PHY 770 -- Statistical Mechanics
12:00* - 1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 24

Review and perspective; multicomponent systems
(Chapter 3 in 3rd edition of Reichl)

- ❑ **Affinity; degree of reaction**
- ❑ **Equilibrium relationships**
- ❑ **Rates of reaction**
- ❑ **Course assessment forms**

***Partial make-up lecture -- early start time**

	Thur: 03/13/2014		Spring break (no class meeting)		
14	Tue: 03/18/2014	Chap. 6	Fermi and Bose particles (class 12-1:45 PM; Exam due)	#13	03/25/2014
15	Thur: 03/20/2014	Chap. 6	Interacting particles (class 12-1:45 PM)	#14	03/25/2014
16	Tue: 03/25/2014	Chap. 7	Langevin equation (class 12-1:45 PM)	#15	04/01/2014
17	Thur: 03/27/2014	Chap. 7	Fokker-Planck equation (class 12-1:45 PM)	#16	04/03/2014
18	Tue: 04/01/2014	Chap. 7	Linear Response (class 12-1:45 PM)	#17	04/10/2014
19	Thur: 04/03/2014	Chap. 9	Transport theory (class 12-1:45 PM)	#18	04/10/2014
20	Tue: 04/08/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#19	04/10/2014
21	Thur: 04/10/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#20	04/17/2014
22	Tue: 04/15/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#21	04/17/2014
23	Thur: 04/17/2014		Review and highlights (class 12-1:45 PM)		
24	Tue: 04/22/2014		Review and highlights (class 12-1:45 PM)		
	Thur: 04/24/2014		Presentations Part I (class 11-1:45 PM)		
	Tue: 04/29/2014		Presentations Part II (class 11-1:45 PM)		

General comments about presentations:

This exercise is designed to allow you to study a topic (related to statistical and thermal physics) of your choosing in some detail.

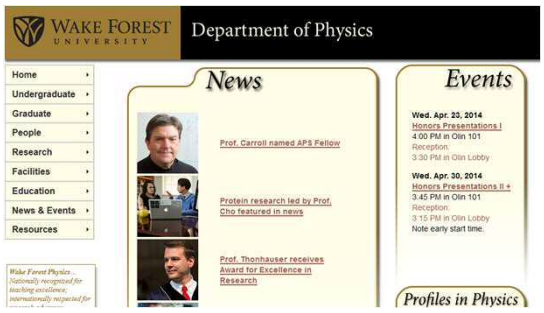
- Please plan your presentation for 10-15 minutes and allow at least 5 minutes for questions
- After your presentation, please hand in or email:
  - ❑ Your presentation
  - ❑ Any additional notes, computer programs, maple or mathematica sheets
  - ❑ A list of references including a copy of any seminal references
- Extra points will be awarded for audience questions and discussion

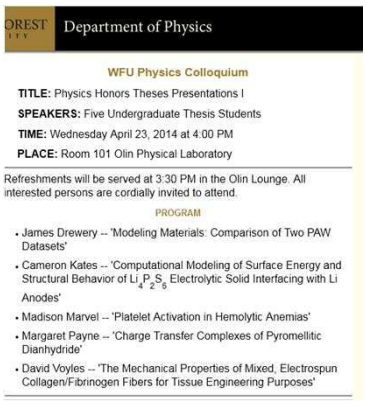
Presentations on Thursday 4/24/2014 in Olin 107

Time	Name	Title
11:00-11:20 AM	David Montgomery	Chemical Reactions
11:25-11:45 AM	Hyunsu Lee???	
11:50-12:10 PM	Zach Lamport	Steam Engines - The Rankine Cycle
12:15-12:35 PM	Xiaohua Liu	Osmosis
12:40-1:00 PM	Junwei	Negative temperature state
1:05-1:25 PM	Jiajie Xiao	Physics in DNA-protein binding prediction

Presentations on Tuesday 4/29/2014 in Olin 107

Time	Name	Title
11:00-11:20 AM	Sam Flynn	The ledenfrost effect
11:25-11:45 AM	Calvin Arter	"Statistical mechanics and the interaction potential"
11:50-12:10 PM	Evan Welchman	Monte Carlo
12:15-12:35 PM	Ahmad Al-Qawasmeh	Linear Response Theory and Dielectric properties
12:40-1:00 PM	Chaochao Dun	Mo/CZTS interface instability
1:05-1:25 PM	Eric Chapman	Analysis of the Stirling Engine





WAKE FOREST UNIVERSITY Department of Physics

WFU Physics Colloquium

TITLE: Physics Honors Theses Presentations I

SPEAKERS: Five Undergraduate Thesis Students

TIME: Wednesday April 23, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

PROGRAM

- James Drewery -- 'Modeling Materials: Comparison of Two PAW Datasets'
- Cameron Kates -- 'Computational Modeling of Surface Energy and Structural Behavior of $Li_4P_2S_6$ Electrolytic Solid Interfacing with Li Anodes'
- Madison Marvel -- 'Platelet Activation in Hemolytic Anemias'
- Margaret Payne -- 'Charge Transfer Complexes of Pyromellitic Dianhydride'
- David Voyles -- 'The Mechanical Properties of Mixed, Electrospun Collagen/Fibrinogen Fibers for Tissue Engineering Purposes'

Properties of the Gibb's free energy -- multicomponent ideal gas

$$G = \sum_i \mu_i N_i$$

For example, consider a reaction at fixed T and P:

$2H_2 + O_2 \leftrightarrow 2H_2O$

$-2H_2O + 2H_2 + O_2 \leftrightarrow 0$ General notation: $\sum_{i=1}^{n} \nu_i X_i \leftrightarrow 0$

Define "degree of reaction" ξ such that the change in number of particles of type i is given by $dN_i = \nu_i d\xi$

Change in Gibbs free energy with fixed T and P:

$$dG = \sum_{i=1}^{n} \mu_i dN_i = \sum_{i=1}^{n} \mu_i \nu_i d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{n} \mu_i \nu_i = \alpha \qquad \text{affinity}$$

Properties of the Gibb's free energy -- multicomponent ideal gas

Change in Gibbs free energy with fixed T and P:

$$dG = \sum_{i=1}^{n} \mu_i dN_i = \sum_{i=1}^{n} \mu_i \nu_i d\xi$$

At equilibrium: $dG = 0 \quad \Rightarrow \alpha \equiv \sum_{i=1}^{n} \mu_i \nu_i = 0$

Note that if $\alpha \neq 0$, there is a "driving force" for the reaction.

Multicomponent ideal gas and possible chemical reactions -- continued

Equilibrium condition for Gibbs free energy with fixed T and P:

$$\sum_{i=1}^{n} \mu_i(T,P)\nu_i = 0$$

Estimation of the chemical potentials:

- For each i, assume independent ideal gas particles with internal energies determined by electronic, internal and kinetic energies:
  $Z_i = Z_i^{\text{electronic}} Z_i^{\text{internal}} Z_i^{\text{kinetic}}$
- $Z_i^{\text{kinetic}} = \frac{1}{N_i!}\left(\frac{V}{\lambda_i^3}\right)^{N_i}$ with thermal wavelength $\lambda_i = \left(\frac{\hbar^2}{2\pi m_i kT}\right)^{1/2}$
- Canonical partition function for system: $Z = \prod_{i=1}^{n} Z_i$

Estimation of chemical potential continued

Note that if we can show that $\mu_i(T,P) = \mu_i^0(T,P) + kT\ln c_i$ where $c_i \equiv \frac{N_i}{N}$,

Then the equilibrium condition $\sum_{i=1}^{n} \mu_i(T,P)\nu_i = 0$ has the following analysis

$$\sum_{i=1}^{n} \left(\mu_i^0(T,P) + kT\ln(c_i)\right)\nu_i = 0$$

$$\sum_{i=1}^{n} \left(\frac{\nu_i \mu_i^0(T,P)}{kT} + \nu_i \ln(c_i)\right) = 0$$

Define: $\ln(K(T,P)) \equiv -\sum_{i=1}^{n}\left(\frac{\nu_i \mu_i^0(T,P)}{kT}\right)$

$$\Rightarrow \sum_{i=1}^{n} \ln\left(c_i^{\nu_i}\right) = \ln\left(\prod_{i=1}^{n}\left(c_i^{\nu_i}\right)\right) = \ln(K(T,P))$$

$$\Rightarrow \prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = K(T,P) = \mathrm{e}^{-\sum_{i=1}^{n}\left(\frac{\nu_i \mu_i^0(T,P)}{kT}\right)}$$

Multicomponent ideal gas and possible chemical reactions -- continued

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = K(T,P)$$

Example:

$-2\mathrm{H_2O} + 2\mathrm{H_2} + \mathrm{O_2} \leftrightarrow 0$

$\nu_i : -2 \quad 2 \quad 1$

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = \frac{[\mathrm{H_2}]^2[\mathrm{O_2}]}{[\mathrm{H_2O}]^2} = K(T,P)$$

Multicomponent ideal gas and possible chemical reactions -- continued

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right)=\frac{\left[\mathrm{H_2}\right]^2\left[\mathrm{O_2}\right]}{\left[\mathrm{H_2O}\right]^2}=K(T,P)$$

$2\mathrm{H_2}+\mathrm{O_2}\leftrightarrow 2\mathrm{H_2O}$

Suppose $\left[\mathrm{H_2O}\right]=1-x$

$\left[\mathrm{H_2}\right]=x$

$\left[\mathrm{O_2}\right]=x/2$

$$\frac{x^3}{2(1-x)^2}=K(T,P)=\mathrm{e}^{-\sum_{i=1}^{n}\left(\frac{\nu_i\mu_i^0(T,P)}{kT}\right)}$$

Estimation of chemical potential continued

Want to show that $\mu_i(T,P)=\mu_i^0(T,P)+kT\ln c_i$ where $c_i\equiv\frac{N_i}{N}$,

$Z_i=Z_i^{\text{electronic}}Z_i^{\text{internal}}Z_i^{\text{kinetic}}$

$Z_i^{\text{kinetic}}=\frac{1}{N_i!}\left(\frac{V}{\lambda_i^3}\right)^{N_i}$ with thermal wavelength $\lambda_i=\left(\frac{\hbar^2}{2\pi m_i kT}\right)^{1/2}$

$Z_i^{\text{electronic}}\approx e^{-N_i\varepsilon_1^{\text{electronic}}}$

$Z_i^{\text{internal}}=\left(\zeta_i(T,P)\right)^{N_i}$ (represents vibrations, rotations, etc.)

Canonical partition function for system: $Z=\prod_{i=1}^{n}Z_i$

Estimation of chemical potential continued

Helmholz free energy for this system

$$A=-kT\ln Z=-kT\sum_{i=1}^{n}\ln Z_i\approx\sum_{i=1}^{n}N_i\left(\varepsilon_i^{el}-kT\ln\zeta_i(T,P)-kT\left(1+\ln\frac{V}{N_i\lambda_i^3}\right)\right)$$

$$\mu_i=\left(\frac{\partial A}{\partial N_i}\right)_{T,V,\{N_j\}}=\varepsilon_i^{el}-kT\ln\zeta_i(T,P)-kT\ln\frac{V}{N_i\lambda_i^3}$$

For an ideal gas: $PV=NkT$ where $\sum_{i=1}^{n}N_i=N$

Let $c_i\equiv\frac{N_i}{N}$ $\mu_i(T,P,c_i)=\varepsilon_i^{el}-kT\ln\zeta_i(T,P)-kT\ln\left(\frac{kT/P}{c_i\lambda_i^3}\right)$

$\Rightarrow\mu_i(T,P,c_i)=\mu_i^0(T,P)+kT\ln(c_i)$

where $\mu_i^0(T,P)=\varepsilon_i^{el}-kT\ln\zeta_i(T,P)-kT\ln\left(\frac{kT}{P\lambda_i^3}\right)$

Multicomponent systems -- continued

Law of "mass action"

$$\prod_{i=1}^{n}\left(c_i^{\nu_i}\right) = K(T,P) = \mathrm{e}^{-\sum_{i=1}^{n}\left(\frac{\nu_i \mu_i^0(T,P)}{kT}\right)}$$

Other relationships:

Gibbs Free Energy: $G(T,P,\{N_i\}) = U - TS + PV$

Enthalpy: $H = U + PV = G + TS$

For $dN_i = \nu_i d\xi$

At equilibrium: $\left(\frac{\partial G}{\partial \xi}\right)^0_{T,P} = 0 = \left(\frac{\partial H}{\partial \xi}\right)^0_{T,P} - T\left(\frac{\partial S}{\partial \xi}\right)^0_{T,P}$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\{N_i\}} \quad \Rightarrow \left(\frac{\partial H}{\partial \xi}\right)^0_{T,P} = -T\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{T,P}\right)_{P,\xi}$$

Example:

Consider the gas phase reaction at constant T and P with initially $N_{N_2O_4} = N_0$:

$N_2O_4 \leftrightarrow 2NO_2$

$$\mu_i(T,P,c_i) = \mu_i^0(T,P) + kT\ln(c_i)$$

where $c_i \equiv \frac{N_i}{N}$ and $\mu_i^0(T,P) = \varepsilon_i^{el} - kT\ln\zeta_i(T,P) - kT\ln\left(\frac{kT}{P\lambda_i^3}\right)$

In this case: $c_{N_2O_4} = \frac{1-\xi}{1+\xi}$ $\qquad c_{NO_2} = \frac{2\xi}{1+\xi}$

$$dG(T,P,\{N_i\}) = \sum_i \nu_i \mu_i(T,P,c_i)\,d\xi = \sum_i \nu_i\left(\mu_i^0(T,P) + kT\ln(c_i)\right)d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \nu_i \mu_i^0(T,P) + kT\ln\left(\frac{(2\xi)^2}{(1+\xi)(1-\xi)}\right)$$

Example continued:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \nu_i \mu_i^0(T,P) + kT\ln\left(\frac{(2\xi)^2}{(1+\xi)(1-\xi)}\right)$$

In this case at standard T and P: $\mu^0_{N_2O_4} = 23.49\text{kcal/mol}$

$\mu^0_{NO_2} = 12.39\text{kcal/mol}$

Solving for equilibrium value of ξ at standard T and P:

$$\frac{4\xi^2}{1-\xi^2} = \exp\left(-\frac{2\mu^0_{NO_2} - \mu^0_{N_2O_4}}{kT}\right) \qquad \Rightarrow \xi_{eq} \approx 0.166$$

Equilibrium concentrations:

$c_{N_2O_4} = \frac{1-\xi}{1+\xi} = 0.715$ $\qquad c_{NO_2} = \frac{2\xi}{1+\xi} = 0.284$

Estimation of chemical potential continued

Extension to other (non ideal gas) systems:

$\mu_i(T,P,c_i) = \mu_i^0(T,P) + kT\ln(c_i) \Rightarrow \mu_i(T,P,c_i) = \mu_i^0(T,P) + kT\ln(\gamma_i c_i)$

$\mu_i^0(T,P) \equiv$ "standard state"

$\gamma_i \equiv$ "activity coefficient"

Extension of analysis to irreversible reactions

Affinity has previously been defined: $\alpha \equiv \sum_{i=1}^{n} \mu_i \nu_i$

Note that if $\alpha \neq 0$, there is a "driving force" for the reaction.

In this case, there is typically an irreversible contribution to the entropy:

$dS_{irr} = \frac{\alpha}{T} d\xi > 0$

Example: $Cl(g) + H_2(g) \leftrightarrow HCl(g) + H(g)$

Typically it is possible to determine the reaction rate:

$\frac{1}{V}\frac{d\xi}{dt} = k_f[Cl][H_2] - k_r[HCl][H]$

Here the forward and reverse reaction rates are estimated from the nearby equilibrium values of the Gibbs Free Energies.