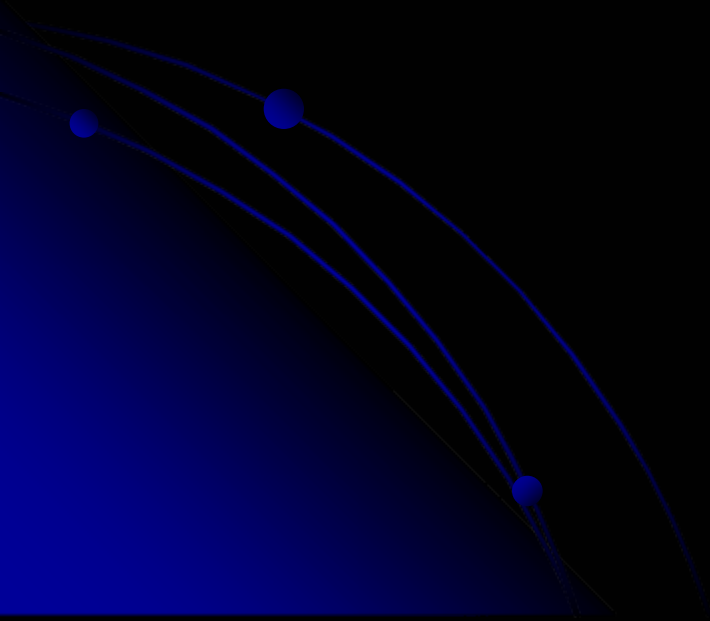
Redox Potential Calculations (2)

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- Redox potentials typically reported relative to a standard electrode...
 - standard hydrogen electrode (SHE)
 - $\text{H}^+ (\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 (\text{g})$
 - reduction potentials: subtract 4.28 V
 - oxidation potentials: add 4.28 V



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 - reduction potentials: subtract 4.28 V
 - oxidation potentials: add 4.28 V
 - other standard electrodes based upon values relative to SHE
 - example: standard calomel electrode (SCE)
$$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq}) \quad E^\circ = +0.24 \text{ V (vs. SHE)}$$
 - reduction potentials: subtract (4.28+0.24) V
 - oxidation potentials: add (4.28+0.24) V