# PHY 341/641 Thermodynamics and Statistical Mechanics
# MWF: Online at 12 PM & FTF at 2 PM

Record!!!

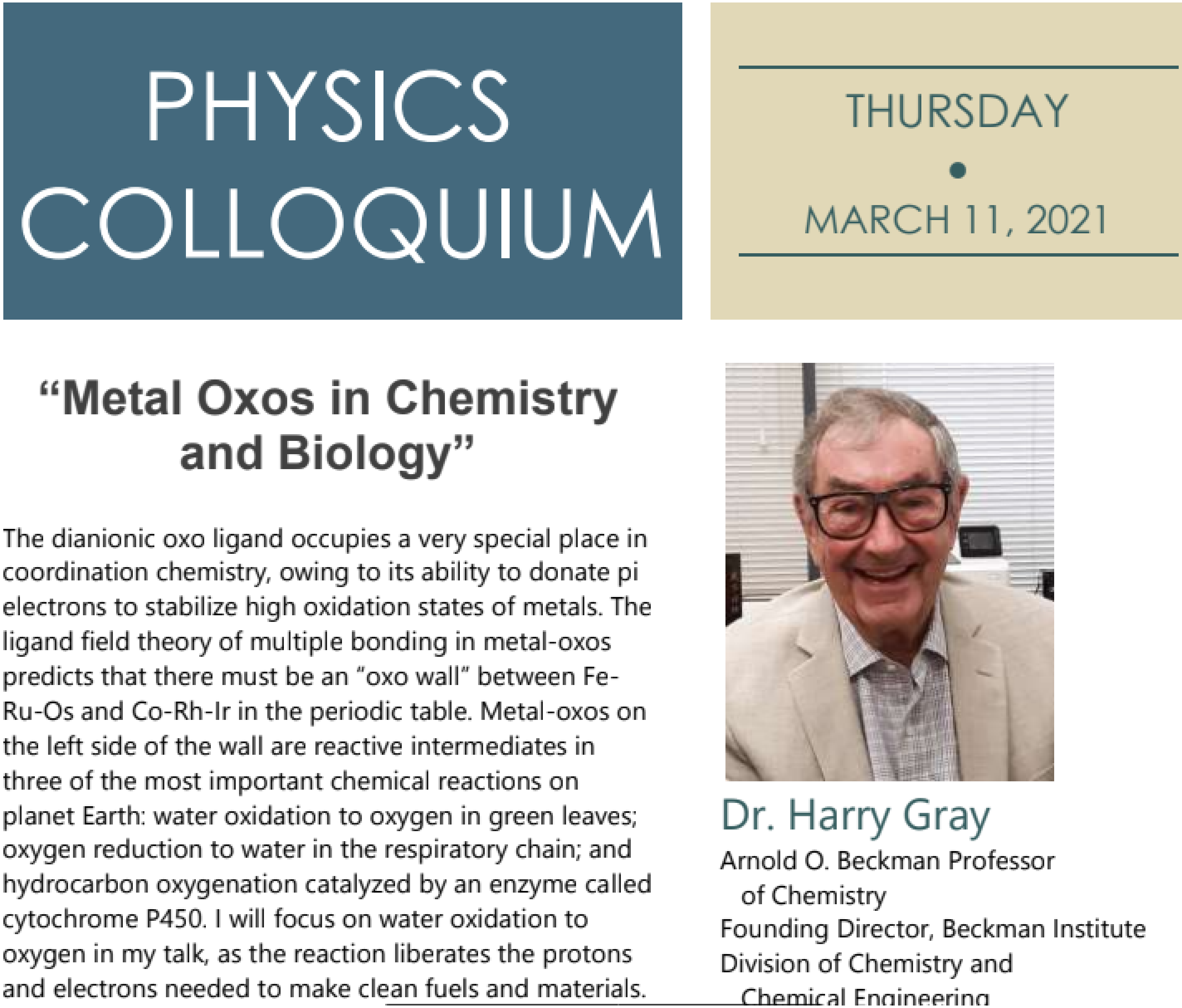
## Discussion for Lecture 19:

**Thermodynamics of equilibrium chemical reactions**

**Reading: Chapter 5.6**

1. **Comment on calculating moles in solution**
2. **Chemical reactions in equilibrium**
3. **Chemical reactions in dilute solutions**

# Physics Colloquium – 4 PM 3/11/2021



PHYSICS COLLOQUIUM

THURSDAY

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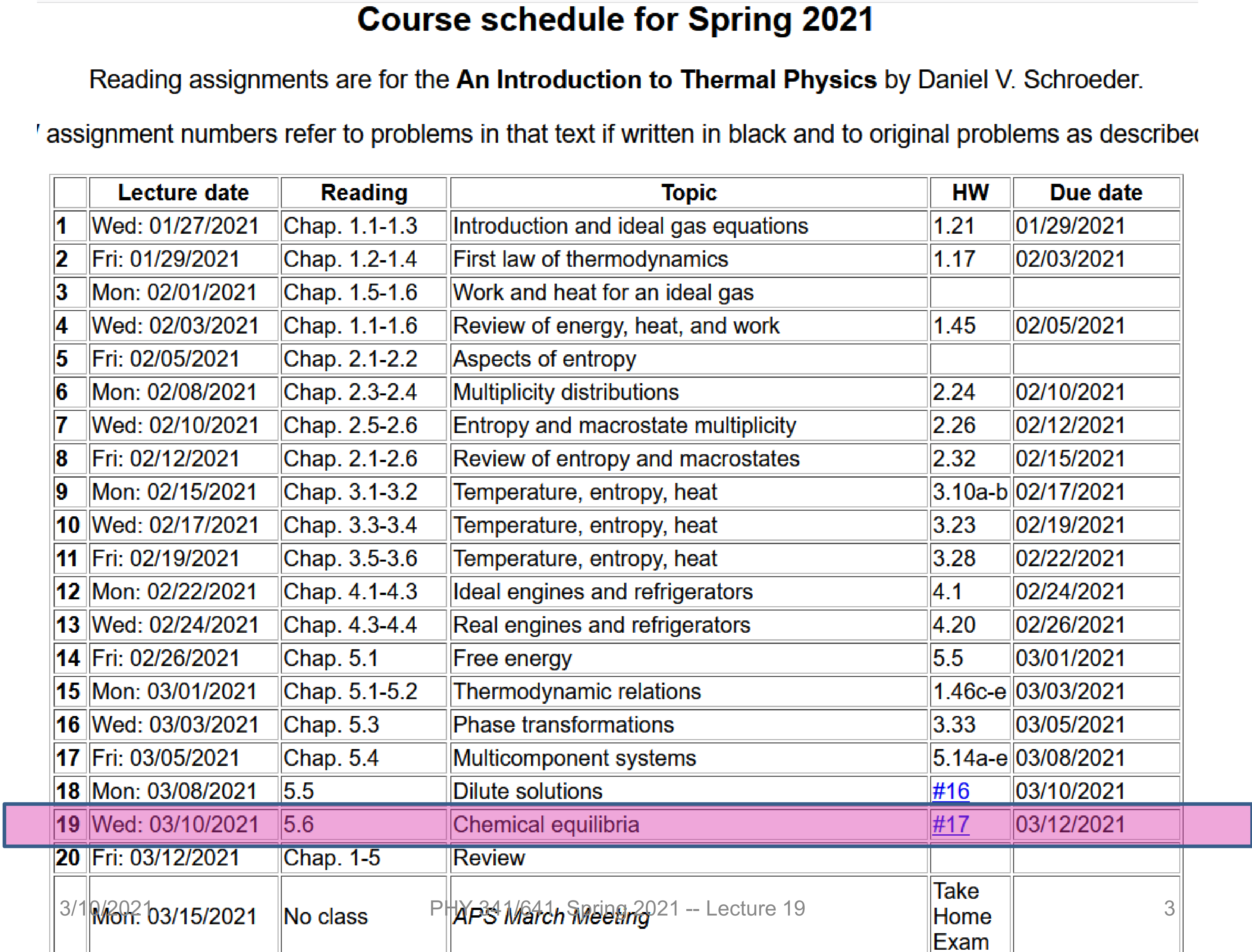
MARCH 11, 2021

## “Metal Oxos in Chemistry and Biology”

The dianionic oxo ligand occupies a very special place in coordination chemistry, owing to its ability to donate pi electrons to stabilize high oxidation states of metals. The ligand field theory of multiple bonding in metal-oxos predicts that there must be an “oxo wall” between Fe-Ru-Os and Co-Rh-Ir in the periodic table. Metal-oxos on the left side of the wall are reactive intermediates in three of the most important chemical reactions on planet Earth: water oxidation to oxygen in green leaves; oxygen reduction to water in the respiratory chain; and hydrocarbon oxygenation catalyzed by an enzyme called cytochrome P450. I will focus on water oxidation to oxygen in my talk, as the reaction liberates the protons and electrons needed to make clean fuels and materials.

**Dr. Harry Gray**

Arnold O. Beckman Professor
of Chemistry
Founding Director, Beckman Institute
Division of Chemistry and
Chemical Engineering



# Course schedule for Spring 2021

Reading assignments are for the **An Introduction to Thermal Physics** by Daniel V. Schroeder.

assignment numbers refer to problems in that text if written in black and to original problems as describe

| | **Lecture date** | **Reading** | **Topic** | **HW** | **Due date** |
|---|---|---|---|---|---|
| **1** | Wed: 01/27/2021 | Chap. 1.1-1.3 | Introduction and ideal gas equations | 1.21 | 01/29/2021 |
| **2** | Fri: 01/29/2021 | Chap. 1.2-1.4 | First law of thermodynamics | 1.17 | 02/03/2021 |
| **3** | Mon: 02/01/2021 | Chap. 1.5-1.6 | Work and heat for an ideal gas | | |
| **4** | Wed: 02/03/2021 | Chap. 1.1-1.6 | Review of energy, heat, and work | 1.45 | 02/05/2021 |
| **5** | Fri: 02/05/2021 | Chap. 2.1-2.2 | Aspects of entropy | | |
| **6** | Mon: 02/08/2021 | Chap. 2.3-2.4 | Multiplicity distributions | 2.24 | 02/10/2021 |
| **7** | Wed: 02/10/2021 | Chap. 2.5-2.6 | Entropy and macrostate multiplicity | 2.26 | 02/12/2021 |
| **8** | Fri: 02/12/2021 | Chap. 2.1-2.6 | Review of entropy and macrostates | 2.32 | 02/15/2021 |
| **9** | Mon: 02/15/2021 | Chap. 3.1-3.2 | Temperature, entropy, heat | 3.10a-b | 02/17/2021 |
| **10** | Wed: 02/17/2021 | Chap. 3.3-3.4 | Temperature, entropy, heat | 3.23 | 02/19/2021 |
| **11** | Fri: 02/19/2021 | Chap. 3.5-3.6 | Temperature, entropy, heat | 3.28 | 02/22/2021 |
| **12** | Mon: 02/22/2021 | Chap. 4.1-4.3 | Ideal engines and refrigerators | 4.1 | 02/24/2021 |
| **13** | Wed: 02/24/2021 | Chap. 4.3-4.4 | Real engines and refrigerators | 4.20 | 02/26/2021 |
| **14** | Fri: 02/26/2021 | Chap. 5.1 | Free energy | 5.5 | 03/01/2021 |
| **15** | Mon: 03/01/2021 | Chap. 5.1-5.2 | Thermodynamic relations | 1.46c-e | 03/03/2021 |
| **16** | Wed: 03/03/2021 | Chap. 5.3 | Phase transformations | 3.33 | 03/05/2021 |
| **17** | Fri: 03/05/2021 | Chap. 5.4 | Multicomponent systems | 5.14a-e | 03/08/2021 |
| **18** | Mon: 03/08/2021 | 5.5 | Dilute solutions | #16 | 03/10/2021 |
| **19** | Wed: 03/10/2021 | 5.6 | Chemical equilibria | #17 | 03/12/2021 |
| **20** | Fri: 03/12/2021 | Chap. 1-5 | Review | | |
| | Mon: 03/15/2021 | No class | *APS March Meeting* | Take Home Exam | |

# PHY 341/641 -- Assignment #16

March 10, 2021

Finish reading Chapter 5 in **Schroeder** .

1. Consider the equilbrium reaction given in Eq. 5.98 of **Schroeder** . Assume that you can represent the number of $N_2$ molecules in terms of the parameter $\chi$ and constant $N_0$ by $N_0(1-\chi)$. Find a consistent representation for the number of $H_2$ and $NH_3$ molecules so that you can estimate the fraction of ammonia molecules which are present at standard temperature pressure. Your textbook gives values for the needed parameters. (You may want to use graphics software for your estimation.)

Please send me suggestions for topics to be covered in Friday's review.

Your questions –

From Kristen – 1. When they talk about Le Chatelier's principle, does a partial pressure increase mean that the number of particles of that compound have increased? 2. How can we assume from the value of K which direction the reaction is most likely to favor?

From Rich -- How would the set-up change for the dissociation of water example if molarity was used instead of molality?

# Comment of boiling point elevation discussion from Lecture 18 --

In terms of Latent heat: $L = T_0\left(S_{gas} - S_{liq}\right)$

$$\Rightarrow T = T_0 + \frac{k_B T_0^2 N_B}{L} = T_0 + \frac{R T_0^2 n_B}{L}$$

Example: Boiling temperature of sea water

$T_0 = 373K$

$L = 2260$ kJ/kg $\qquad n_B \approx 1.2$ moles/kg

$T \approx 373.6K$

How should we estimate $n_B$?

Textbook says that for 1 kg of water there are 35 g of NaCl

Molecular mass of NaCl 58.44 g

$n_B$=0.6 or $n_B$=1.2 ?????

Note that in this lecture we will use “k” for the Boltzmann constant (instead of $k_B$)

# Notion of chemical reactions

$N_2 + 3H_2 \leftrightarrow 2NH_3$

In this case, the reaction of hydrogen and nitrogen gas forming ammonia gas can in principle proceed in either direction, depending on conditions.

Consider the following general reaction with 4 particles $A, B, C, D$:

$-\nu_A A - \nu_B B \rightleftarrows \nu_C C + \nu_D D$ By convention $\nu_A < 0$ and $\nu_B < 0$

We use $N_A, N_B, N_C, N_D$ to denote the number of each of the particles.

We want to use the Gibbs free energy to analyze the reaction at fixed T and P.

In the case that all of the particles are approximately ideal gasses, we can start with Gibbs free energy of each type of particle. For particle A, for example:

$$G(T,P,N_A) = -N_A kT\left(\ln\left(\frac{kT}{P_A}\left(\frac{2\pi M_A kT}{h^2}\right)^{3/2}\right)\right)$$

$$= N_A \mu_A^0\left(T_0,P_0\right) - N_A kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P_A}\right)$$

For $-\nu_A A - \nu_B B \rightleftarrows \nu_C C + \nu_D D$ it follows that

$dN_A = \nu_A d\chi \quad dN_B = \nu_B d\chi \quad dN_C = \nu_C d\chi \quad dN_D = \nu_D d\chi$

where $d\chi$ measures the "degree of reaction".

It is also useful to define the fraction $x_i$ of each type of particle in terms of the partial pressures $P_i = x_i P$.

Additionally, $N = \sum_i N_i$

In these terms, the Gibbs free energy of the system is

$$G(T,P,\{N_i\}) = -\sum_i N_i kT\left(\ln\left(\frac{kT}{P_i}\left(\frac{2\pi M_i kT}{h^2}\right)^{3/2}\right)\right)$$

$$= \sum_i N_i \mu_i^0\left(T_0, P_0\right) - \sum_i N_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P_i}\right)$$

$$= \sum_i N_i \mu_i^0\left(T_0, P_0\right) - \sum_i N_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + \sum_i N_i kT \ln\left(x_i\right)$$

$$= \sum_i N_i \mu_i^0\left(T_0, P_0\right) - NkT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\sum_i \ln\left(x_i^{N_i}\right)$$

Consider the change in the Gibbs free energy

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

where the chemical potentials are

$$\mu_i = \mu_i^0\left(T_0, P_0\right) - kT\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\ln\left(x_i\right)$$

Expressed in terms of the degree of reaction:

$$dG = -SdT + VdP + \sum_i \mu_i \nu_i d\chi$$

$$\left(\frac{\partial G}{\partial \chi}\right)_{T,P} = \sum_i \mu_i \nu_i \equiv \boldsymbol{a} \qquad \text{"affinity"}$$

Note that at constant temperature and pressure, when the reactions is at equilibrium $\boldsymbol{a}^0=0$

# Summary for reaction:

$$-\nu_A A - \nu_B B \rightleftarrows \nu_C C + \nu_D D$$

Chemical potential:

$$\mu_i = \mu_i^0\left(T_0, P_0\right) - kT\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\ln\left(x_i\right)$$

$$\left(\frac{\partial G}{\partial \chi}\right)_{T,P} = \sum_i \mu_i \nu_i \equiv \boldsymbol{a} \qquad \text{"affinity"}$$

At equilibrium $\boldsymbol{a}^0 = 0$

Off equilibrium $\boldsymbol{a}\, d\chi < 0$

$\Rightarrow$ Reaction proceeding to the right: $d\chi > 0$ and $\boldsymbol{a} < 0$

$\Rightarrow$ Reaction proceeding to the left: $d\chi < 0$ and $\boldsymbol{a} > 0$

$$\boldsymbol{a}(T,P,\chi)=\left(\frac{\partial G}{\partial \chi}\right)_{T,P}=\sum_i \mu_i \nu_i$$

$$\boldsymbol{a}(T,P,\chi)=\sum_i \mu_i \nu_i=\sum_i \nu_i \mu_i^0\left(T_0,P_0\right)-\sum_i \nu_i kT\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right)+\sum_i kT\ln\left(x_i^{\nu_i}\right)$$

At equilibrium: $\boldsymbol{a}(T,P,\chi)=0$

$$\ln\left(\frac{x_C^{\nu_C}x_D^{\nu_D}}{x_A^{|\nu_A|}x_B^{|\nu_B|}}\right)=\sum_i \nu_i \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right)-\frac{1}{kT}\underbrace{\sum_i \nu_i \mu_i^0\left(T_0,P_0\right)}_{\Delta G(T_0,P_0)}$$

$$\left(\frac{x_C^{\nu_C}x_D^{\nu_D}}{x_A^{|\nu_A|}x_B^{|\nu_B|}}\right)_{T_0P_0}=e^{-\Delta G(T_0,P_0)/kT_0}\equiv K$$

Consider the gas phase reaction –
$N_2O_4 \leftrightarrow 2NO_2$
$\nu_A=-1 \qquad \nu_C=2$

Ref: L. E. Reichl
A modern course in
Statistical Mechanics

Suppose initially only $N_2O_4$ is present.

$$N_A = N_0(1-\chi) \qquad\qquad N_C = 2N_0\chi$$

$$x_A = \frac{1-\chi}{1+\chi} \qquad\qquad x_C = \frac{2\chi}{1+\chi}$$

$$\boldsymbol{a}(T,P,\chi) = \sum_i \nu_i \mu_i^0\left(T_0,P_0\right) - \sum_i \nu_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\ln\left(\frac{\left(2\chi\right)^2}{\left(1-\chi\right)\left(1+\chi\right)}\right)$$

For our example based on one mole (Avogadro's number of particles) and using $k \rightarrow R$

$$R = 8.315 \text{ J/K}$$

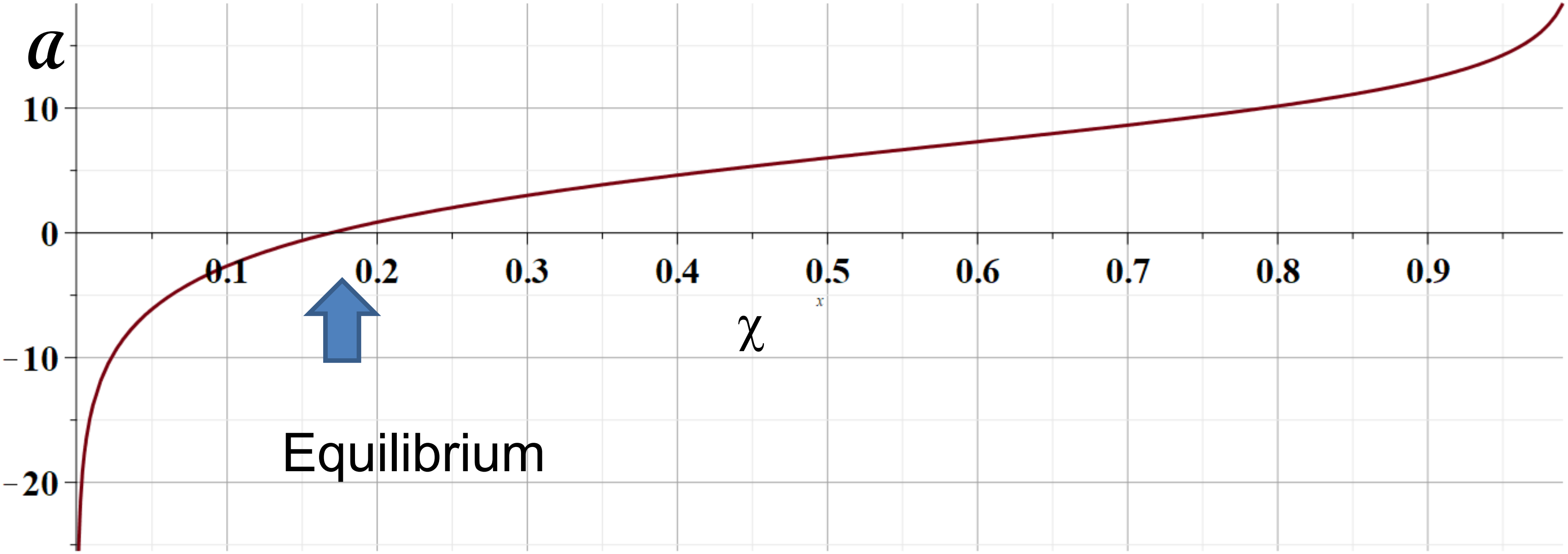
For $N_2O_4$: $\quad \mu_i^0\left(T_0,P_0\right) = 98.3 \text{ kJ}$

For $NO_2$: $\quad \mu_i^0\left(T_0,P_0\right) = 51.8 \text{ kJ}$

Consider the gas phase reaction –

$N_2O_4 \leftrightarrow 2NO_2$

$\nu_A=-1$ $\nu_C=2$ At $T_0=298K$ $P_0=1$ atm



$$x_{N_2O_4}=0.71 \qquad x_{NO_2}=0.29$$

# Another example of equilibrium chemical reactions – processes in dilute solutions

Dissociation of water: $$H_2O \leftrightarrow H^+ + OH^-$$

In this case, we cannot use the ideal gas expressions but the notions of equilibrium and the "affinity" function are still relevant

$$\boldsymbol{a}(T,P,\chi) = \left(\frac{\partial G}{\partial \chi}\right)_{T,P} = \sum_i \mu_i \nu_i \qquad \text{At equilibrium, } \boldsymbol{a}^0(T,P,\chi) = 0 = \sum_i \mu_i \nu_i$$

$$\ln\left(\frac{x_{H^+} x_{OH^-}}{x_{H_2O}}\right) = -\frac{1}{kT}\sum_i \nu_i \mu_i^0\left(T_0, P_0\right)$$

Suppose $$N_{H_2O} = N_0(1-\chi)$$

$$N_{H^+} = N_{HO^-} = N_0\chi$$

$$\left(\frac{x_{H^+} x_{OH^-}}{x_{H_2O}}\right) = e^{-\Delta G(T_0,P_0)/kT_0} \equiv K$$

For $x_{H_2O} = \dfrac{1-\chi}{1+2\chi} \approx 1$ and $x_{H^+} = x_{OH^-} = \dfrac{\chi}{1+2\chi} \approx \chi$

$$\chi^2 \approx K$$

Using the units in your text book:

$$m_{H^+} = m_{OH^-} = \chi(\text{constant}) = \frac{\text{moles of ion}}{\text{kilograms of water}} = 1\times10^{-7}$$

Notion of pH-- $\quad \text{pH} = -\log_{10}(m_{H^+}) = 7$