

# Advanced Materials Thermodynamics

- (1) Robert T. DeHoff, "Thermodynamics in Materials Science", McGraw-Hill, Inc., New York 1993.
- (2) Kerson Huang, "Statistical Mechanics", 2<sup>nd</sup> Edition, John Willey & Sons, 1986

## Contents

<b>(1) Statistical Thermodynamics</b>	<b>1-6<sup>th</sup> weeks</b>
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-2 Condition for Equilibrium in Statistical Thermodynamics	<b>3-4<sup>th</sup> week</b>
-3 Applications of the Algorithm	<b>5-6<sup>th</sup> week</b>
<b>(2) Defects in Crystal</b>	<b>6-9<sup>th</sup> weeks</b>
<b>(3) Electrochemistry:</b>	<b>10-13<sup>th</sup> weeks</b>

# “Thermodynamics”

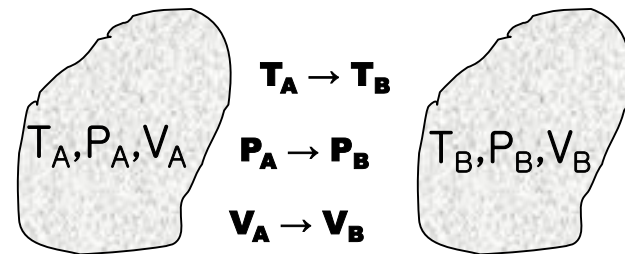
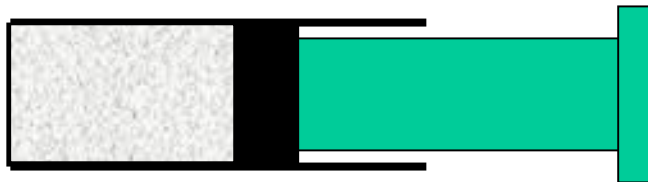
What is the purpose of thermodynamics?



Prediction of the future of our **system** at a given condition

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**a subset of the universe of interest**



State A



State B

**Process**



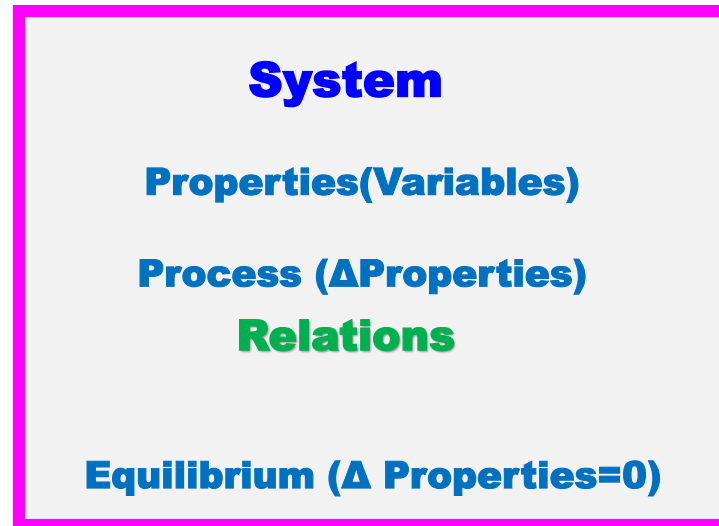
**Relationship**

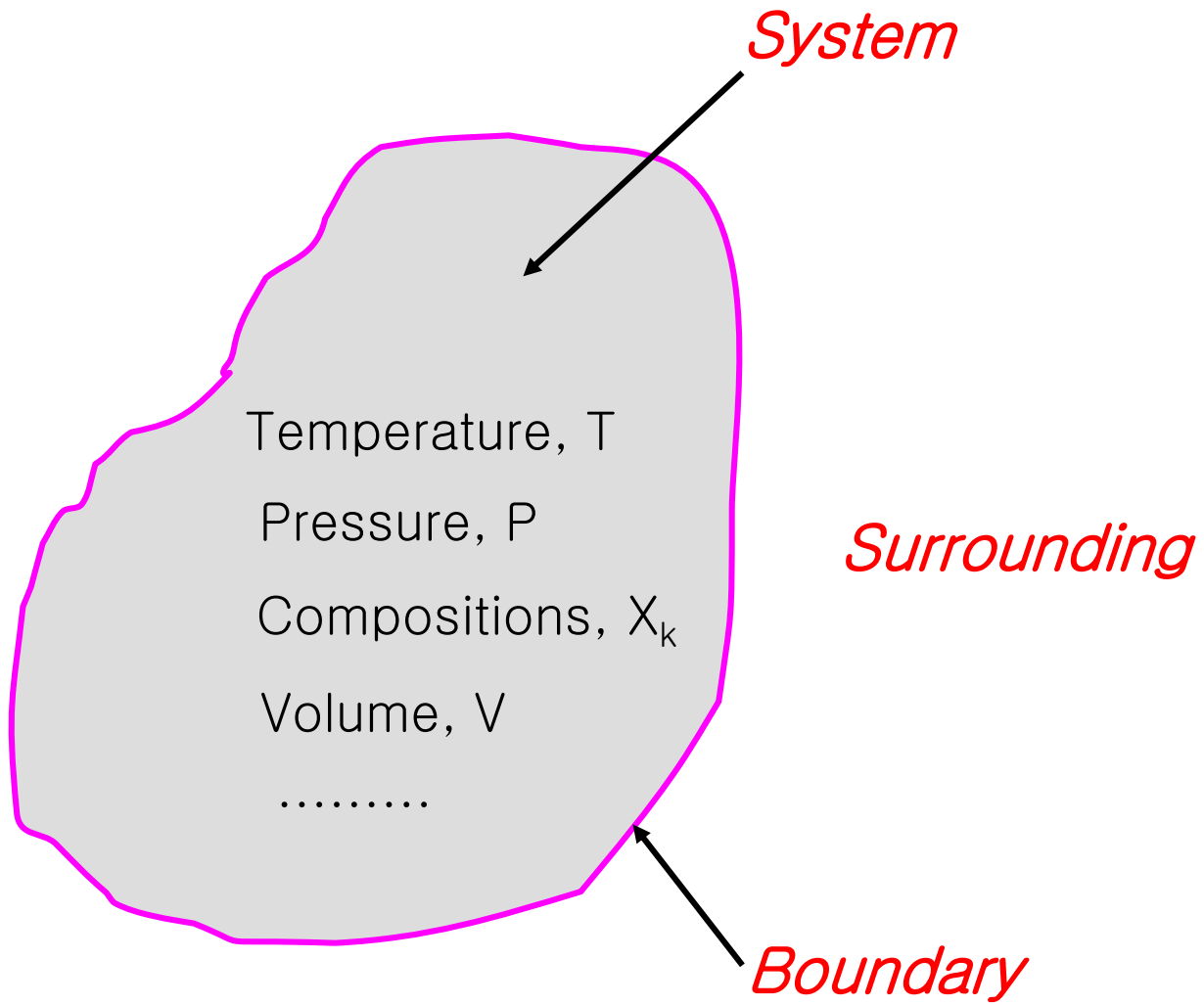
$$PV = RT$$

In practice, the focus of thermodynamics is on a subset of the universe, called a ***system***.

**Surrounding**

**Boundary**





The condition of the system at the time of observation is described in terms of its **properties**, quantities that report aspects of the condition of the system such as its temperature, T, its pressure, P, its volume, V, its chemical composition, and so on.

As the system is caused to pass through a **process**, its properties experience changes.

**A very common application of thermodynamics** is the **calculation of the changes in the properties of a specified system** as it is taken through some specified process.

Thus, an important aspect of the development of thermodynamics is the deduction of **relationships** between the properties of a system.

## The Laws of Thermodynamics

- (1) There exists a property of the universe, called its **energy**, which cannot change no matter what processes occur in the universe.
- (2) There exists a property of the universe, called its **entropy**, which can only change in one direction no matter what processes occur in the universe.
- (3) A universal absolute temperature scale exists and has a minimum value, defined to be **absolute zero**, and the entropy of all substances is the same at that temperature.



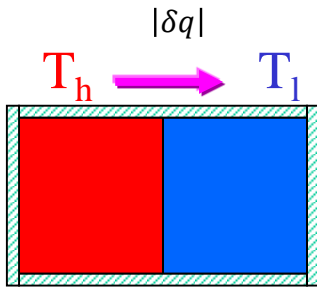
$$\Delta U = Q + W + W'$$

$$\delta Q_{rev} = TdS$$

$$T = 0K$$



$$dU = \delta Q + \delta W + \delta W' = TdS - PdV + \delta W'$$

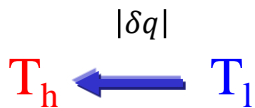


an isolated system

$$\begin{aligned}
 dS &= dS_h + dS_l & dS_h &= \frac{-|\delta q|}{T_h} & dS_l &= \frac{|\delta q|}{T_l} \\
 &= \left( \frac{1}{T_l} - \frac{1}{T_h} \right) |\delta q| & &= \left( \frac{T_h - T_l}{T_h T_l} \right) |\delta q| & &
 \end{aligned}$$

$$dS > 0$$

**Spontaneous Process**



$$\begin{aligned}
 dS &= dS_h + dS_l & dS_h &= \frac{|\delta q|}{T_h} & dS_l &= \frac{-|\delta q|}{T_l} \\
 &= \left( \frac{1}{T_h} - \frac{1}{T_l} \right) |\delta q| & &= \left( \frac{T_l - T_h}{T_h T_l} \right) |\delta q| & &
 \end{aligned}$$

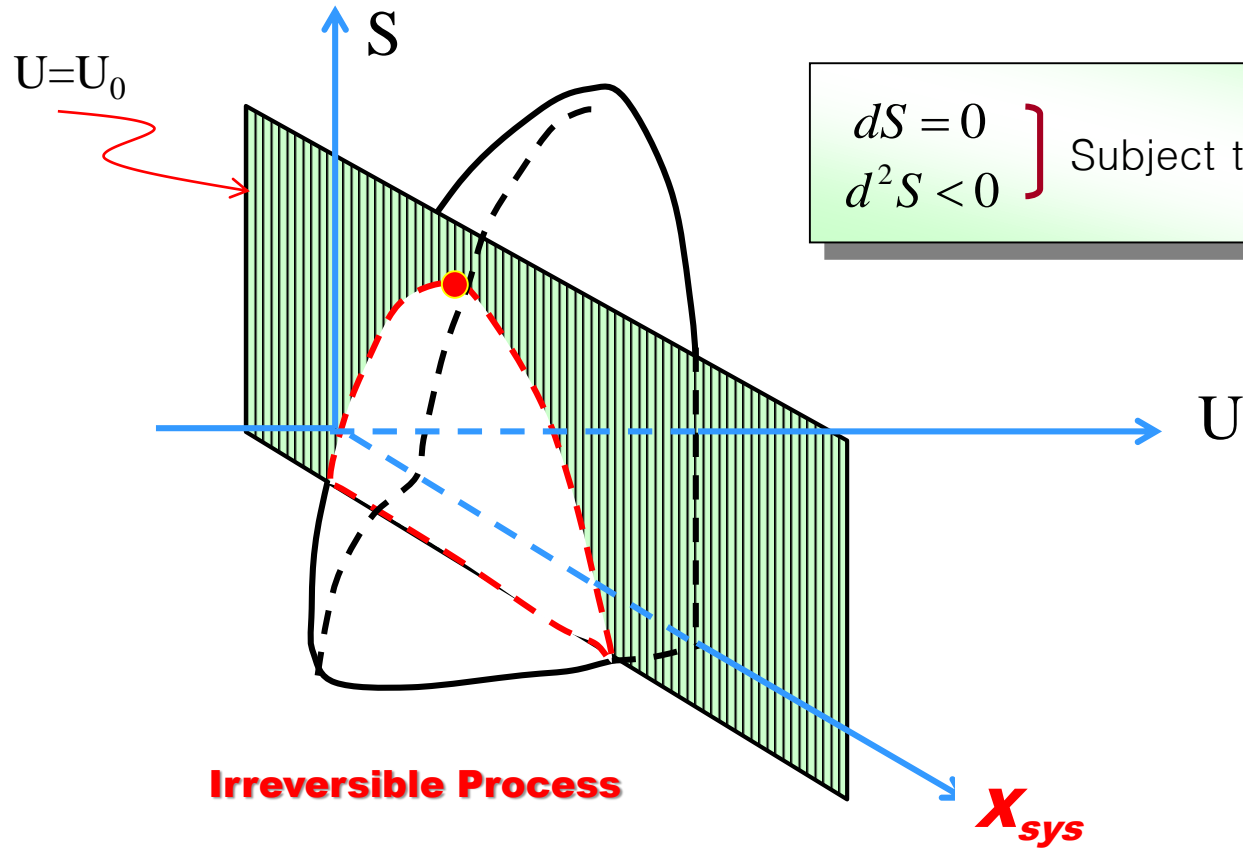
$$dS < 0$$

**Non-spontaneous Process**



***In an isolated system, the entropy is a maximum at equilibrium.***

# For an isolated composite system



# Chapter 6 : Statistical Thermodynamics

## 6-1 Introduction

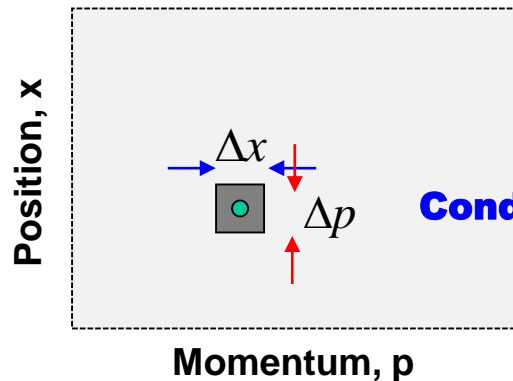
<Phenomenological (classical) thermodynamics>

No use has been made of the idea that the substance of the system is actually composed of atoms or molecules and the behavior of the system is somehow related to the properties of the particles that compose it.

<Statistical (atomistic) thermodynamics>

In a system consisting of a single atom, position ( $x$ ) and momentum ( $p$ ) should be specified for a complete description of its state.

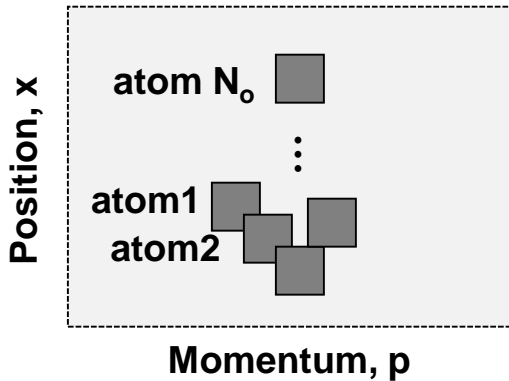
**'Heisenberg uncertainty principle'**  $\Delta x \Delta p \geq h$



**Condition of the system = State  
= ( $x, p$ )**

**State A ( $x_A, p_A$ )  $\neq$  State B ( $x_B, p_B$ )**

In a system consisting of  $N_o$  atoms, position ( $x$ ) and momentum ( $p$ ) for all those atoms should be specified respectively for a complete description of its state.



Condition of the system= State

=  $\{(x_1, p_1), (x_2, p_2), \dots, (x_{N_o}, p_{N_o})\}$  : **Microstate**

$\neq \{(x'_1, p'_1), (x'_2, p'_2), \dots, (x'_{N_o}, p'_{N_o})\}$ : a different **Microstate**

## 6-2 Microstates, Macrostates and Entropy

For simplicity, let us consider a system consisting of 4 particles (a,b,c,d) arranged over only two energy level ( $\epsilon_1, \epsilon_2$ ).

Particles: a,b,c,d & States: $\epsilon_1, \epsilon_2$
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Microstates ( $2^4=16$ )
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A complete description of  $x$  and  $p$  for all those atoms comprising the system

A complete description of how many atoms arranged over all  $x$  and  $p$  coordinates

State	$\epsilon_1$	$\epsilon_2$	$n_1$	$n_2$
A	a,b,c,d	–	4	0
B	a,b,c	d	3	1
C	a,b,d	c	3	1
D	a,c,d	b	3	1
E	b,c,d	a	3	1
F	a,b	c,d	2	2
G	a,c	b,d	2	2
H	a,d	b,c	2	2
I	b,c	a,d	2	2
J	b,d	a,c	2	2
K	c,d	a,b	2	2
L	a	b,c,d	1	3
M	b	a,c,d	1	3
N	c	a,b,d	1	3
O	d	a,b,c	1	3
P	–	a,b,c,d	0	4

Particles: a,b,c,d & States: $\epsilon_1, \epsilon_2$				
Microstates ( $2^4=16$ )				
State	$\epsilon_1$	$\epsilon_2$		
A	a,b,c,d	-	4	0
B	a,b,c	d	3	1
C	a,b,d	c	3	1
D	a,c,d	b	3	1
E	b,c,d	a	3	1
F	a,b	c,d	2	2
G	a,c	b,d	2	2
H	a,d	b,c	2	2
I	b,c	a,d	2	2
J	b,d	a,c	2	2
K	c,d	a,b	2	2
L	a	b,c,d	1	3
M	b	a,c,d	1	3
N	c	a,b,d	1	3
O	d	a,b,c	1	3
P	-	a,b,c,d	0	4

Particles: a,b,c,d & States: $\epsilon_1, \epsilon_2$				
Macrostates (=5)				
State	$\epsilon_1$	$\epsilon_2$		
I	4	0	A	1
II	3	1	B,C,D,E	4
III	2	2	F,G,H,I,J,K	6
IV	1	3	L,M,N,O	4
V	0	4	P	1



Since the particles are assumed to be physically identical, the macroscopically observable behavior of the system is not dependent on **which** particles exist in a given state, but merely on **how many** particles are in that state.

Microstates listed as B, C, D and E in Table 6-1 give the same values for the macroscopic properties of the system. Each of these microstates corresponds to the condition “two particles are in state  $e_1$  and two particles are in state  $e_2$ ” This observation gives to a much more efficient and useful way of describing the state of a system at an atomic level, called the **macrostate** for the system.

To specify the macrostate of a system at a given instant in time, focus not upon the particles but upon the list of possible conditions or states that the individual atoms can exhibit.

In general case, a macrostate is specified by assigning a number of particles to each of the  $r$  available states.

$\epsilon_1$	$\epsilon_2$	$\epsilon_3$	...	$\epsilon_i$	...	$\epsilon_r$
$n_1$	$n_2$	$n_3$	...	$n_i$	...	$n_r$

The set of numbers  $(n_1, \dots, n_r)$  is a distribution function specifying how the atoms are distributed over the energy levels. This distribution describes the **macrostate** for the system.

**The number of microstates that corresponds to a given macrostate** is a central quantity in the development of statistical thermodynamics.

From the atomistic point of view a thermodynamic process, which is a change in the macroscopic state of the system, corresponds to a redistribution of the atoms over their allowable states, or to a collection of changes in the number of particles in each atomic energy state.

For a general system composed of  $N_o$  particles distributed over  $r$  states, the description of a particular macrostate has the form of a distribution function:

$$(n_1, n_2, n_3, \dots, n_i, \dots, n_r) \quad \text{where } n_i \text{ is the number of particle in state } e_i.$$

How many microstates correspond to the macrostate  $(n_1, n_2, n_3, \dots, n_i, \dots, n_r)$ ?

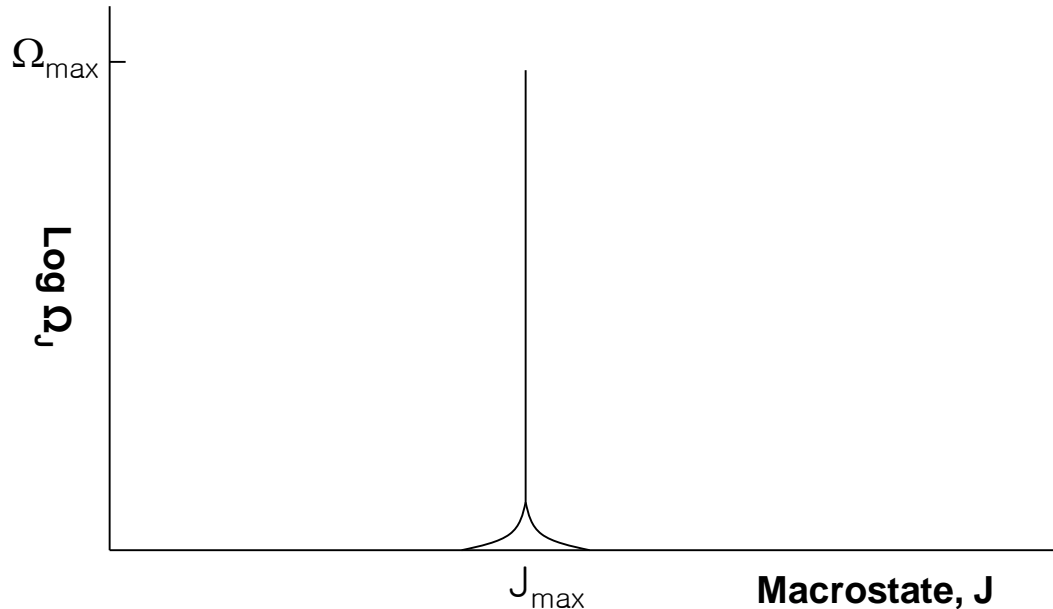
How many different ways can  $N_o$  balls be arranged in  $r$  boxes such that there are  $n_1$  balls in the first box,  $n_2$  in the second and so on to  $n_r$  balls in the  $r^{\text{th}}$  box?

$$\Omega = \frac{N_o!}{n_1!n_2!\cdots n_r!} = \frac{N_o!}{\prod_{i=1}^r n_i!}$$

The probability that the system exists in a given macrostate is the ratio of the number of microstates  $\Omega_J$  that correspond to the  $J^{\text{th}}$  macrostate to the total number of microstates the system may exhibit.

$$P_J = \frac{\Omega_J}{r^{N_o}} = \frac{N_o!}{\prod_{i=1}^r n_i!} \frac{1}{r^{N_o}}$$

Of all the macrostates that can exist for a system, one contains more microstates than any other. This macrostate has the maximum value of  $\Omega$  and the maximum probability of appearing at any instant in time.



Macrostates that differ significantly from the maximum probability state have negligible probability of occurrence. Thus, the maximum probability state, or those very near to it, are observed almost all of the time. If this most likely state is interpreted as the macrostate that correspond to the equilibrium state for the system, then this hypothesis forms the basis for connecting the statistical, atomistic description of the system with phenomenological thermodynamics.

In the phenomenological thermodynamics the equilibrium state is also characterized by an extremum; the entropy of an isolated system is a maximum at equilibrium.

This correspondence suggests a connection between entropy and  $\Omega$ , the number of microstates corresponding a given macrostate. If the functional relationship between these quantities is monotonic, that is, both either increase together or decrease together, then when one function maximizes, so does the other.

These considerations lead to the basic assumption that connects the atomistic and phenomenological descriptions known as the **Boltzmann hypothesis**:

$$S = k \ln \Omega$$

## 6-3 Conditions for Equilibrium in Statistical Thermodynamics

In the atomistic description of the thermodynamic behavior of a system, the equilibrium state is that particular macrostate which maximizes the entropy of the system when it is isolated.

<General strategy for finding conditions for equilibrium>

1. Write an expression for the change in entropy of the system in terms of the variables that define its state. In statistical thermodynamics, these variables are  $(n_1, n_2, \dots, n_r)$
2. Write expressions for the constraints on the variation of these variables imposed by the limitation of an isolated system.
3. Derive the set of equations that must be satisfied in order for the entropy function to be a maximum, subject to the isolation constraints.

## 6-3.1 Evaluation of Entropy

The entropy of a macrostate  $S = k \ln \Omega = k \ln \left( \frac{N_o!}{\prod_{i=1}^r n_i!} \right)$

Stirling's approximation:  $\ln x! \cong x \ln x - x$

$$S = k \ln \left( \frac{N_o!}{\prod_{i=1}^r n_i!} \right) = k \left[ \ln N_o! - \ln \prod_{i=1}^r n_i! \right] = k \left[ \ln N_o! - \sum_{i=1}^r \ln n_i! \right]$$

$$= k \left[ (N_o \ln N_o - N_o) - \sum_{i=1}^r (n_i \ln n_i - n_i) \right] = k \left[ (N_o \ln N_o - N_o) - \sum_{i=1}^r n_i \ln n_i + \sum_{i=1}^r n_i \right]$$

$$= k \left[ (N_o \ln N_o - N_o) - \sum_{i=1}^r n_i \ln n_i + N_o \right] = k \left[ N_o \ln N_o - \sum_{i=1}^r n_i \ln n_i \right]$$

$$N_o = \sum_{i=1}^r n_i$$

$$S = k \left[ N_o \ln N_o - \sum_{i=1}^r n_i \ln n_i \right] = k \left[ \sum_{i=1}^r n_i \ln N_o - \sum_{i=1}^r n_i \ln n_i \right] = k \left[ \sum_{i=1}^r n_i (\ln N_o - \ln n_i) \right]$$

$$= k \sum_{i=1}^r n_i \left( \ln \frac{N_o}{n_i} \right) = -k \sum_{i=1}^r n_i \left( \ln \frac{n_i}{N_o} \right) \quad N_o = \sum_{i=1}^r n_i$$

$$S = -k \sum_{i=1}^r n_i \left( \ln \frac{n_i}{N_o} \right)$$

The change in entropy for an arbitrary change in state

$$dS = -k d \left[ \sum_{i=1}^r n_i \left( \ln \frac{n_i}{N_o} \right) \right] = -k \sum_{i=1}^r d \left[ n_i \left( \ln \frac{n_i}{N_o} \right) \right] = -k \sum_{i=1}^r d [n_i \ln n_i - n_i \ln N_o]$$

$$= -k \sum_{i=1}^r dn_i \ln n_i + n_i d \ln n_i - dn_i \ln N_o - n_i d \ln N_o$$

$$= -k \sum_{i=1}^r dn_i \ln n_i + n_i \left( \frac{1}{n_i} \right) dn_i - dn_i \ln N_o - n_i \left( \frac{1}{N_o} \right) dN_o$$

$$dS = -k \sum_{i=1}^r dn_i \ln n_i + n_i \left( \frac{1}{n_i} \right) dn_i - dn_i \ln N_o - n_i \left( \frac{1}{N_o} \right) dN_o$$

$$= -k \sum_{i=1}^r \left[ dn_i \ln n_i + dn_i - dn_i \ln N_o - n_i \left( \frac{1}{N_o} \right) dN_o \right]$$

$$= -k \left[ \sum_{i=1}^r (\ln n_i - \ln N_o) dn_i + \sum_{i=1}^r dn_i - \sum_{i=1}^r \left( \frac{n_i}{N_o} \right) dN_o \right]$$

$$N_o = \sum_{i=1}^r n_i \quad \sum_{i=1}^r \left( \frac{n_i}{N_o} \right) = 1$$

$$= -k \sum_{i=1}^r (\ln n_i - \ln N_o) dn_i$$

$$dN_o = \sum_{i=1}^r dn_i$$

$$dS = -k \sum_{i=1}^r \ln \left( \frac{n_i}{N_o} \right) dn_i$$

No restrictions are imposed upon the nature of the redistribution of the particles over their energy levels.

## 6-3.2 Evaluation of the Isolation Constraints

Recall that the application of the criterion for equilibrium requires that the system be isolated from its surroundings.

Isolation from the surroundings implies that, whatever processes occur inside the system, the total number of particles cannot change and the internal energy of the system cannot change.

$$U = \sum_{i=1}^r \varepsilon_i n_i \quad dU = \sum_{i=1}^r (\varepsilon_i dn_i + n_i d\varepsilon_i) = \sum_{i=1}^r \varepsilon_i dn_i = 0 \quad d\varepsilon_i = 0$$

$$N_o = \sum_{i=1}^r n_i \quad dN_o = \sum_{i=1}^r dn_i = 0$$

Energy levels over which the particles are distributed, the  $\varepsilon_i$ , do not change during a process.

Processes are viewed to occur as a redistribution of the particles on a fixed set of energy levels.

## 6-3.3 The Constrained Maximum in the Entropy Function

A general procedure for solving this class of mathematical problems exists, and is known as the method of Lagrange multipliers.

$$dS = -k \sum_{i=1}^r \ln\left(\frac{n_i}{N_o}\right) dn_i \quad dS = -k \sum_{i=1}^r \ln\left(\frac{n_i}{N_o}\right) dn_i + \alpha \cdot dN_o + \beta \cdot dU$$

$$dU = \sum_{i=1}^r \varepsilon_i dn_i = 0 \quad \beta \cdot dU = \beta \cdot \sum_{i=1}^r \varepsilon_i dn_i = 0$$

$$dN_o = \sum_{i=1}^r dn_i = 0 \quad \alpha \cdot dN_o = \alpha \cdot \sum_{i=1}^r dn_i = 0$$

At equilibrium  $dS = -k \sum_{i=1}^r \ln\left(\frac{n_i}{N_o}\right) dn_i + \alpha \cdot dN_o + \beta \cdot dU = 0$

$$-k \sum_{i=1}^r \ln\left(\frac{n_i}{N_o}\right) dn_i + \alpha \cdot \sum_{i=1}^r dn_i + \beta \cdot \sum_{i=1}^r \varepsilon_i dn_i = 0 \quad \sum_{i=1}^r \left[ -k \ln\left(\frac{n_i}{N_o}\right) dn_i + \alpha \cdot dn_i + \beta \cdot \varepsilon_i dn_i \right] = 0$$

$$\sum_{i=1}^r \left[ -k \ln \left( \frac{n_i}{N_o} \right) dn_i + \alpha \cdot dn_i + \beta \cdot \varepsilon_i dn_i \right] = 0$$

$$\sum_{i=1}^r \left[ -k \ln \left( \frac{n_i}{N_o} \right) + \alpha + \beta \cdot \varepsilon_i \right] dn_i = 0 \quad -k \ln \left( \frac{n_i}{N_o} \right) + \alpha + \beta \cdot \varepsilon_i = 0 \quad (i = 1, 2, \dots, r)$$

$$\left( \frac{n_i}{N_o} \right) = e^{\frac{\alpha + \beta \cdot \varepsilon_i}{k}} \quad (i = 1, 2, \dots, r)$$

Equilibrium macrostate is characterized by this relationship: the fraction of particles in the  $i^{\text{th}}$  energy level ( $n_i/N_o$ ) is exponentially related to the value of the energy for that level  $\varepsilon_i$ .

It remains to evaluate the Lagrange multipliers  $\alpha$  and  $\beta$  in terms of the thermodynamic properties of the system.

$$\sum_{i=1}^r \left( \frac{n_i}{N_o} \right) = 1 = \sum_{i=1}^r e^{\frac{\alpha + \beta \varepsilon_i}{k}} = \sum_{i=1}^r e^{\frac{\alpha}{k}} e^{\frac{\beta \varepsilon_i}{k}} = e^{\frac{\alpha}{k}} \sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}} \quad e^{\frac{\alpha}{k}} = \frac{1}{\sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}}} = \frac{1}{P} \quad P \equiv \sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}}$$

$$\sum_{i=1}^r \left( \frac{n_i}{N_o} \right) = 1 = e^{\frac{\alpha}{k}} \sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}}$$

$$P \equiv \sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}}$$

**Partition Function, P, for the system**

$$e^{\frac{\alpha}{k}} = \frac{1}{\sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}}} = \frac{1}{P}$$

$$\left( \frac{n_i}{N_o} \right) = e^{\frac{\alpha + \beta \cdot \varepsilon_i}{k}} = \frac{1}{P} e^{\frac{\beta \cdot \varepsilon_i}{k}}$$

It remains to evaluate  $\beta$ .

$$dS = -k \sum_{i=1}^r \ln \left( \frac{n_i}{N_o} \right) dn_i = -k \sum_{i=1}^r \ln \left( \frac{1}{P} e^{\frac{\beta \varepsilon_i}{k}} \right) dn_i = -k \sum_{i=1}^r \left( \ln \left( \frac{1}{P} \right) + \ln \left( e^{\frac{\beta \varepsilon_i}{k}} \right) \right) dn_i$$

$$= -k \sum_{i=1}^r \left( \ln \left( \frac{1}{P} \right) + \frac{\beta \varepsilon_i}{k} \right) dn_i = -k \sum_{i=1}^r \left( \frac{\beta \varepsilon_i}{k} - \ln P \right) dn_i = \sum_{i=1}^r (-\beta \varepsilon_i + k \ln P) dn_i$$

$$= -\beta \sum_{i=1}^r \varepsilon_i dn_i + k \ln P \sum_{i=1}^r dn_i$$

$$dU = \sum_{i=1}^r \varepsilon_i dn_i$$

$$dN_o = \sum_{i=1}^r dn_i$$

$$dS = -\beta dU + k \ln P dN_o$$

$$dU = TdS - PdV + \mu dN_o$$

For an open system

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN_o \leftarrow dU = TdS - PdV + \mu dN_o$$

$$dS = -\beta dU + k \ln P dN_o$$

$$\beta = -\frac{1}{T} \quad k \ln P = -\frac{\mu}{T}$$

In this introductory development of statistical thermodynamics it is assumed that the average volume occupied by an atom is the same for all energy level. Therefore, no counterpart in the statistical expression for the entropy.

$$\left( \frac{n_i}{N_o} \right) = \frac{1}{P} e^{\frac{\beta \cdot \varepsilon_i}{k}} = \frac{1}{P} e^{-\frac{\varepsilon_i}{kT}} \quad P = \sum_{i=1}^r e^{\frac{\beta \varepsilon_i}{k}} = \sum_{i=1}^r e^{-\frac{\varepsilon_i}{kT}}$$

$$\frac{n_i}{N_o} = \frac{1}{P} e^{-\frac{\varepsilon_i}{kT}}$$

$$P = \sum_{i=1}^r e^{-\frac{\varepsilon_i}{kT}}$$

## 6-3.4 Calculation of the Macroscopic Properties from the Partition Function

The value of the entropy for the equilibrium distribution

$$S = -k \sum_{i=1}^r n_i \left( \ln \frac{n_i}{N_o} \right) = -k \sum_{i=1}^r n_i \ln \left( \frac{1}{P} e^{-\frac{\epsilon_i}{kT}} \right) = -k \sum_{i=1}^r n_i \left[ \ln \left( \frac{1}{P} \right) + \ln \left( e^{-\frac{\epsilon_i}{kT}} \right) \right] = -k \sum_{i=1}^r n_i \left[ -\ln P - \frac{\epsilon_i}{kT} \right]$$
$$= \sum_{i=1}^r n_i \left[ k \ln P + \frac{\epsilon_i}{T} \right] = k \ln P \sum_{i=1}^r n_i + \frac{1}{T} \sum_{i=1}^r n_i \epsilon_i = k \ln P N_o + \frac{1}{T} U$$

$$S = \frac{1}{T} U + k N_o \ln P$$

$$F \equiv U - TS = U - T \left( \frac{1}{T} U + k N_o \ln P \right) = -N_o k T \ln P$$

$$dF = -SdT - PdV + \delta W'$$

↓

$$S = - \left( \frac{\partial F}{\partial T} \right)_V$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_V = - \left( \frac{\partial}{\partial T} (-N_o k T \ln P) \right)_V = N_o k \ln P + N_o k T \left( \frac{\partial \ln P}{\partial T} \right)_V$$

$$F \equiv U - TS$$

$$F = -N_o k T \ln P$$

$$S = N_o k \ln P + N_o k T \left( \frac{\partial \ln P}{\partial T} \right)_v$$

$$U = F + TS = -N_o k T \ln P + T \left[ N_o k \ln P + N_o k T \left( \frac{\partial \ln P}{\partial T} \right)_v \right] = N_o k T^2 \left( \frac{\partial \ln P}{\partial T} \right)_v$$

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v = \left( \frac{\partial}{\partial T} N_o k T^2 \left( \frac{\partial \ln P}{\partial T} \right)_v \right)_v = 2 N_o k T \left( \frac{\partial \ln P}{\partial T} \right)_v + N_o k T^2 \left( \frac{\partial^2 \ln P}{\partial T^2} \right)_v$$

Computation of the remaining thermodynamic state functions,  $V$ ,  $H$ ,  $G$ , and  $C_p$ , requires a formulation that includes the volume dependence of the partition function.



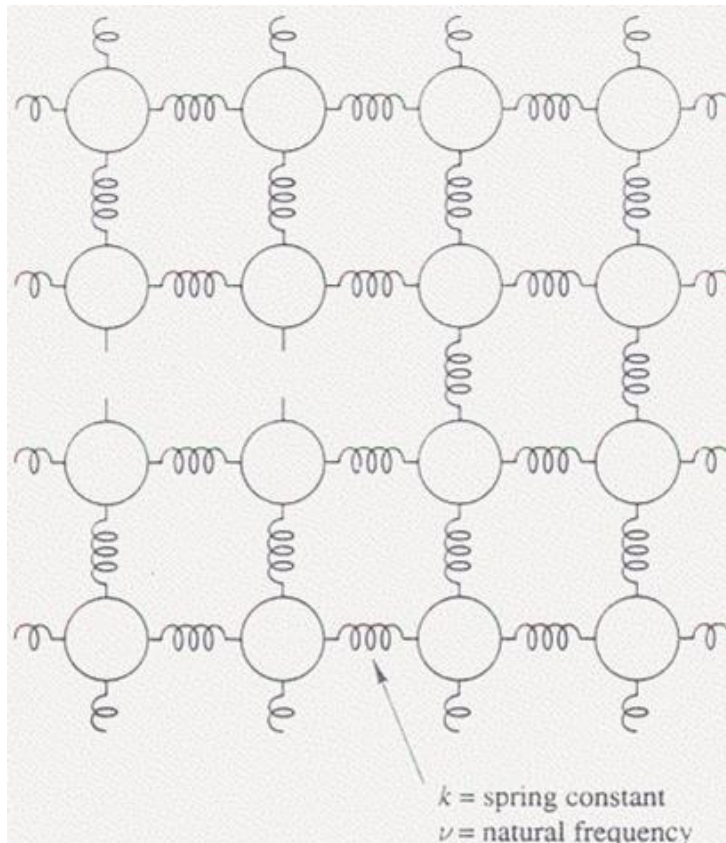
- (1) An atomistic model for the thermodynamic behavior of a system begins with a complete list of the energy levels that the particles in the system may exhibit.
- (2) Given this list and no other information, the partition function for the model can be computed.
- (3) Given the partition function, all the macroscopic thermodynamic properties of the system can be computed.

## 6-4 Application of the Algorithm

### 6-4.1 Einstein's Model of a Crystal

Consider a cubic crystal consisting of  $N_0$  atoms contains  $3N_0$  bonds.

Since all the springs connecting pairs of atoms are coupled together in the crystal, analysis of coupled oscillators show that only certain discrete vibrational frequencies can occur in such a system.



Einstein showed that the list of allowable energies for bonds could be described by:

$$\varepsilon_i = \left(i + \frac{1}{2}\right) \hbar \nu$$

The characteristic frequency  $\nu$  is related to the spring constant and hence the strength of the binding energy in the crystal.

i) Evaluation of the partition function:

$$P = \sum_{i=1}^r e^{-\frac{\varepsilon_i}{kT}} = \sum_{i=0}^r e^{-\frac{(i+\frac{1}{2})\hbar\nu}{kT}} = \sum_{i=0}^r e^{-i\frac{\hbar\nu}{kT}} e^{-\frac{\hbar\nu}{2kT}} = e^{-\frac{\hbar\nu}{2kT}} \sum_{i=0}^r e^{-i\frac{\hbar\nu}{kT}}$$

$$= e^{-\frac{\hbar\nu}{2kT}} \sum_{i=0}^r \left( e^{-\frac{\hbar\nu}{kT}} \right)^i = e^{-\frac{\hbar\nu}{2kT}} \frac{1}{1 - e^{-\frac{\hbar\nu}{kT}}} = \frac{e^{-\frac{\hbar\nu}{2kT}}}{1 - e^{-\frac{\hbar\nu}{kT}}} \quad \leftarrow \sum_{i=0}^{\infty} x^i = \frac{1}{1-x}, (x \ll 1)$$

$$\ln P = \ln \frac{e^{-\frac{\hbar\nu}{2kT}}}{1 - e^{-\frac{\hbar\nu}{kT}}} = \ln e^{-\frac{\hbar\nu}{2kT}} - \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right) = \underline{-\frac{\hbar\nu}{2kT} - \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right)}$$

ii) Calculation of thermodynamic properties from the given partition function:

$$F = -N_o kT \ln P = -3N_o kT \ln P = -3N_o kT \left( -\frac{\hbar\nu}{2kT} - \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right) \right)$$

$$= \frac{3}{2} N_o \hbar\nu + 3N_o kT \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right)$$



$$S = -\left( \frac{\partial F}{\partial T} \right)_V = -\left( \frac{\partial}{\partial T} \left( \frac{3}{2} N_o \hbar\nu + 3N_o kT \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right) \right) \right)_V = -3N_o k \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right) - 3N_o kT \frac{-e^{-\frac{\hbar\nu}{kT}}}{1 - e^{-\frac{\hbar\nu}{kT}}} \left( \frac{\hbar\nu}{kT^2} \right)$$

$$= -3N_o k \ln \left( 1 - e^{-\frac{\hbar\nu}{kT}} \right) + \frac{e^{-\frac{\hbar\nu}{kT}}}{1 - e^{-\frac{\hbar\nu}{kT}}} \left( 3 \frac{N_o \hbar\nu}{T} \right)$$

$$U = F + TS = \frac{3}{2} N_o \hbar \nu + 3 N_o k T \ln \left( 1 - e^{-\frac{\hbar \nu}{kT}} \right) + T \left( -3 N_o k \ln \left( 1 - e^{-\frac{\hbar \nu}{kT}} \right) + \frac{e^{-\frac{\hbar \nu}{kT}}}{1 - e^{-\frac{\hbar \nu}{kT}}} \left( 3 \frac{N_o \hbar \nu}{T} \right) \right)$$

$$= \frac{3}{2} N_o \hbar \nu + (3 N_o \hbar \nu) \left( \frac{e^{-\frac{\hbar \nu}{kT}}}{1 - e^{-\frac{\hbar \nu}{kT}}} \right) = \frac{3}{2} N_o \hbar \nu \left( 1 + 2 \left( \frac{e^{-\frac{\hbar \nu}{kT}}}{1 - e^{-\frac{\hbar \nu}{kT}}} \right) \right) = \frac{3}{2} N_o \hbar \nu \left( 1 + 2 \left( \frac{x}{1-x} \right) \right)$$

$$x \equiv e^{-\frac{\hbar \nu}{kT}}$$

$$= \frac{3}{2} N_o \hbar \nu \left( \frac{1-x+2x}{1-x} \right) = \frac{3}{2} N_o \hbar \nu \left( \frac{1+x}{1-x} \right)$$

$$U = \frac{3}{2} N_o \hbar \nu \left( \frac{1+x}{1-x} \right)$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial}{\partial T} \frac{3}{2} N_o \hbar \nu \left( \frac{1+e^{-\frac{\hbar \nu}{kT}}}{1-e^{-\frac{\hbar \nu}{kT}}} \right) \right)_V = \frac{3}{2} N_o \hbar \nu \left( \frac{\partial}{\partial T} \left( \frac{1+e^{-\frac{\hbar \nu}{kT}}}{1-e^{-\frac{\hbar \nu}{kT}}} \right) \right)_V$$

$$x \equiv e^{-\frac{\hbar \nu}{kT}}$$

$$= 3 N_o \left( \frac{\hbar \nu}{kT} \right)^2 \frac{e^{-\frac{\hbar \nu}{kT}}}{\left( 1 - e^{-\frac{\hbar \nu}{kT}} \right)^2}$$

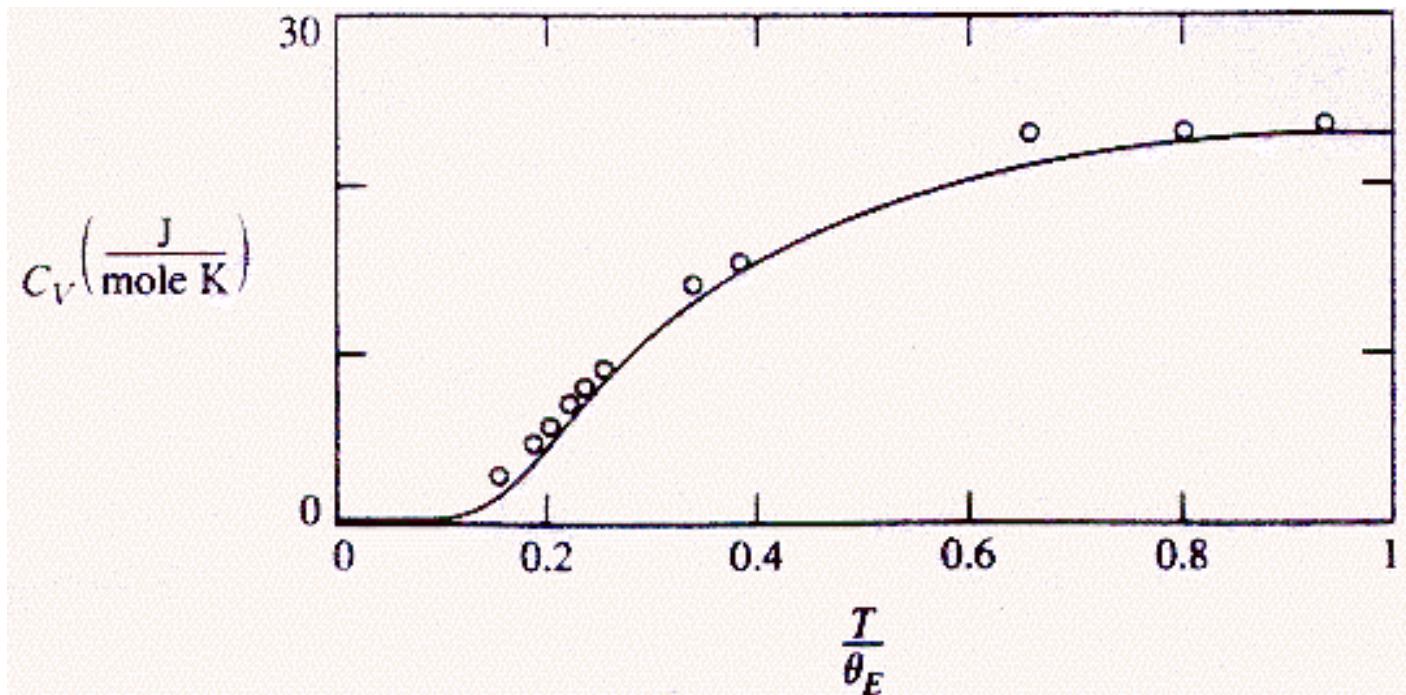


Fig. 6.3 Comparison of experimentally measured heat capacity for diamond with that computed from Einstein one parameter model.  $\theta_E=1320$  K.

## 6-4.2 Monatomic Gas Model

Consider a gas composed of identical particles, each of which is a single atom.

Assume that the energy contributed by each particle is simply the kinetic energy associated with its translation through space.

It is necessary to specify the values of six variables to specify the state of a gas atom in the system.

The energy exhibited by a particle in this model:  $\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$

Because the variables involved are continuous, the summation over all the available states that constitute the partition function must be replaced by an integral over all states.

i) Evaluation of the partition function:

$$P = \sum_{i=1}^r e^{-\frac{\epsilon_i}{kT}} \quad \Rightarrow \quad P = \int_0^{\infty} e^{-\frac{\epsilon}{kT}} d\epsilon = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \quad \text{at a point}$$

$$P = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \quad \text{at a point}$$



$$P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z dx dy dz \quad \text{in a volume}$$

$$P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} e^{-\frac{mv_y^2}{2kT}} e^{-\frac{mv_z^2}{2kT}} dv_x dv_y dv_z dx dy dz$$

The position and velocity coordinates are independent of each other.

$$P = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dx dy dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} e^{-\frac{mv_y^2}{2kT}} e^{-\frac{mv_z^2}{2kT}} dv_x dv_y dv_z = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dx dy dz \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} dv_x \int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2kT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2kT}} dv_z$$

$$= V \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} dv_x \int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2kT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2kT}} dv_z$$

$$V = \int_0^{l_z} \int_0^{l_y} \int_0^{l_x} dx dy dz$$

$$= V \left[ \frac{2\pi kT}{m} \right]^{\frac{3}{2}} \longleftarrow \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}v^2} dv = \sqrt{\frac{2\pi kT}{m}} \longleftarrow \int_{-\infty}^{\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a}$$

$$P = V \left[ \frac{2\pi kT}{m} \right]^{\frac{3}{2}} \quad \ln P = \ln V \left[ \frac{2\pi kT}{m} \right]^{\frac{3}{2}} = \ln V + \frac{3}{2} \ln \frac{2\pi kT}{m} = \ln V + \frac{3}{2} \ln \frac{2\pi k}{m} + \frac{3}{2} \ln T$$

$$\left( \frac{\partial \ln P}{\partial T} \right)_V = \frac{3}{2} \frac{1}{T}$$

ii) Calculation of thermodynamic properties from the given partition function:

$$F = -N_o kT \ln P = -3N_o kT \ln V \left[ \frac{2\pi kT}{m} \right]^{\frac{3}{2}}$$

$$S = N_o k \ln P + N_o kT \left( \frac{\partial \ln P}{\partial T} \right)_V = N_o k \ln \left( V \left[ \frac{2\pi kT}{m} \right]^{\frac{3}{2}} \right) + \frac{3}{2} N_o k$$

$$U = N_o kT^2 \left( \frac{\partial \ln P}{\partial T} \right)_V = N_o kT^2 \frac{3}{2T} = \frac{3}{2} N_o kT \dots \rightarrow C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N_o k$$

$$dF = -SdT - PdV + \delta W' \qquad -P = \left( \frac{\partial F}{\partial V} \right)_T$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = - \left( \frac{\partial (-N_o k T \ln P)}{\partial V} \right)_T = N_o k T \left( \frac{\partial \ln P}{\partial V} \right)_T \leftarrow \text{-----} \ln P = \ln V + \frac{3}{2} \ln \frac{2\pi k}{m} + \frac{3}{2} \ln T$$


$$= N_o k T \left( \frac{\partial}{\partial V} \left( \ln V + \frac{3}{2} \ln \frac{2\pi k}{m} + \frac{3}{2} \ln T \right) \right)_T = N_o k T \frac{1}{V} \quad \text{-----} \rightarrow \underline{PV = N_o k T}$$

## 6-5 Alternate Statistical Formulations

In the formulation presented here, no restrictions are placed upon the number of particles.

In distributing electrons in their allowable energy levels, however, this restriction (Pauli exclusion principle) must be strictly obeyed; a modified combinational analysis must be devised.

Three different forms of the relationship between microstates and macrostates have been prominent in the development of statistical thermodynamics.

(1) Maxwell-Boltzmann statistics  $\frac{n_i}{N} = 1/P_{MB} e^{\frac{\epsilon_i}{kT}}$    $\frac{n_i}{N_o} = \frac{1}{P} e^{-\frac{\epsilon_i}{kT}}$

(2) Bose-Einstein statistics  $\frac{n_i}{N} = 1/P_{BE} \left( e^{\frac{\epsilon_i}{kT}} - 1 \right)$

(3) Fermi-Dirac statistics  $\frac{n_i}{N} = 1/P_{FD} \left( e^{\frac{\epsilon_i}{kT}} + 1 \right)$

# Chapter 13 : Defects in Crystals

## 13-1 Introduction

<Solid crystals are not perfect>

Imperfections in the arrangement of the atoms in space occur as isolated points, along lines, or as surfaces in the structure.

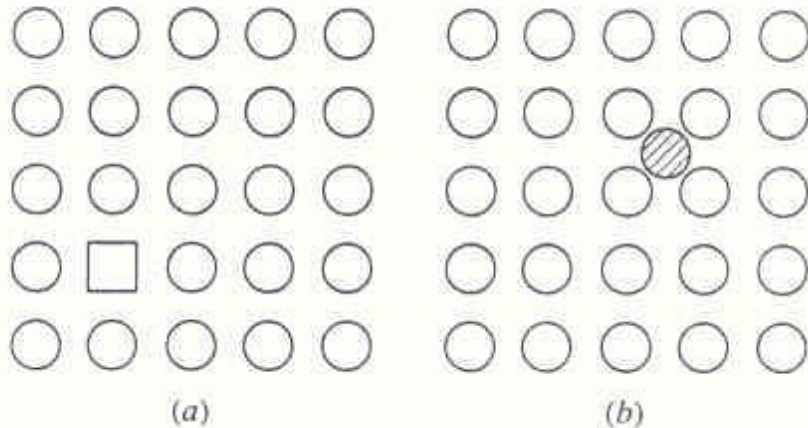
Perhaps the most important role played by point defects in the behavior of solids is in diffusion, that is, the atom-by-atom transport of components through the crystal lattice. Most processes in materials science that produce changes in microstructure involve diffusion. The elemental step in diffusion is the motion of an atom from a normal crystal site into an adjacent point defect.

Processes such as precipitation, phase changes, sintering, oxidation, solid state bonding, and some forms of creep depend on the presence of point defects in the system. Point defects influence the resistivity of conductors, the losses in insulators, and the conductivity of semiconductors.

## 13-2 Point Defects in Elemental Crystals

The two primary classes of point defects found to exist in elemental crystals are **vacancies** and **interstitials**.

While each defect contributes an increase to the energy of the crystal, each defect also increases the entropy of the crystal. These effects combine to guarantee that at equilibrium a crystal contains some point defects.



**FIGURE 13.1**

Two classes of point defects in an elemental crystal: (a) vacancy, and (b) an interstitial.

## 13-2.1 Conditions for Equilibrium in a Crystal with Vacant Lattice Sites

Consider a system composed of a homogeneous crystalline phase (a) and its vapor (g).

$$U' = U'(S', V', N') \quad U' = U'(S', V', n_1, n_2, \dots, n_r)$$

$$U'^{\alpha} = U'^{\alpha}(S'^{\alpha}, V'^{\alpha}, n_1^{\alpha}, n_2^{\alpha}, \dots, n_c^{\alpha}, n_V^{\alpha}) \quad dU'^{\alpha} = T^{\alpha} dS'^{\alpha} - P^{\alpha} dV'^{\alpha} + \sum_{k=1}^c \mu_k^{\alpha} dn_k^{\alpha} + \mu_V^{\alpha} dn_V^{\alpha}$$

$$U'^g = U'^g(S'^g, V'^g, n_1^g, n_2^g, \dots, n_c^g) \quad dU'^g = T^g dS'^g - P^g dV'^g + \sum_{k=1}^c \mu_k^g dn_k^g$$

$$dU'^{\alpha} = T^{\alpha} dS'^{\alpha} - P^{\alpha} dV'^{\alpha} + \sum_{k=1}^c \mu_k^{\alpha} dn_k^{\alpha} + \mu_V^{\alpha} dn_V^{\alpha}$$

$$dU'^g = T^g dS'^g - P^g dV'^g + \sum_{k=1}^c \mu_k^g dn_k^g$$

$$dS'^{\alpha} = \frac{1}{T^{\alpha}} dU'^{\alpha} + \frac{P^{\alpha}}{T^{\alpha}} dV'^{\alpha} - \frac{1}{T^{\alpha}} \sum_{k=1}^c \mu_k^{\alpha} dn_k^{\alpha} - \frac{1}{T^{\alpha}} \mu_V^{\alpha} dn_V^{\alpha}$$

$$dS'^g = \frac{1}{T^g} dU'^g + \frac{P^g}{T^g} dV'^g - \frac{1}{T^g} \sum_{k=1}^c \mu_k^g dn_k^g$$

$$dS'_{sys} = dS'^{\alpha} + dS'^g = \frac{1}{T^{\alpha}} dU'^{\alpha} + \frac{P^{\alpha}}{T^{\alpha}} dV'^{\alpha} - \frac{1}{T^{\alpha}} \sum_{k=1}^c \mu_k^{\alpha} dn_k^{\alpha} - \frac{1}{T^{\alpha}} \mu_V^{\alpha} dn_V^{\alpha} \\ + \frac{1}{T^g} dU'^g + \frac{P^g}{T^g} dV'^g - \frac{1}{T^g} \sum_{k=1}^c \mu_k^g dn_k^g$$

$$= \left( \frac{1}{T^{\alpha}} - \frac{1}{T^g} \right) dU'^{\alpha} + \left( \frac{P^{\alpha}}{T^{\alpha}} - \frac{P^g}{T^g} \right) dV'^{\alpha} - \sum_{k=1}^c \left( \frac{\mu_k^{\alpha}}{T^{\alpha}} - \frac{\mu_k^g}{T^g} \right) dn_k^{\alpha} - \frac{1}{T^{\alpha}} \mu_V^{\alpha} dn_V^{\alpha}$$

Because the system is isolated from its surrounding,

$$dU'_{sys} = dU'^{\alpha} + dU'^g = 0$$

$$dU'^g = -dU'^{\alpha}$$

$$dV'_{sys} = dV'^{\alpha} + dV'^g = 0$$

$$dV'^g = -dV'^{\alpha}$$

$$dn_{k,sys} = dn_k^{\alpha} + dn_k^g = 0$$

$$dn_k^g = -dn_k^{\alpha}$$

$$dS'_{sys,iso} = \left( \frac{1}{T^\alpha} - \frac{1}{T^g} \right) dU'^\alpha + \left( \frac{P^\alpha}{T^\alpha} - \frac{P^g}{T^g} \right) dV'^\alpha - \sum_{k=1}^c \left( \frac{\mu_k^\alpha}{T^\alpha} - \frac{\mu_k^g}{T^g} \right) dn_k^\alpha - \frac{1}{T^\alpha} \mu_V^\alpha dn_V^\alpha = 0 \quad \text{at Equilibrium}$$

$$\left( \frac{1}{T^\alpha} - \frac{1}{T^g} \right) = 0$$

$$\left( \frac{P^\alpha}{T^\alpha} - \frac{P^g}{T^g} \right) = 0$$

$$\left( \frac{\mu_k^\alpha}{T^\alpha} - \frac{\mu_k^g}{T^g} \right) = 0$$

$$\frac{\mu_V^\alpha}{T^\alpha} = 0$$

: Equilibrium Condition



$$\left( \begin{array}{l} T^\alpha = T^g \\ P^\alpha = P^g \\ \mu_k^\alpha = \mu_k^g \\ \underline{\mu_V^\alpha = 0} \end{array} \right)$$

## 13-2.2 The Concentration of Vacancies in a Crystal at Equilibrium

A mixture of vacant sites with sites occupied by normal atoms can be considered to be a dilute solution of vacancies and normal atoms.

**The chemical potential of any component is identical with the partial molal Gibbs free energy.**

$$\begin{aligned} \bar{G}_i &= \mu_i & \Delta\mu_i &= \Delta\bar{G}_i = \Delta\bar{G}_i^{xs} + \Delta\bar{G}_i^{id} = (\Delta\bar{H}_i^{xs} - T\Delta\bar{S}_i^{xs}) + (\Delta\bar{H}_i^{id} - T\Delta\bar{S}_i^{id}) \\ & & &= \Delta\bar{H}_i^{xs} - T\Delta\bar{S}_i^{xs} + kT \ln X_i^\alpha & \Delta\bar{H}_i^{id} &= 0 \\ & & & & \Delta\bar{S}_i^{id} &= -k \ln X_i^\alpha \end{aligned}$$

$$\mu_i^\alpha - \mu_i^{o,\alpha} = \Delta\bar{H}_i^{xs} - T\Delta\bar{S}_i^{xs} + kT \ln X_i^\alpha$$

$$\mu_V^\alpha - \mu_V^{o,\alpha} = \Delta\bar{H}_V^{xs} - T\Delta\bar{S}_V^{xs} + kT \ln X_V^\alpha$$

$$\mu_V^{o,\alpha} \equiv 0$$

$$\mu_V^\alpha = \Delta\bar{H}_V^{xs} - T\Delta\bar{S}_V^{xs} + kT \ln X_V^\alpha = 0 \quad \text{at Equilibrium}$$

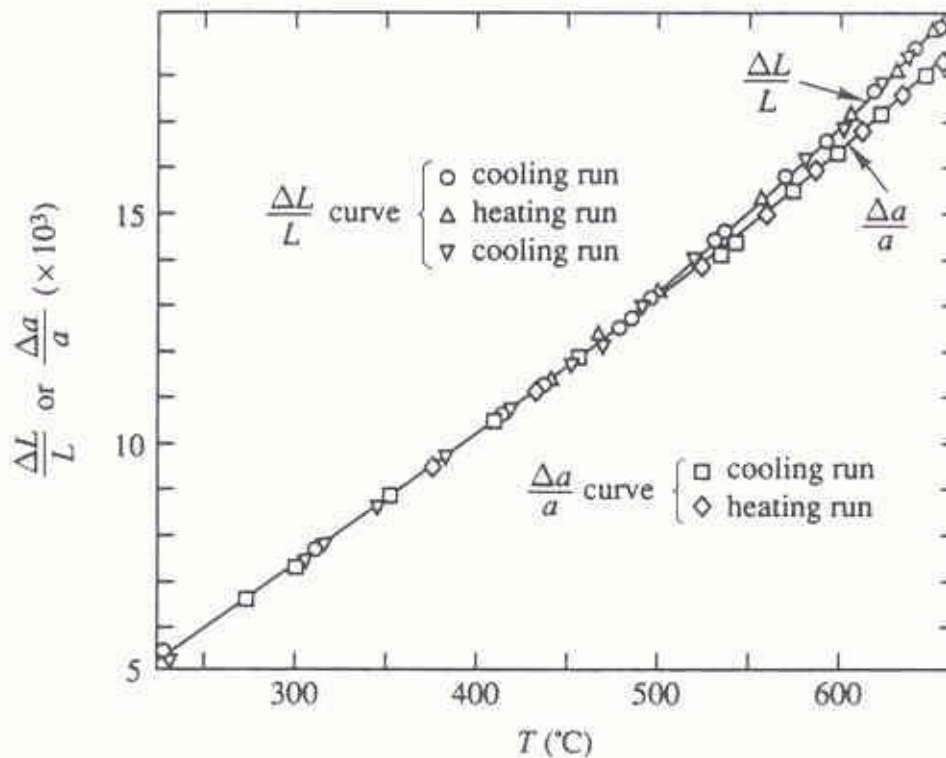
$$kT \ln X_V^\alpha = -\Delta\bar{H}_V^{xs} + T\Delta\bar{S}_V^{xs} \quad \ln X_V^\alpha = -\Delta\bar{H}_V^{xs} / kT + \Delta\bar{S}_V^{xs} / k$$

$$X_V^\alpha = e^{-\Delta\bar{H}_V^{xs} / kT} e^{\Delta\bar{S}_V^{xs} / k}$$

$$X_V^a = e^{-\Delta\bar{H}_V^{xs}/kT} e^{\Delta\bar{S}_V^{xs}/k}$$

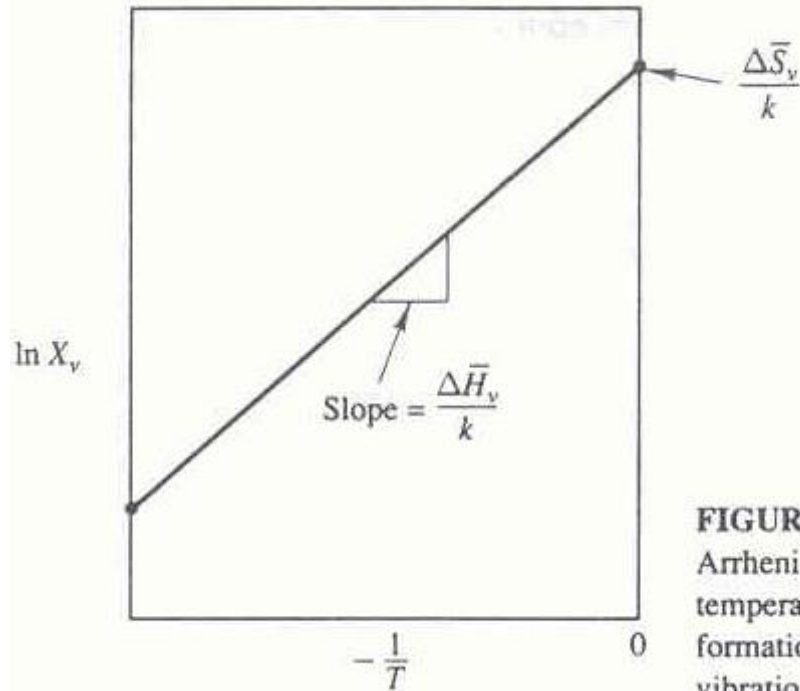
$\Delta\bar{H}_V^{xs}$  : Enthalpy of formation of a vacancy from a perfect crystal  
 $\Delta\bar{S}_V^{xs}$  : Excess entropy associated with this process, physically associated with changes in the vibrational behavior of atoms surrounding the vacant site

[Direct measurements of the equilibrium vacancy concentration]



**FIGURE 13.2**

Comparison of the molar volume of a crystal computed from dilatometric measurements and X-ray lattice parameter measurements. The difference between these curves at any temperature is the volume of vacancies in the crystal [13.1].



**FIGURE 13.3**

Arrhenius plot of atom fraction of vacancies versus temperature; the slope is proportional to the enthalpy of formation of a vacancy and the intercept gives the vibrational entropy of a vacancy.

**TABLE 13.1**

**Properties of vacancies for some typical metals** [13.3]

Metal	$X_v(T_m)^*$	$\Delta \bar{S}_v$ (J/gm-atom K)	$\Delta \bar{H}_v$ (KJ/gm-atom)
Aluminum	$9.0 \times 10^{-4}$	19	74
Copper	$1.9 \times 10^{-4}$	12	113
Gold	$7.2 \times 10^{-4}$	10	92
Lead	$2.0 \times 10^{-4}$	21	56
Platinum	$6.0 \times 10^{-4}$	9	135
Silver	$1.7 \times 10^{-4}$	12	101

## 13-2.3 Interstitial Defects and Divacancies

These arguments easily extend to other defects in elemental crystals with analogous results. At equilibrium, the chemical potential of an interstitial defect is zero, implying a relation between defect concentration and temperature of the general form:

$$X_D^\alpha = f_D e^{\Delta \bar{S}_D^{xs}/k} e^{-\Delta \bar{H}_D^{xs}/kT}$$

$$[M_i] \equiv \frac{N_i}{N_{available,i}} = \frac{N_i}{f_i N_o} = \frac{1}{f_i} X_i$$

Where  $f_D$  is the ratio the number of interstitial sites to the number of normal lattice sites in the crystal.

Defects may occur in combinations in an elemental crystal. 1) the most common of these is the divacancy, which is a pair of adjacent vacant lattice sites.

$$X_{VV}^\alpha = e^{\Delta \bar{S}_{VV}^{xs}/k} e^{-\Delta \bar{H}_{VV}^{xs}/kT}$$

- (1) The separate formation of two vacancies from a perfect crystal.
- (2) The formation of the divacancy configuration from two separated single vacancies.

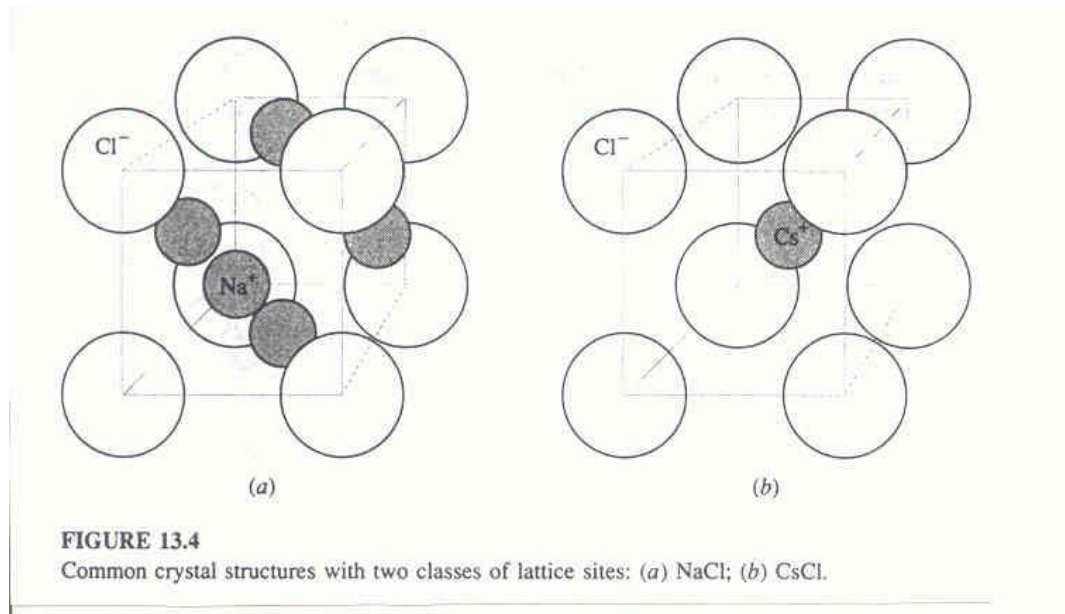
$$\Delta \bar{H}_{VV}^{xs} = 2\Delta \bar{H}_V^{xs} + \Delta \bar{H}_{int}$$

$$\Delta \bar{S}_{VV}^{xs} = 2\Delta \bar{S}_V^{xs} + \Delta \bar{S}_{int}$$

They are the interaction enthalpy and entropy for the pair of vacancies, both of which can be expected to be negative.

$$\begin{aligned}
 X_{VV}^{\alpha} &= e^{\Delta\bar{S}_{VV}^{xs}/k} e^{-\Delta\bar{H}_{VV}^{xs}/kT} = e^{(2\Delta\bar{S}_{V}^{xs} + \Delta\bar{S}_{\text{int}}^{xs})/k} e^{-(2\Delta\bar{H}_{V}^{xs} + \Delta\bar{H}_{\text{int}}^{xs})/kT} = e^{(2\Delta\bar{S}_{V}^{xs})/k} e^{-(2\Delta\bar{H}_{V}^{xs})/kT} e^{(\Delta\bar{S}_{\text{int}}^{xs})/k} e^{-(\Delta\bar{H}_{\text{int}}^{xs})/kT} \\
 &= \left( e^{(\Delta\bar{S}_{V}^{xs})/k} e^{-(\Delta\bar{H}_{V}^{xs})/kT} \right)^2 e^{(\Delta\bar{S}_{\text{int}}^{xs})/k} e^{-(\Delta\bar{H}_{\text{int}}^{xs})/kT} = \left( X_V^{\alpha} \right)^2 e^{(\Delta\bar{S}_{\text{int}}^{xs})/k} e^{-(\Delta\bar{H}_{\text{int}}^{xs})/kT}
 \end{aligned}$$

It is concluded that at equilibrium the concentration of divacancies is somewhat larger than the square of the concentration of single vacancies.



## 13-3 Point Defects in Stoichiometric Compound Crystals

Many intermediate phases and line compounds have crystal structures that have two (or more) distinct classes of lattice sites, Fig. 13.4, called sublattices.

In the following description the anion (or more electronegative) component in a compound crystal is designated generically as **X**, The other more metallic (cation) element in the system is designated with an **M**. A vacant lattice site is designated with a **V**. These components (atoms or ions) can occupy cation (M) sites, anion (X) sites, or interstitial (i) sites. Finally, each entity visualized has as associated electronic charge.

A widely accepted notation was devised by Kröger and Vink:

1. The entity occupying the defect site (M, X, V or substitutional elements)
2. A subscript for the type of site occupied ( $\text{M}_M$ ,  $\text{X}_X$ , or  $\text{V}_i$ )
3. A superscript for the excess charge associated with the site,  $(\text{M}_M^x)$ ,  $(\text{X}_X^y)$ , or  $(\text{V}_i^z)$

Some generic examples of this notation are reviewed in Table 13.2

Table 13.2 Defect designation using the Kroger-Vink notation applied to a compound with nominal composition MX and normal valence of M as +2, X as -2

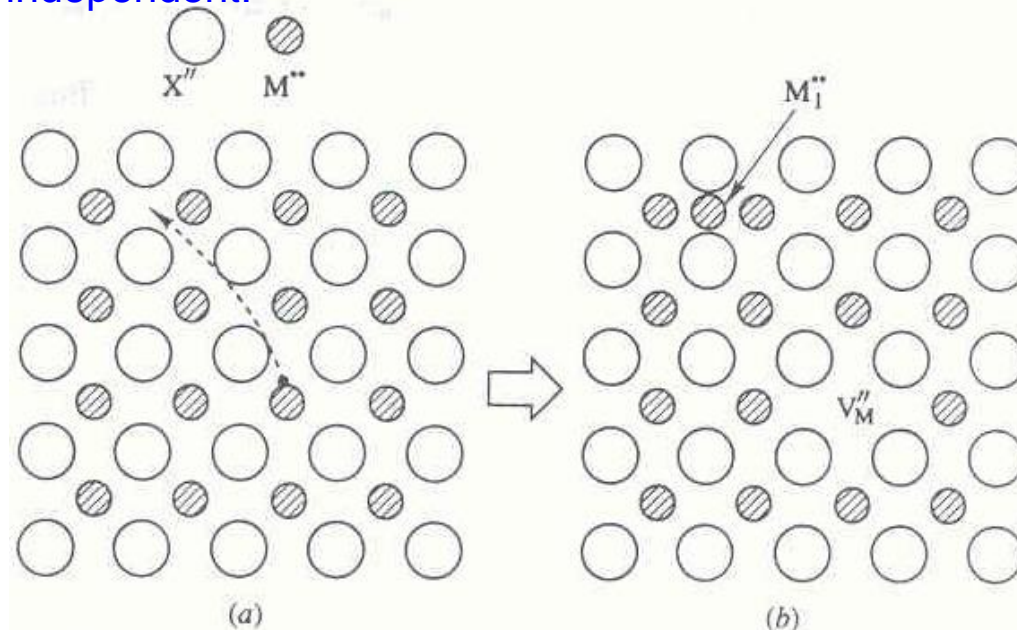
Defect	Excess charge	Symbol
Vacancy on M sublattice	-2	$V_M''$
Vacancy on X sublattice	+2	$V_X^{..}$
M atom in interstitial site	+2	$M_i^{2+}$
X atom in interstitial site	-2	$X_i^{2-}$
M atom on X site	+4	$M_X^{4+}$
X atom on M site	-4	$X_M^{4-}$
Divacancy on M and X sites	0	$(V_M V_X)$
M interstitial paired with M on X site	+6	$(M_i M_X)^{6+}$
Solute cation L with +3 charge on M site	+1	$L_M^+$
Solute anion Y with -1 charge on X site	+1	$Y_X^-$
Free (unattached) electron	-1	$e'$
Electron hole	+1	$h'$

## 13-3.1 Frenkel Defects

A Frenkel defect is formed on the cation sublattice by removing an M ion from a normal M site and placing it in an interstitial site. It is also possible to form a Frenkel defect on the anion sublattice.

Consider a crystal MX; four distinct entities exist in such a crystal:  $M_M^x$ ,  $X_X^x$ ,  $V_M''$ ,  $M_i''$

The number of each of these entities can be varied in the crystal; however, these variations are not independent.



**FIGURE 13.5**

A Frenkel defect is formed on the cation sublattice by removing an M atom from a normal cation lattice site and placing it in an interstitial site.

To find the conditions for equilibrium,

(1) Write an expression for the entropy of this homogeneous crystalline phase incorporating changes in the numbers of each possible entity.

$$dS'_{\text{sys}} = \frac{1}{T} dU' + \frac{P}{T} dV' - \frac{1}{T} \sum_{k=1}^c \mu_k dn_k = \frac{1}{T} dU' + \frac{P}{T} dV' - \frac{1}{T} (\mu_{M_M} dn_{M_M} + \mu_{X_X} dn_{X_X} + \mu_{V_M} dn_{V_M} + \mu_{M_i} dn_{M_i})$$

(2) In an isolated system,  $dU' = 0$        $dV' = 0$        $dm_M = 0$        $dm_X = 0$

$$dm_M = dn_{M_M} + dn_{M_i} = 0 \qquad dm_X = dn_{X_X} = 0 \qquad \underline{dn_{M_i} = dn_{V_M}}$$

(3) Insertion of these constraints,

$$dS'_{\text{sys,iso}} = -\frac{1}{T} (\mu_{M_M} (-dn_{M_i}) + 0 + \mu_{V_M} (dn_{M_i}) + \mu_{M_i} dn_{M_i}) = -\frac{1}{T} (\mu_{V_M} + \mu_{M_i} - \mu_{M_M}) dn_{M_i}$$

$$M_M = V_M + M_i \qquad A_{M_i} \equiv \Delta\mu_{M_i} = (\mu_{M_i} + \mu_{V_M} - \mu_{M_M})$$

(4) The condition for equilibrium,

$$dS'_{\text{sys,iso}} = -\frac{1}{T} (\mu_{V_M} + \mu_{M_i} - \mu_{M_M}) dn_{M_i} = 0 \quad \Rightarrow \quad A_{M_i} = (\mu_{M_i} + \mu_{V_M} - \mu_{M_M}) = 0$$

$$A_{M_i} = (\mu_{M_i} + \mu_{V_M} - \mu_{M_M}) = 0$$

$$\Delta\mu_k = \mu_k - \mu_k^o = \Delta\bar{G}_k = \Delta\bar{G}_k^{xs} + \Delta\bar{G}_k^{id} = \Delta\bar{G}_k^{xs} + kT \ln X_k = (\bar{G}_k^{xs} - \bar{G}_k^o) + kT \ln X_k = (\bar{G}_k^{xs} - \mu_k^o) + kT \ln X_k$$

$$\mu_k = \bar{G}_k^{xs} + kT \ln X_k \quad (k = M_i, V_M, M_M)$$

$$A_{M_i} = (\mu_{M_i} + \mu_{V_M} - \mu_{M_M}) = (\bar{G}_{M_i}^{xs} + kT \ln X_{M_i} + \bar{G}_{V_M}^{xs} + kT \ln X_{V_M} - (\bar{G}_{M_M}^{xs} + kT \ln X_{M_M})) = 0$$

$$= (\bar{G}_{M_i}^{xs} + \bar{G}_{V_M}^{xs} - \bar{G}_{M_M}^{xs} + kT \ln X_{M_i} + kT \ln X_{V_M} - kT \ln X_{M_M})$$

$$= (\bar{G}_{M_i}^{xs} + \bar{G}_{V_M}^{xs} - \bar{G}_{M_M}^{xs}) + kT (\ln X_{M_i} + \ln X_{V_M} - \ln X_{M_M}) = \Delta\bar{G}_{fd}^{xs} + kT \ln \left( \frac{X_{M_i} X_{V_M}}{X_{M_M}} \right) = 0$$

$$\Delta\bar{G}_{fd}^{xs} = -kT \ln K_{fd}$$

$$\Delta\bar{G}_{fd}^{xs} \equiv (\bar{G}_{M_i}^{xs} + \bar{G}_{V_M}^{xs} - \bar{G}_{M_M}^{xs})$$

$$K_{fd} \equiv \left( \frac{X_{M_i} X_{V_M}}{X_{M_M}} \right)$$

$$\Delta \bar{G}_{fd}^{xs} = -kT \ln K_{fd}$$

$$K_{fd} = \left( \frac{X_{M_i} X_{V_M}}{X_{M_M}} \right) = \exp \left( -\frac{\Delta \bar{G}_{fd}^{xs}}{kT} \right)$$

For a low defect concentration regime  $X_{M_M} \approx 1$

$$X_{M_i} X_{V_M} \approx \exp \left( -\frac{\Delta \bar{G}_{fd}^{xs}}{kT} \right)$$

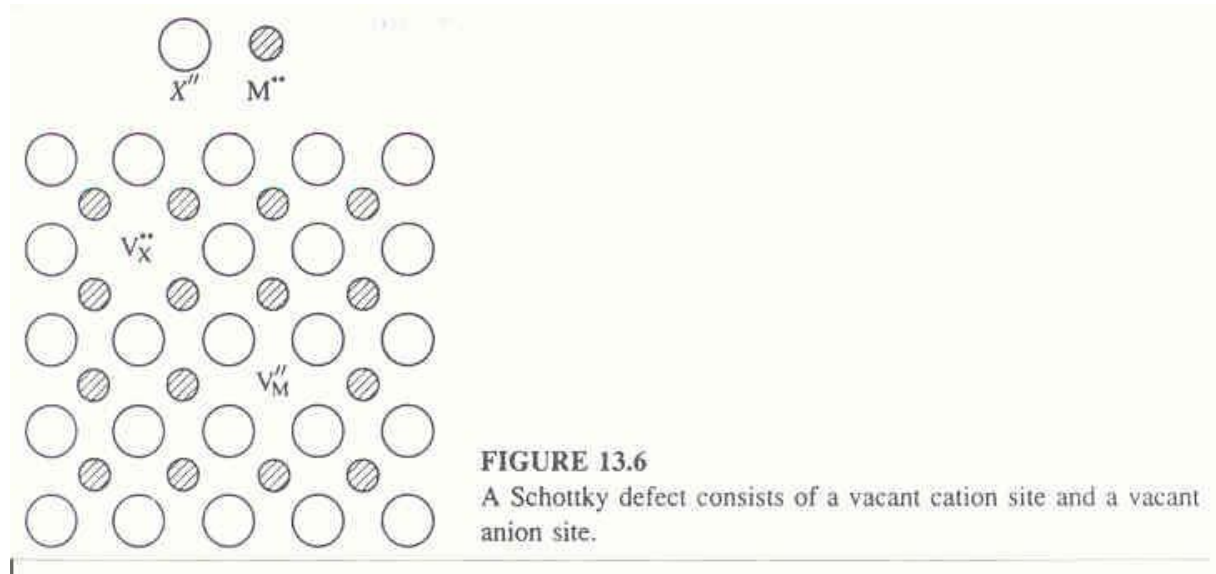
For a stoichiometric compound  $X_{M_i} = X_{V_M} \equiv X_{fd}$

$$X_{fd} \approx \exp \left( -\frac{\Delta \bar{G}_{fd}^{xs}}{2kT} \right) = \exp \left( -\frac{\Delta \bar{H}_{fd}^{xs} - T \Delta \bar{S}_{fd}^{xs}}{2kT} \right) = e^{\frac{\Delta \bar{S}_{fd}^{xs}}{2k}} e^{-\frac{\Delta \bar{H}_{fd}^{xs}}{2kT}}$$


---

## 13-3.2 Schottky Defects

In an MX crystal a Schottky defect consists of a vacant site and a vacant anion site.



With an expression for the change in entropy

$$\begin{aligned}
 dS'_{sys} &= \frac{1}{T} dU' + \frac{P}{T} dV' - \frac{1}{T} \left( \mu_{M_M} dn_{M_M} + \mu_{X_X} dn_{X_X} + \mu_{V_M} dn_{V_M} + \mu_{V_X} dn_{V_X} \right) \\
 &= -\frac{1}{T} \left( \mu_{V_M} dn_{V_M} + \mu_{V_X} dn_{V_X} \right) = -\frac{1}{T} \left( \mu_{V_M} dn_{V_M} + \mu_{V_X} dn_{V_M} \right) = \underline{-\frac{1}{T} \left( \mu_{V_M} + \mu_{V_X} \right) dn_{V_M}} = 0
 \end{aligned}$$

The isolation constraints

$$dU' = 0 \quad dV' = 0 \quad dm_M = dn_{M_M} = 0 \quad dm_X = dn_{X_X} = 0 \quad dn_{V_M} = dn_{V_X}$$

$$dS'_{sys,iso} = -\frac{1}{T}(\mu_{V_M} + \mu_{V_X})dn_{V_M} = 0$$

The equilibrium condition :

$$null = V_M + V_X \quad A_{V_M, V_X} = (\mu_{V_M} + \mu_{V_X}) = 0$$

$$X_{sd} \approx \exp\left(-\frac{\Delta\bar{G}_{sd}^{xs}}{2kT}\right) = \exp\left(-\frac{\Delta\bar{H}_{sd}^{xs} - T\Delta\bar{S}_{sd}^{xs}}{2kT}\right) = e^{\frac{\Delta\bar{S}_{sd}^{xs}}{2k}} e^{-\frac{\Delta\bar{H}_{sd}^{xs}}{2kT}}$$

$\Delta\bar{S}_{sd}^{xs}$  : the excess entropy associated with the formation of the pair of vacancies from a perfect crystal

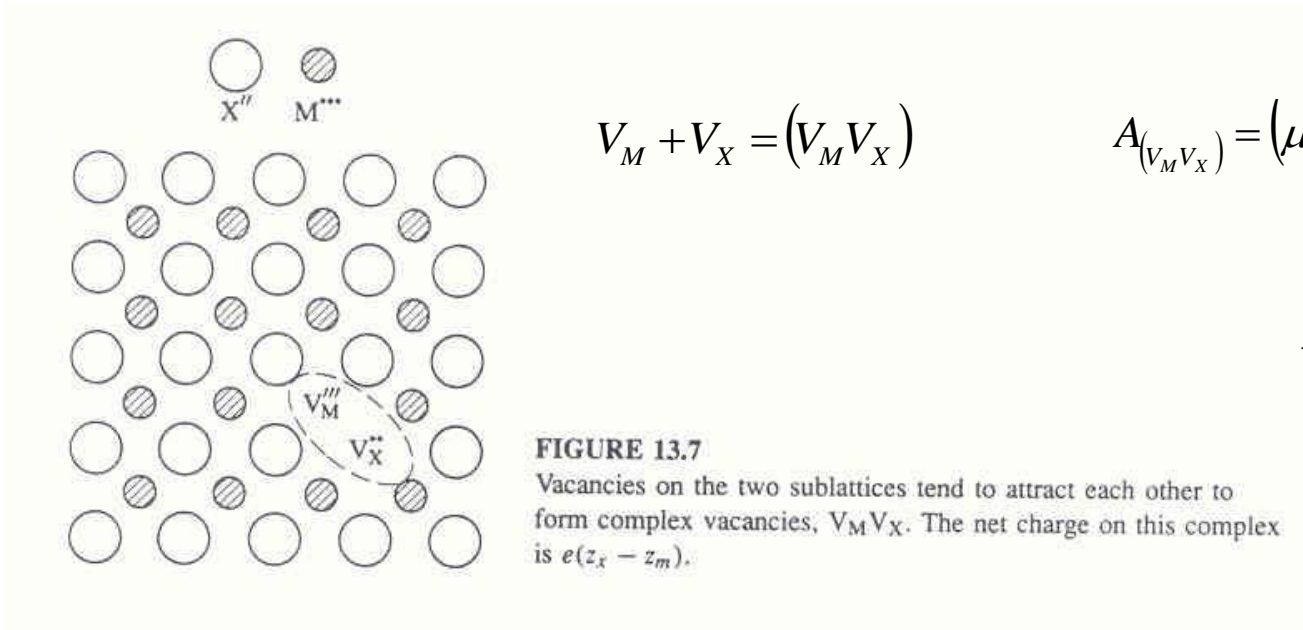
$\Delta\bar{H}_{sd}^{xs}$  : the corresponding enthalpy change

In a crystal with formula  $M_uX_v$ , in which the ratio of M to X sites is  $u/v$ , conservation of the ratio of anion to cation sites dictated by the geometry of the crystalline arrangement requires that a Schottky defect be made up of  $u$  cation vacancies and  $v$  anion vacancies.

$$null = uV_M + vV_X \quad A_{V_M, V_X} = (u\mu_{V_M} + v\mu_{V_X}) = 0$$

### 13-3.3 Combined Defects in Binary Compounds

The oppositely charged entities in a crystal can be expected to attract each other to form a cation-anion vacancy pair.



$\Delta \bar{S}_{mx}^{xs}$  : the excess entropy associated with the formation of the associate

$\Delta \bar{H}_{mx}^{xs}$  : the enthalpy change for the process

## 13-3.4 Multivariate Equilibrium Among Defects in a Stoichiometric Compound

The strategy for determining defect concentrations in a crystal of the compound  $M_U X_V$  that is isolated from its surroundings.

The entities that may exist in this crystal when it comes to equilibrium include

$$M_M^x, V_M, M_i, X_X^x, V_X, X_i$$

Defect complexes may also exist but are neglected in this development.

(1) Expression for the change in entropy

$$dS'_{sys} = \frac{1}{T} dU' + \frac{P}{T} dV' - \frac{1}{T} \left( \mu_{M_M} dn_{M_M} + \mu_{V_M} dn_{V_M} + \mu_{M_i} dn_{M_i} + \mu_{X_X} dn_{X_X} + \mu_{V_X} dn_{V_X} + \mu_{X_i} dn_{X_i} \right)$$

(2) Applying the usual isolation constraints on changes in internal energy and volume

$$dS'_{sys} = -\frac{1}{T} \left( \mu_{M_M} dn_{M_M} + \mu_{V_M} dn_{V_M} + \mu_{M_i} dn_{M_i} + \mu_{X_X} dn_{X_X} + \mu_{V_X} dn_{V_X} + \mu_{X_i} dn_{X_i} \right)$$

(3) In addition, applying the following three constraining equations that operate on the changes in the numbers of each entity in this isolated crystal:

① Conservation of M atoms  $dm_M = dn_{M_M} + dn_{M_i} = 0 \Rightarrow dn_{M_M} = -dn_{M_i}$

② Conservation of X atoms  $dm_X = dn_{X_X} + dn_{X_i} = 0 \Rightarrow dn_{X_X} = -dn_{X_i}$

③ Conservation of the ratio of sites in the two sublattices  $v[dn_{M_M} + dn_{V_M}] = u[dn_{X_X} + dn_{V_X}]$

$$u:v = n_{S_M}:n_{S_X} \longrightarrow vn_{S_M} = un_{S_X} \longrightarrow vdn_{S_M} = udn_{S_X} \xrightarrow{\uparrow}$$

$$dn_{V_M} = \frac{u}{v} [dn_{X_X} + dn_{V_X}] - dn_{M_M}$$

$$dS'_{sys} = -\frac{1}{T} \left( \mu_{M_M} dn_{M_M} + \mu_{V_M} dn_{V_M} + \mu_{M_i} dn_{M_i} + \mu_{X_X} dn_{X_X} + \mu_{V_X} dn_{V_X} + \mu_{X_i} dn_{X_i} \right)$$

$$= -\frac{1}{T} \left( \mu_{M_M} (-dn_{M_i}) + \mu_{V_M} dn_{V_M} + \mu_{M_i} dn_{M_i} + \mu_{X_X} (-dn_{X_i}) + \mu_{V_X} dn_{V_X} + \mu_{X_i} dn_{X_i} \right)$$

$$= -\frac{1}{T} \left( (\mu_{M_i} - \mu_{M_M}) dn_{M_i} + \mu_{V_M} dn_{V_M} + (\mu_{X_i} - \mu_{X_X}) dn_{X_i} + \mu_{V_X} dn_{V_X} \right)$$

$$\begin{aligned}
dS'_{sys,iso} &= -\frac{1}{T} \left( (\mu_{M_i} - \mu_{M_M}) dn_{M_i} + \mu_{V_M} dn_{V_M} + (\mu_{X_i} - \mu_{X_X}) dn_{X_i} + \mu_{V_X} dn_{V_X} \right) \\
&\qquad\qquad\qquad dn_{V_M} = \frac{u}{v} [dn_{X_X} + dn_{V_X}] - dn_{M_M} = \frac{u}{v} [-dn_{X_i} + dn_{V_X}] + dn_{M_i} \\
&= -\frac{1}{T} \left( (\mu_{M_i} - \mu_{M_M}) dn_{M_i} + \mu_{V_M} \left( \frac{u}{v} [-dn_{X_i} + dn_{V_X}] + dn_{M_i} \right) + (\mu_{X_i} - \mu_{X_X}) dn_{X_i} + \mu_{V_X} dn_{V_X} \right) \\
&= -\frac{1}{T} \left( (\mu_{M_i} + \mu_{V_M} - \mu_{M_M}) dn_{M_i} + \left( \mu_{X_i} - \frac{u}{v} \mu_{V_M} - \mu_{X_X} \right) dn_{X_i} + \left( \frac{u}{v} \mu_{V_M} + \mu_{V_X} \right) dn_{V_X} \right) \\
&= -\frac{1}{T} \left( (\mu_{M_i} + \mu_{V_M} - \mu_{M_M}) dn_{M_i} + (\mu_{X_i} + \mu_{V_X} - \mu_{X_X}) dn_{X_i} + \left( \frac{u}{v} \mu_{V_M} + \mu_{V_X} \right) dn_{V_X} \right) = 0
\end{aligned}$$

(4) To find the conditions for equilibrium, set the coefficient equal to zero.

$$\begin{array}{l}
(\mu_{M_i} + \mu_{V_M} - \mu_{M_M}) = 0 \\
(\mu_{X_i} + \mu_{V_X} - \mu_{X_X}) = 0 \\
\left( \frac{u}{v} \mu_{V_M} + \mu_{V_X} \right) = 0
\end{array}
\quad \Rightarrow \quad
\begin{array}{l}
M_M = M_i + V_M \\
X_X = X_i + V_X \\
null = uV_M + vV_X
\end{array}$$

(5) It is customary to describe the concentrations of each of the entities as a fraction of the sites in the corresponding sublattice. These measures of composition are designated with brackets.

$$[V_M] = \frac{n_{V_M}}{n_{S_M}} = \frac{n_{V_M}}{uN_o}, [M_i] = \frac{n_{M_i}}{n_{S_M}} = \frac{n_{M_i}}{uN_o}$$

$$[V_X] = \frac{n_{V_X}}{n_{S_X}} = \frac{n_{V_X}}{vN_o}, [X_i] = \frac{n_{X_i}}{n_{S_X}} = \frac{n_{X_i}}{vN_o}$$

$$[M_M] \cong 1$$

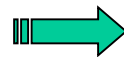
$$\frac{[M_i][V_M]}{[M_M]} = K_{fd,c} = K_{fd,c}^o e^{-(\Delta\bar{H}_{fd,c}/kT)}$$

$$\Rightarrow [M_i][V_M] \approx K_{fd,c}^o e^{-(\Delta\bar{H}_{fd,c}/kT)}$$

$$M_M = M_i + V_M$$

$$X_X = X_i + V_X$$

$$null = uV_M + vV_X$$



$$[M_i][V_M] \approx K_{fd,c}^o e^{-(\Delta\bar{H}_{fd,c}/kT)}$$

$$[X_i][V_X] \approx K_{fd,a}^o e^{-(\Delta\bar{H}_{fd,a}/kT)}$$

$$[V_M]^u [V_X]^v \approx K_{sd}^o e^{-(\Delta\bar{H}_{sd}/kT)}$$

(6) The condition for charge neutrality in the crystal

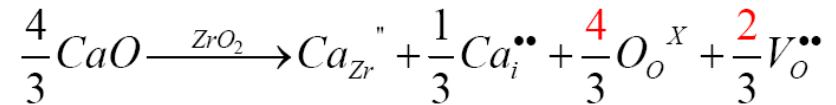
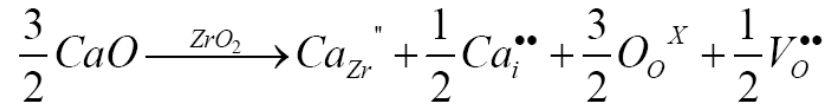
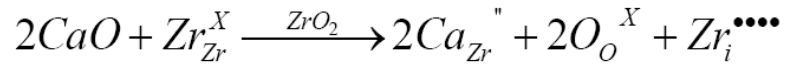
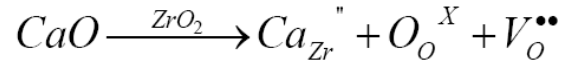
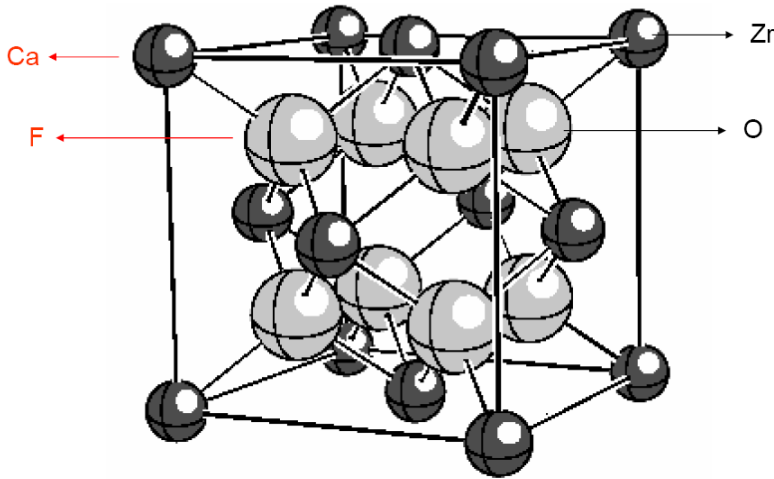
$$\left[ V_M^{-z} \right] \left[ M_i^{+z} \right] \left[ V_X^{\left(\frac{u}{v}\right)z} \right], \left[ X_i^{-\left(\frac{u}{v}\right)z} \right]$$

$$-zn_{V_M} + zn_{M_i} + \frac{u}{v}zn_{V_X} - \frac{u}{v}zn_{X_i} = 0$$

$$\boxed{-\left[ V_M^{-z} \right] + \left[ M_i^{+z} \right] + \frac{u}{v} \left[ V_X^{\left(\frac{u}{v}\right)z} \right] - \frac{u}{v} \left[ X_i^{-\left(\frac{u}{v}\right)z} \right] = 0}$$

# 13-3.5 Extrinsic Defects in Stoichiometric Compound Crystals

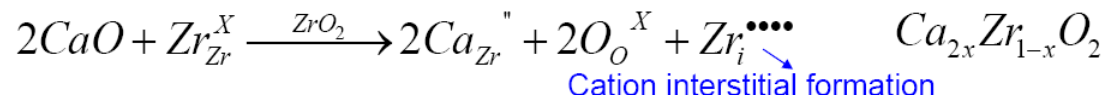
Ex)  $ZrO_2$  doped with  $CaO$

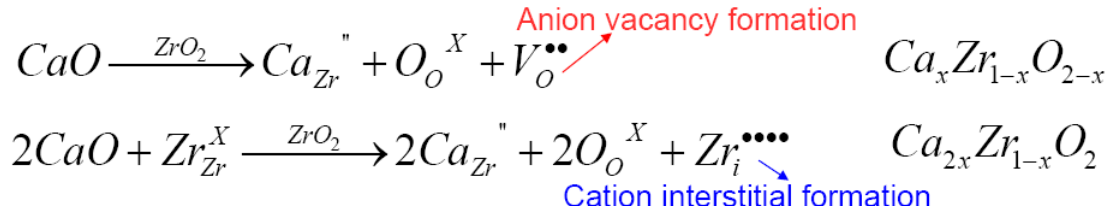


Ion size, crystal structure, density, electrical properties

.....

→ Determine Proper Incorporation Reaction.





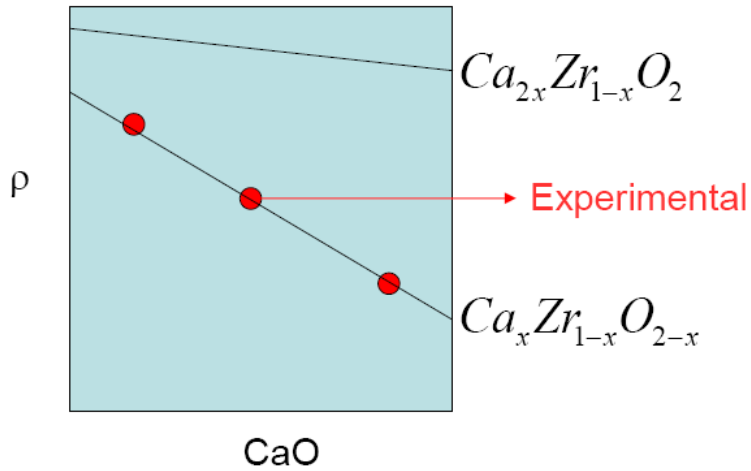
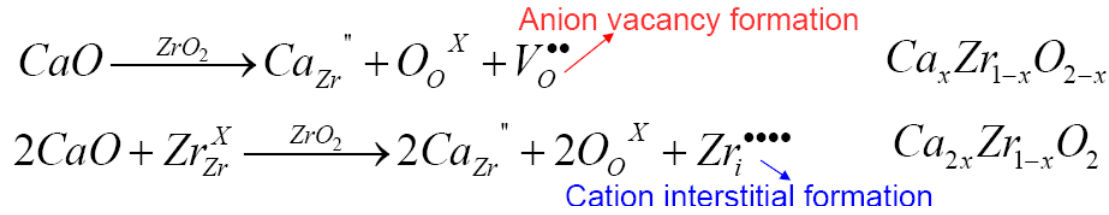
$x=0.15$   $a=5.1535\text{\AA}$  determined by x-ray diffraction
 
$$\rho = \frac{z(x M_{\text{CaO}} + (1-x) M_{\text{ZrO}_2})}{N_A V_C}$$

**Anion vacancy:  $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$**

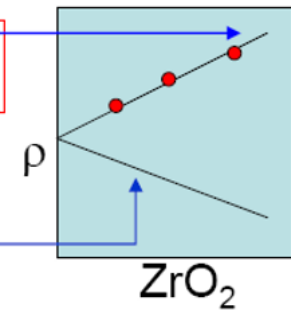
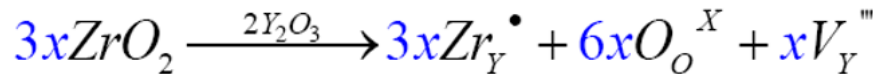
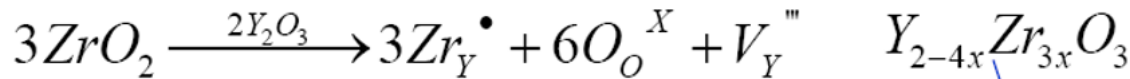
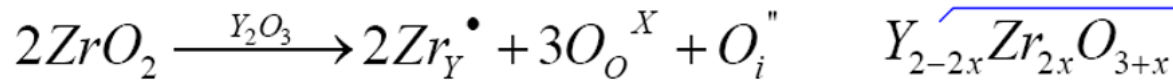
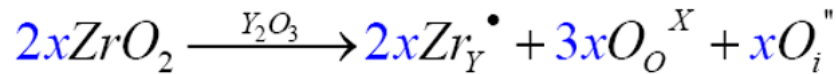
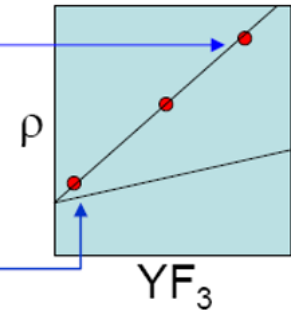
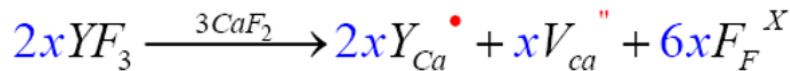
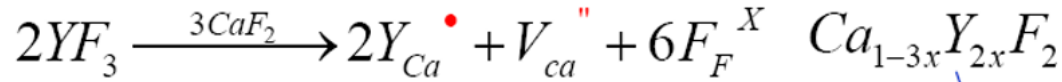
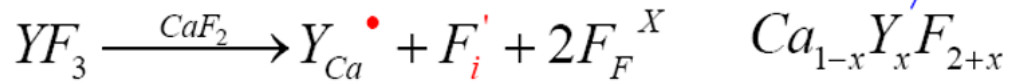
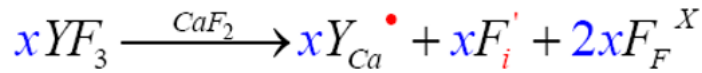
$$\rho = \frac{4(0.15 M_{\text{CaO}} + 0.85 M_{\text{ZrO}_2})}{N_A (5.1535 \times 10^{-8} \text{ cm})^3} = 5.52 \text{ g / cm}^3$$

**Cation interstitial:  $\text{Ca}_{0.30}\text{Zr}_{0.85}\text{O}_2$**

$$\rho = \frac{4(0.3 M_{\text{CaO}} + 0.85 M_{\text{ZrO}_2})}{N_A (5.1535 \times 10^{-8} \text{ cm})^3} = 5.92 \text{ g / cm}^3$$



**When sintered at 1600°C, the density profiles coincide with anion model**



## 13-4 Nonstoichiometric Compound Crystals

When elements M and X combine to form a crystalline compound  $M_uX_v$ , the resulting structure forms in two sublattices, one normally occupied by M atoms and the other by X atoms.

The geometry of the crystal structure that the numbers of the two kinds of sites occur in the ratio (v/u) and **the ratio of sites is stoichiometric.**

If the crystal contains only intrinsic defects, **the composition is still stoichiometric.**

The defect structure of real crystals is not confined to intrinsic defects. Interactions with the surroundings may produce defects that are not simply equivalent to an internal rearrangement of atoms on sites in the crystal.

In an oxidizing atmosphere, the compound  $M_uO_v$  may dissolve more oxygen atoms than the number given by the stoichiometric ratio (v/u). **The composition of the compound departs from its stoichiometric ratio** and becomes oxygen rich. **However, the geometric requirements of the crystal lattice for the compound require that the ratio of sites remains at (u/v)**

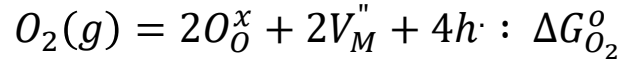
In the case of oxygen rich, the excess oxygen atoms must be accommodated either by

- (1) Placing oxygen ions in interstitial positions (oxygen excess:  $M_uO_{v+\delta}$ ), or
- (2) Placing the oxygen ions on normal anion sublattice sites and simultaneously creating vacancies in the cation sublattice (metal deficient:  $M_{u-\delta}O_v$ ).

If, in contrast, the ratio of metal to oxygen in the system is less than ( $v/u$ ), the compound is metal rich. This excess of metal relative to oxygen can be accommodated by

- (1) Placing metal ions in interstitial positions (metal excess:  $M_{u+\delta}O_v$ ), or
- (2) Placing the metal ions on normal cation sublattice sites and simultaneously creating vacancies in the anion sublattice (oxygen deficient:  $M_uO_{v-\delta}$ ).

$$MO: (P_M = P_M^{Eq}, P_{O_2} > P_{O_2}^{Eq})$$



$$\Delta G_{O_2}^o = -RT \ln K_{O_2}$$

$$K_{O_2} = e^{-\frac{\Delta G_{O_2}^o}{RT}} = \frac{X_{O_O^x}^2 X_{V_M''}^2 p^4}{P_{O_2}} \approx \frac{X_{V_M''}^2 p^4}{P_{O_2}} = \frac{K_{sd} p^4}{P_{O_2}}$$

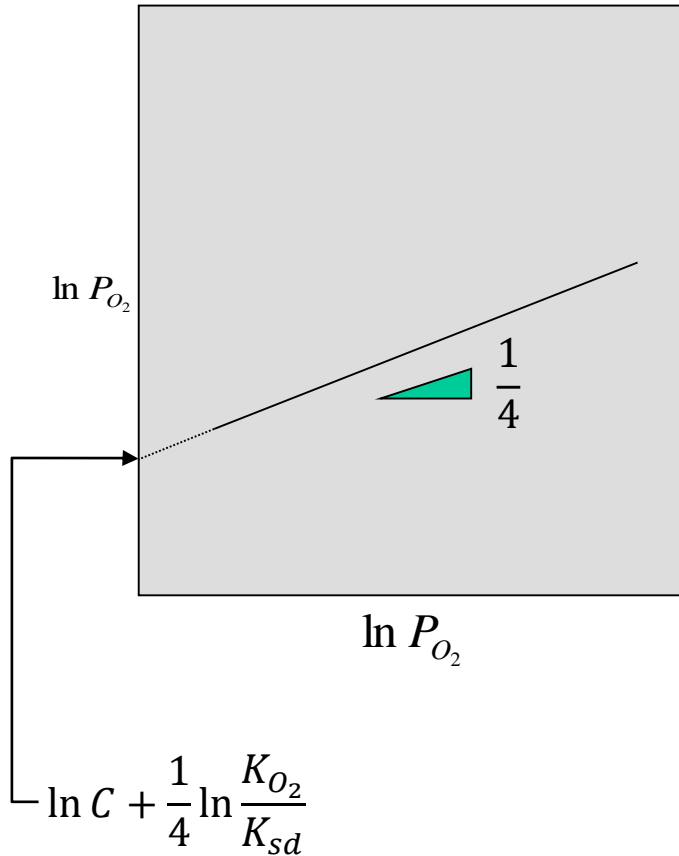
If Schottky defect is dominant

$$p^4 = \frac{K_{O_2}}{K_{sd}} P_{O_2}$$

$$p = \sqrt[4]{\frac{K_{O_2}}{K_{sd}} P_{O_2}^{\frac{1}{4}}} \propto \sigma$$

$$\sigma = C \sqrt[4]{\frac{K_{O_2}}{K_{sd}} P_{O_2}^{\frac{1}{4}}}$$

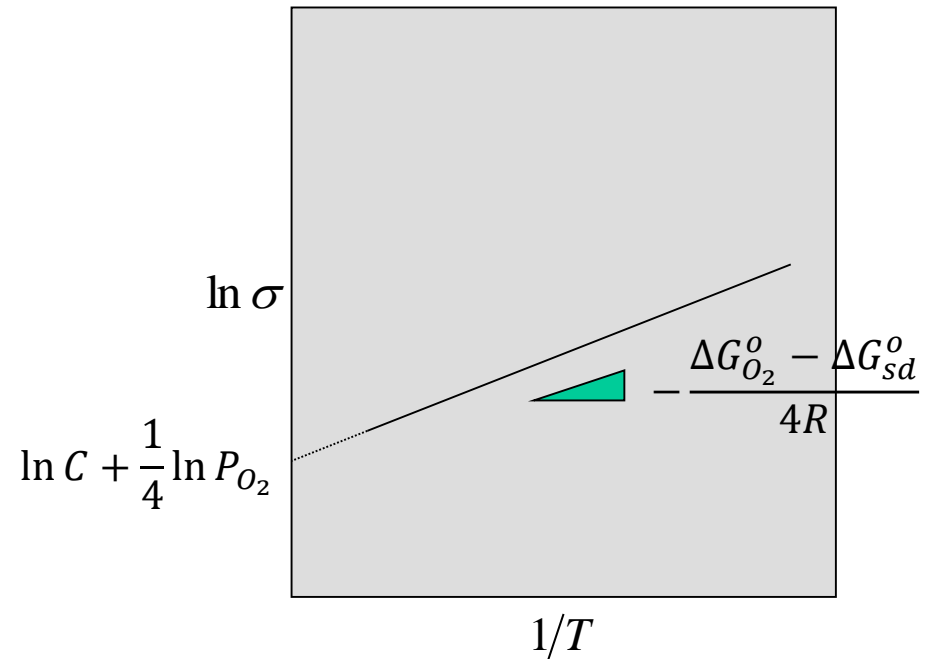
$$\ln \sigma = \ln C + \frac{1}{4} \ln \frac{K_{O_2}}{K_{sd}} + \frac{1}{4} \ln P_{O_2}$$



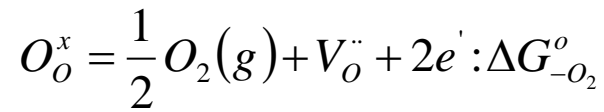
$$\ln \sigma = \ln C + \frac{1}{4} \ln \frac{K_{O_2}}{K_{sd}} + \frac{1}{4} \ln P_{O_2} = \ln C + \frac{1}{4} \ln \frac{e^{-\frac{\Delta G_{O_2}^o}{RT}}}{e^{-\frac{\Delta G_{sd}^o}{RT}}} + \frac{1}{4} \ln P_{O_2} = \ln C + \frac{1}{4} \ln P_{O_2} + \ln e^{-\frac{\Delta G_{O_2}^o - \Delta G_{sd}^o}{4RT}}$$

$$\ln \sigma = \ln C + \frac{1}{2} \ln P_{O_2} - \frac{\Delta G_{O_2}^o - \Delta G_{sd}^o}{2RT}$$

$$\ln \sigma = \ln C + \frac{1}{4} \ln P_{O_2} - \frac{\Delta G_{O_2}^o - \Delta G_{sd}^o}{4RT}$$



$$MO: (P_M = P_M^{Eq}, P_{O_2} < P_{O_2}^{Eq})$$



$$\Delta G_{-O_2}^o = -RT \ln K_{-O_2}$$

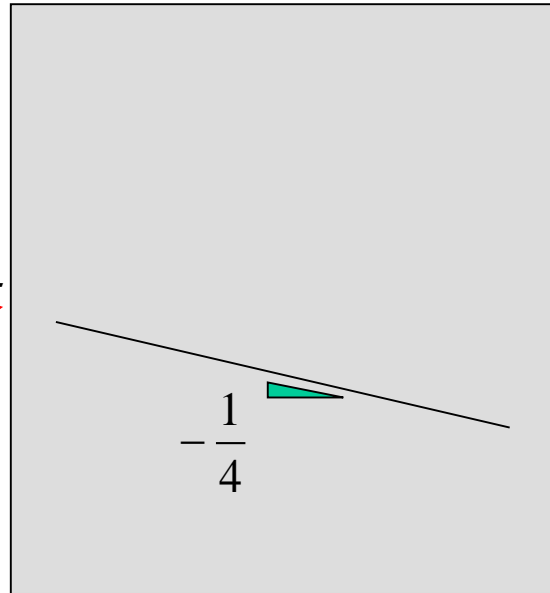
$$K_{-O_2} = e^{-\frac{\Delta G_{-O_2}^o}{RT}} = \frac{P_{O_2}^{\frac{1}{2}} X_{V_O^{\cdot\cdot}} n^2}{X_{O_O^x}} \approx \frac{P_{O_2}^{\frac{1}{2}} X_{V_O^{\cdot\cdot}} n^2}{1} = P_{O_2}^{\frac{1}{2}} K_{sd}^{\frac{1}{2}} n^2$$

If Schottky defect is dominant

$$n = \sqrt{\frac{K_{-O_2}}{K_{sd}^{\frac{1}{2}}}} P_{O_2}^{-\frac{1}{4}} \propto \sigma$$

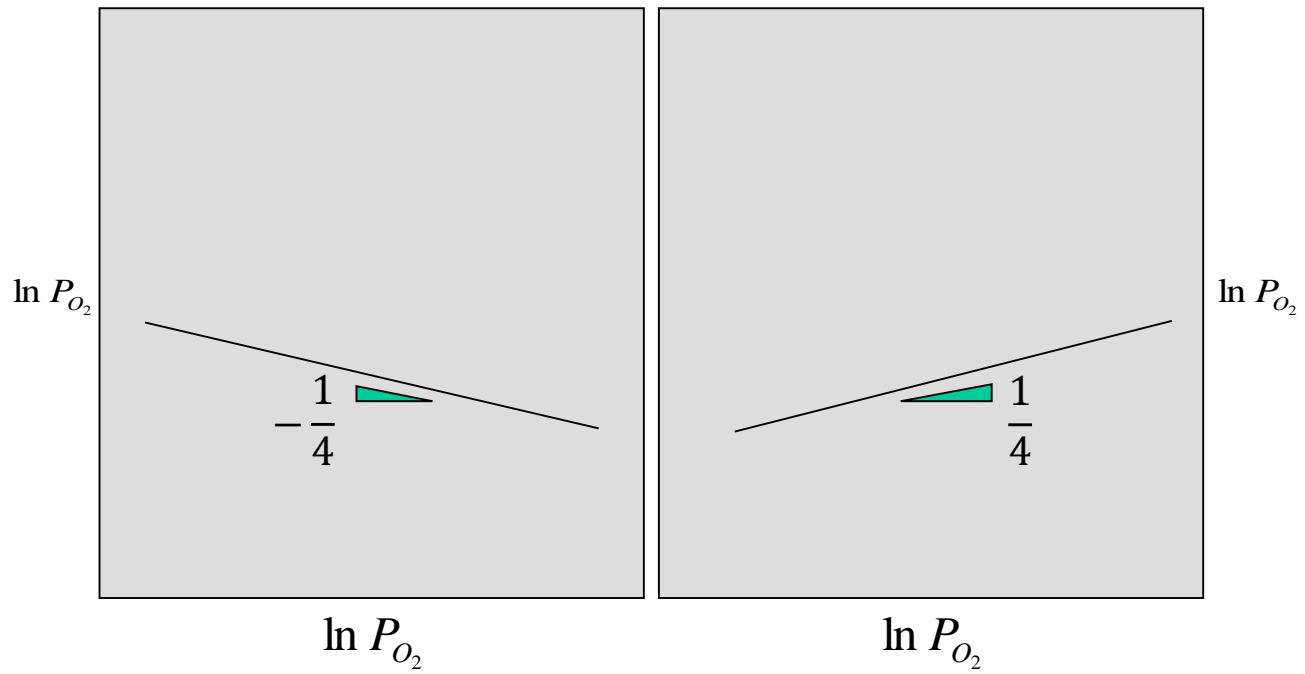
$$\sigma = C \sqrt{\frac{K_{-O_2}}{K_{sd}^{\frac{1}{2}}}} P_{O_2}^{-\frac{1}{4}}$$

$$\ln \sigma = \ln C + \ln \sqrt{\frac{K_{-O_2}}{K_{sd}^{\frac{1}{2}}}} - \frac{1}{4} \ln P_{O_2}$$



$\ln P_{O_2}$

$$\ln C + \ln \sqrt{\frac{K_{-O_2}}{K_{sd}^{\frac{1}{2}}}}$$



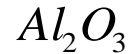
## 13-4.1 Equilibrium in Compound Crystals with a Variety of Defects

The strategy for determining defect concentrations in a crystal of the compound  $M_uX_v$  that is equilibrium with its surrounding atmosphere.

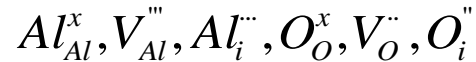
- (1) List the entities that may exist in the crystal of concern
- (2) Determine the number of independent defect reactions  
[C<sup>α</sup>+C<sup>β</sup>-E-2]
- (3) Construction of balanced defect chemistry equation
  - ① Mass Conservation
  - ② Site Ratio Conservation
  - ③ Charge Neutrality
- (4) The affinity for every reaction is equal to zero

## 13-4.2 Illustration of the Conditions for Equilibrium of Alumina

Assume that an alumina crystal is in equilibrium with its vapor and neglect the presence of impurities

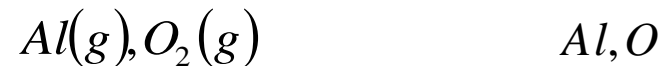
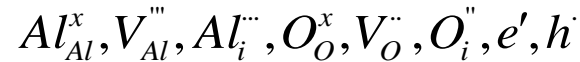


- (1) List the entities that may exist in the crystal of concern



- (2) Determine the number of independent defect reactions

$$[C^{\alpha} + C^{\beta} - E - 2] = [8 + 2 - 2 - 2] = 6$$



- (3) Construction of balanced defect chemistry equation

- ① Mass Conservation + ② Site Ratio Conservation + ③ Charge Neutrality

$$null = 2V_{Al}''' + 3V_O''$$

$$null = e' + h$$

$$Al(g) = Al_i''' + 3e'$$



$$\Delta \bar{G}_r^{xs} = -kT \ln K_r$$

$$O_2(g) = 2O_i'' + 4h$$

$$Al(g) + V_{Al}''' = Al_{Al}^x + 3e'$$

$$3O_2(g) = 6O_O^x + 4V_{Al}''' + 12h$$

- (4) The affinity for every reaction is equal to zero

$$null = 2V_{Al}''' + 3V_{O}'' \quad : K_{sd}$$

$$null = e' + h \quad : K_{np}$$

$$Al(g) = Al_i''' + 3e' \quad : K_{Al_i}$$

$$O_2(g) = 2O_i'' + 2h \quad : K_{O_i}$$

$$Al(g) + V_{Al}''' = Al_{Al}^x + 3e' \quad : K_{-V_{Al}}$$

$$3O_2(g) = 6O_O^x + 4V_{Al}''' + 12h \quad : K_{V_{Al}}$$

$$\Delta \bar{G}_r^{xs} = -kT \ln K_r$$

$$K_r = e^{-\frac{\Delta \bar{G}_r^{xs}}{kT}}$$

$$K_{sd} = \frac{X_{V_{Al}'''}^2 X_{V_{O}''}^3}{1}$$

8 Unknowns

$$K_{np} = \frac{np}{1}$$

+  
6 Equations

$$K_{Al_i} = \frac{X_{Al_i}''' n^3}{P_{Al}}$$

||  
2 Unknowns

$$K_{O_i} = \frac{X_{O_i}'' p^2}{P_{O_2}}$$

$$K_{-V_{Al}} = \frac{n^3}{P_{Al} X_{V_{Al}'''}}$$

$$K_{V_{Al}} = \frac{X_{V_{Al}'''}^4 p^{12}}{P_{O_2}^3}$$

$$3X_{V_{Al}''} + 2X_{O_i}'' + n = 2X_{V_{O}''} + 3X_{Al_i}''' + p$$

$$P = P_{Al} + P_{O_2} + P_{Others} = 1 \text{ atm}$$

8 Unknowns

+

8 Equations

||

0 Unknowns

# \* Brouwer Diagram

$$\text{System} = f(T, P, X)$$

## Defect Generation Reaction:

**Neutrality:**  $2[V_O^{\bullet\bullet}] + p = 2[V_M^{\bullet\bullet}] + n$

– Intrinsic

Ionic:

$$\text{null} = V_M^{\bullet\bullet} + V_O^{\bullet\bullet} \quad K_s = [V_M^{\bullet\bullet}][V_O^{\bullet\bullet}]$$

$$M_M^X = M_i^{\bullet\bullet} + V_M^{\bullet\bullet} \quad K_F = [M_i^{\bullet\bullet}][V_M^{\bullet\bullet}]$$

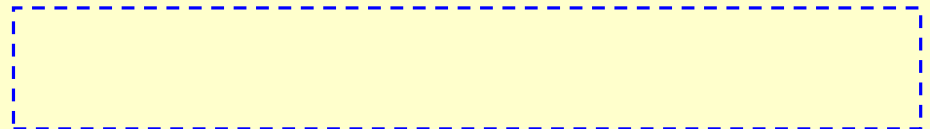
$$O_O^X = O_i^{\bullet\bullet} + V_O^{\bullet\bullet} \quad K_{AF} = [O_i^{\bullet\bullet}][V_O^{\bullet\bullet}]$$

Electronic:

$$\text{nil} = e' + h \quad K_i = np$$

– Extrinsic

Ionic:



Electronic:

$$O_O^X = \frac{1}{2} O_2(g) + V_O^{\bullet\bullet} + 2e' \quad K_R = [V_O^{\bullet\bullet}] n^2 P_{O_2}^{1/2}$$

$$(M(g) = M_i^{\bullet\bullet} + 2e')$$

$$\frac{1}{2} O_2(g) = O_O^X + V_M^{\bullet\bullet} + 2h \quad K_O = [V_M^{\bullet\bullet}] p^2 P_{O_2}^{-1/2}$$

$$\left(\frac{1}{2} O_2(g) = O_i^{\bullet\bullet} + 2h\right)$$

# \*-1. Intrinsic

## Defect Generation Reaction:

**Neutrality:**  $2[V_O^{\bullet\bullet}] + p = 2[V_M^{\prime\prime}] + n$

- Intrinsic

Ionic:

$$null = V_M^{\prime\prime} + V_O^{\bullet\bullet}$$

$$K_s = [V_M^{\prime\prime}][V_O^{\bullet\bullet}]$$

Electronic:

$$nil = e' + h\cdot$$

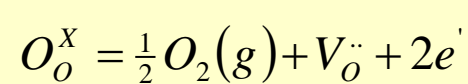
$$K_i = np$$

- Extrinsic

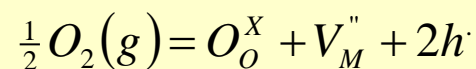
Ionic:



Electronic:



$$K_R = [V_O^{\bullet\bullet}] n^2 P_{O_2}^{1/2}$$



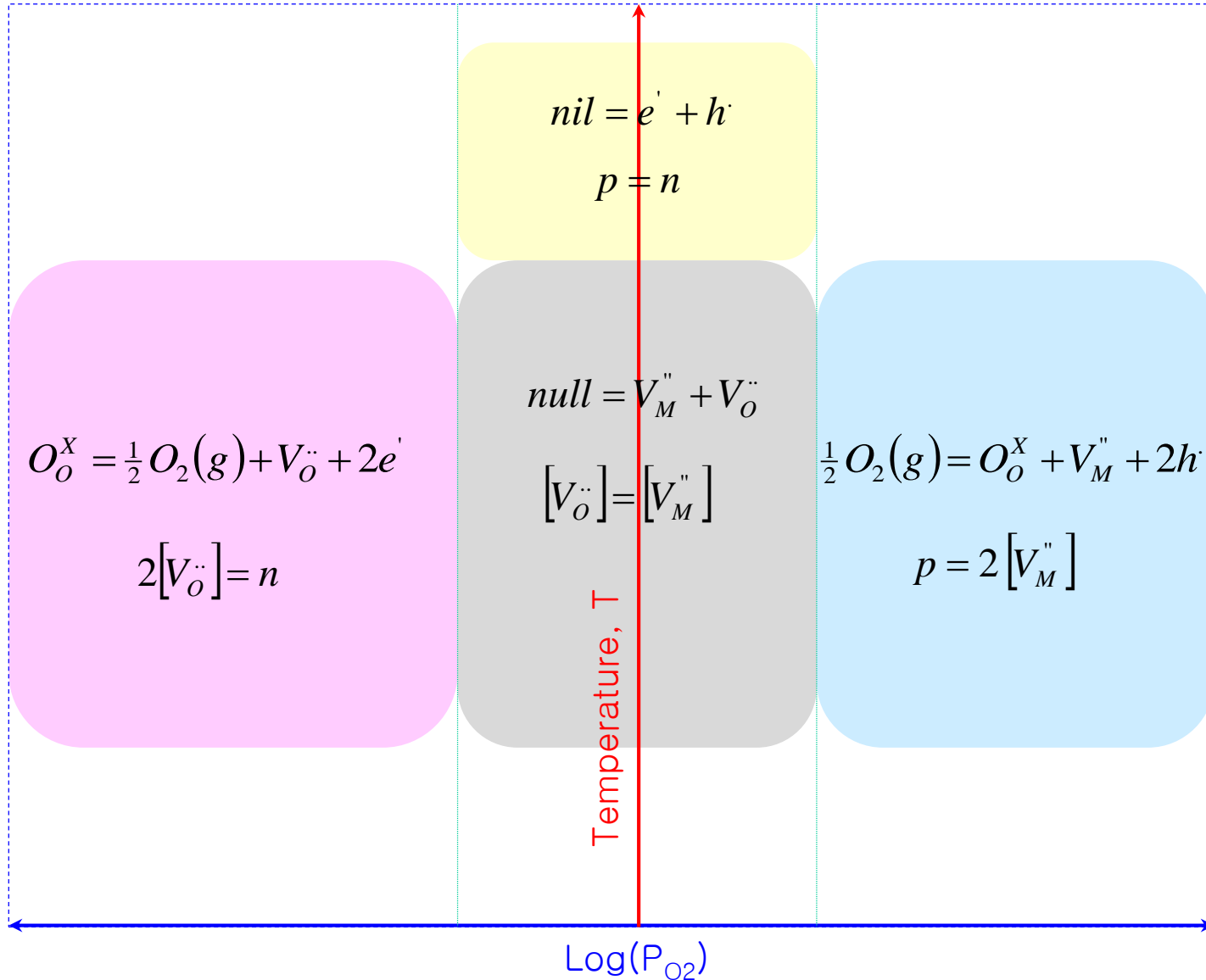
$$K_O = [V_M^{\prime\prime}] p^2 P_{O_2}^{-1/2}$$

## Regime ON

**Regime OD**

$$2[V_{\ddot{O}}] + p = 2[V_M''] + n$$

**Regime OE**



## For Regime ON

$$null = V_M'' + V_O''$$

$$K_S = [V_M''] [V_O'']$$

$$[V_O''] = [V_M'']$$

$$[V_M''] = [V_O''] = K_S^{\frac{1}{2}}$$

$$nil = e' + h'$$

$$K_i = np$$

$$p = K_i n^{-1} = K_i K_R^{-\frac{1}{2}} K_S^{\frac{1}{4}} P_{O_2}^{\frac{1}{4}}$$

$$O_O^X = \frac{1}{2} O_2(g) + V_O'' + 2e'$$

$$K_R = P_{O_2}^{\frac{1}{2}} [V_O''] n^2 = P_{O_2}^{\frac{1}{2}} K_S^{\frac{1}{2}} n^2$$

$$n^2 = K_R P_{O_2}^{-\frac{1}{2}} K_S^{-\frac{1}{2}}$$

$$n = K_R^{\frac{1}{2}} K_S^{-\frac{1}{4}} P_{O_2}^{-\frac{1}{4}}$$

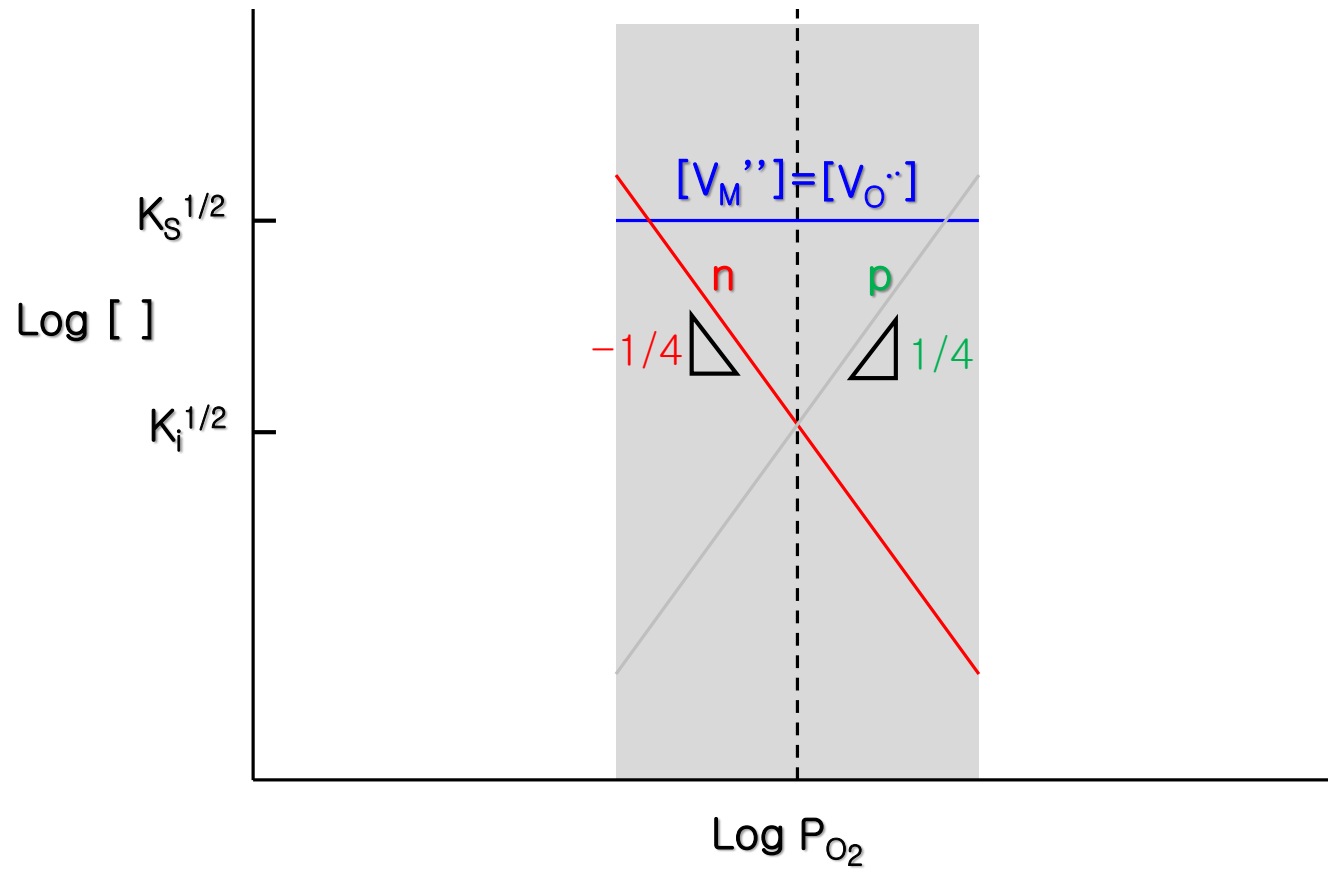
$$\frac{1}{2} O_2(g) = O_O^X + V_M'' + 2h'$$

$$K_O = P_{O_2}^{-\frac{1}{2}} [V_M''] p^2$$

$$[V_M''] = [V_O^{\bullet\bullet}] = K_S^{1/2}$$

$$n = K_R^{1/2} K_S^{-1/4} P_{O_2}^{-1/4}$$

$$p = K_i K_R^{-1/2} K_S^{1/4} P_{O_2}^{1/4}$$



## For Regime OD

$$O_O^X = \frac{1}{2} O_2(g) + V_O \ddot{\cdot} + 2e'$$

$$K_R = P_{O_2}^{\frac{1}{2}} [V_O \ddot{\cdot}] n^2 \quad [V_O \ddot{\cdot}] = \frac{1}{2} n$$

$$K_R = P_{O_2}^{\frac{1}{2}} [V_O \ddot{\cdot}] 4 [V_O \ddot{\cdot}]^2$$

$$[V_O \ddot{\cdot}] = \left( \frac{1}{4} K_R P_{O_2}^{-\frac{1}{2}} \right)^{\frac{1}{3}} = \left( \frac{1}{4} K_R \right)^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

$$n = 2 [V_O \ddot{\cdot}] = 2 \left( \frac{1}{4} K_R \right)^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

$$null = V_M \ddot{\cdot} + V_O \ddot{\cdot}$$

$$K_S = [V_M \ddot{\cdot}] [V_O \ddot{\cdot}]$$

$$[V_M \ddot{\cdot}] = K_S [V_O \ddot{\cdot}]^{-1} = K_S \left( \frac{1}{4} K_R \right)^{-\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$nil = e' + h'$$

$$K_i = np$$

$$p = K_i n^{-1} = K_i \frac{1}{2} \left( \frac{1}{4} K_R \right)^{-\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$\frac{1}{2} O_2(g) = O_O^X + V_M \ddot{\cdot} + 2h'$$

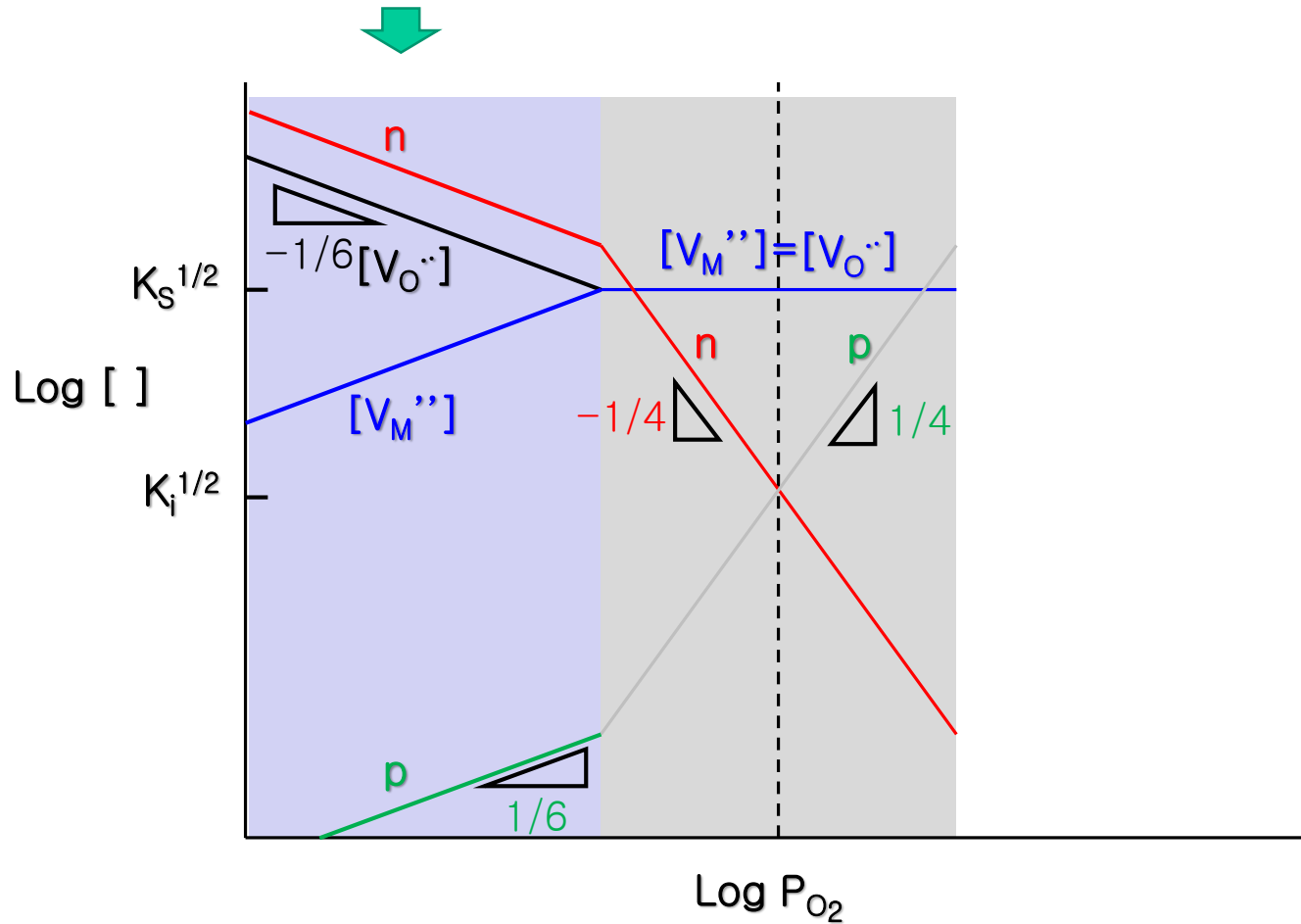
$$K_O = P_{O_2}^{-\frac{1}{2}} [V_M \ddot{\cdot}] p^2$$

$$[V_{O^{\bullet\bullet}}] = \left(\frac{1}{4} K_R\right)^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

$$n = 2\left(\frac{1}{4} K_R\right)^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

$$[V_M''] = K_S \left(\frac{1}{4} K_R\right)^{-\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$p = K_i \frac{1}{2} \left(\frac{1}{4} K_R\right)^{-\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$



## For Regime OE

$$\frac{1}{2} O_2(g) = O_O^X + V_M'' + 2h'$$

$$K_O = P_{O_2}^{-\frac{1}{2}} [V_M''] p^2 \quad [V_M''] = \frac{1}{2} p$$

$$K_O = P_{O_2}^{-\frac{1}{2}} [V_M''] 4[V_M'']^2$$

$$[V_M''] = \left( \frac{1}{4} K_O P_{O_2}^{\frac{1}{2}} \right)^{\frac{1}{3}} = \left( \frac{1}{4} K_O \right)^{\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$p = 2[V_M''] = 2 \left( \frac{1}{4} K_O \right)^{\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$null = V_M'' + V_O''$$

$$K_S = [V_M''] [V_O'']$$

$$[V_O''] = K_S [V_M'']^{-1} = K_S \left( \frac{1}{4} K_O \right)^{-\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

$$nil = e' + h'$$

$$K_i = np$$

$$n = K_i p^{-1} = K_i \frac{1}{2} \left( \frac{1}{4} K_O \right)^{-\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

$$O_O^X = \frac{1}{2} O_2(g) + V_O'' + 2e'$$

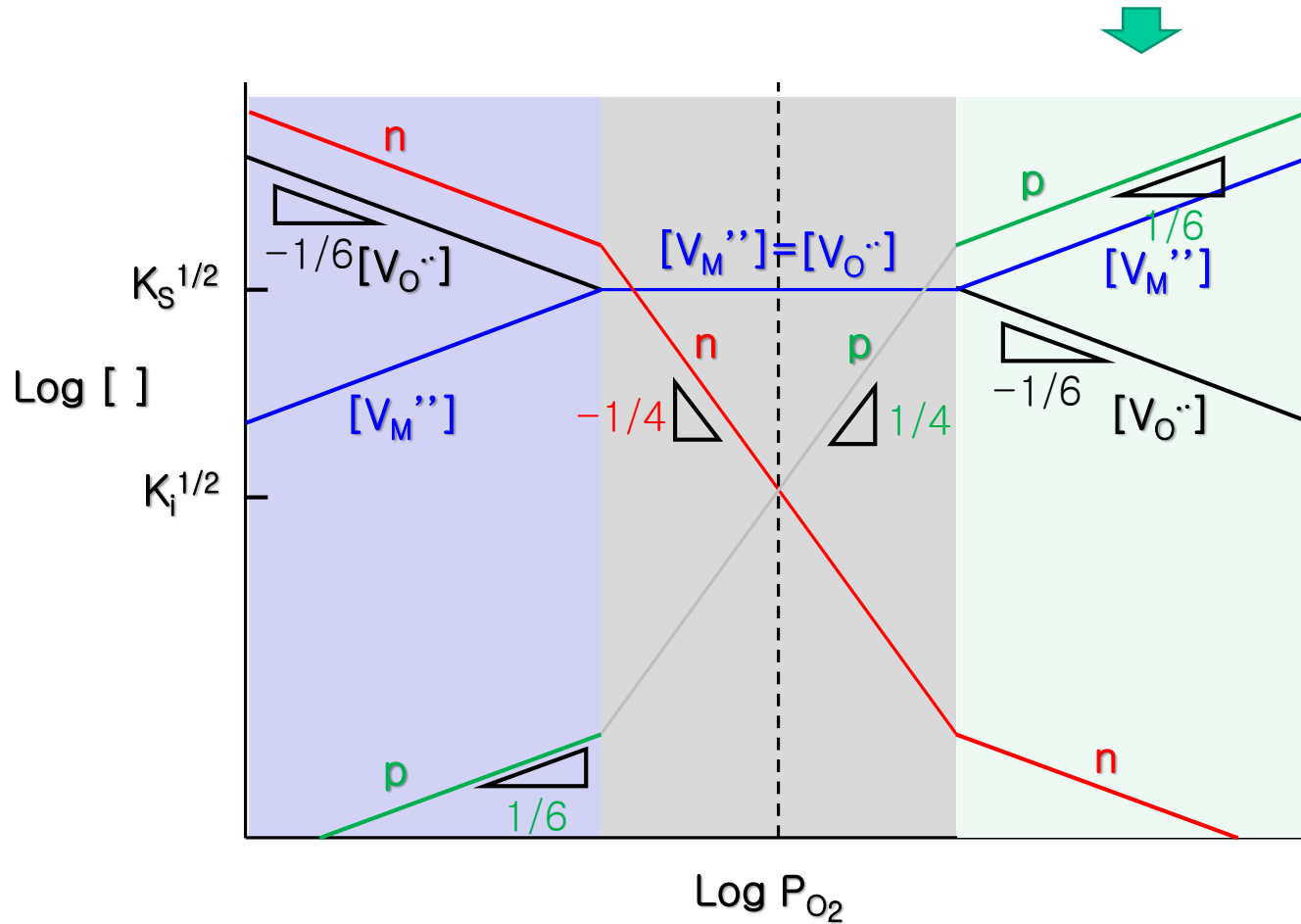
$$K_R = P_{O_2}^{\frac{1}{2}} [V_O''] n^2$$

$$[V_M''] = \left(\frac{1}{4} K_O\right)^{\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$p = 2\left(\frac{1}{4} K_O\right)^{\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$$

$$[V_O^{\bullet\bullet}] = K_S \left(\frac{1}{4} K_O\right)^{-\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$

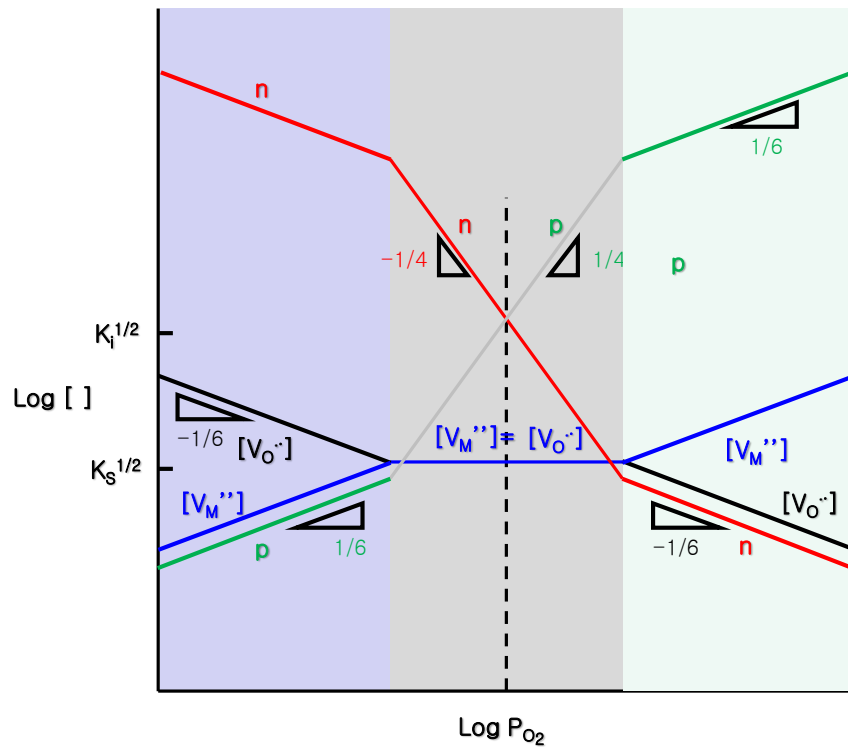
$$n = K_i \frac{1}{2} \left(\frac{1}{4} K_O\right)^{-\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$$



$$K_s = \exp\left(\frac{-\Delta G_s^\circ}{RT}\right) \approx \exp\left(\frac{-\Delta H_s^\circ}{RT}\right)$$

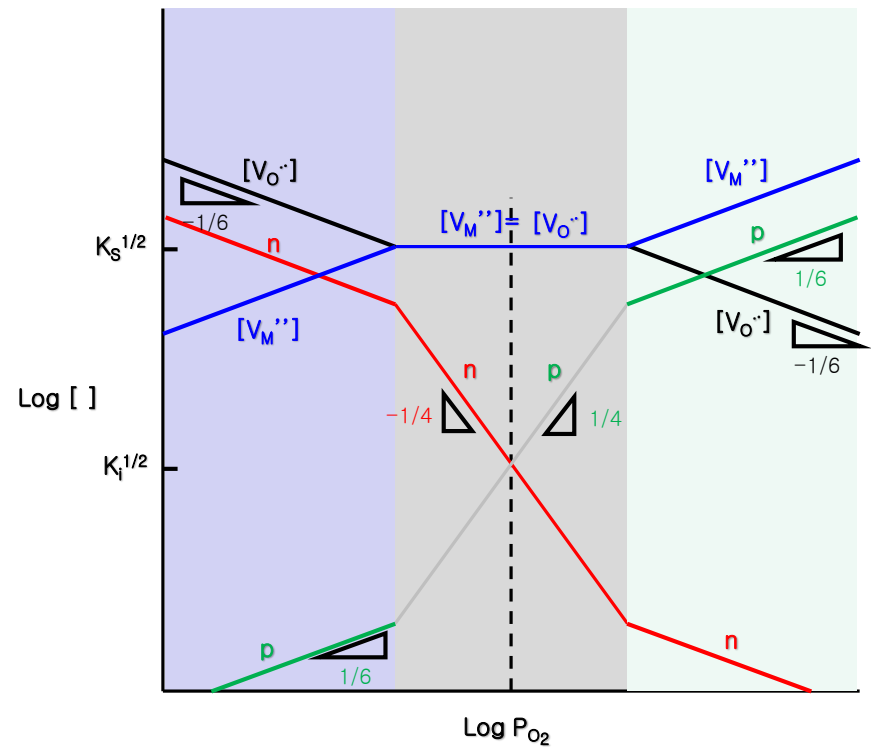
$$K_i = \exp\left(\frac{-\Delta G_i^\circ}{RT}\right) \approx \exp\left(\frac{-\Delta H_i^\circ}{RT}\right) = \exp\left(\frac{-E_g}{RT}\right)$$

When  $\Delta H_s^\circ > \Delta H_i^\circ \Rightarrow K_s \ll K_i$



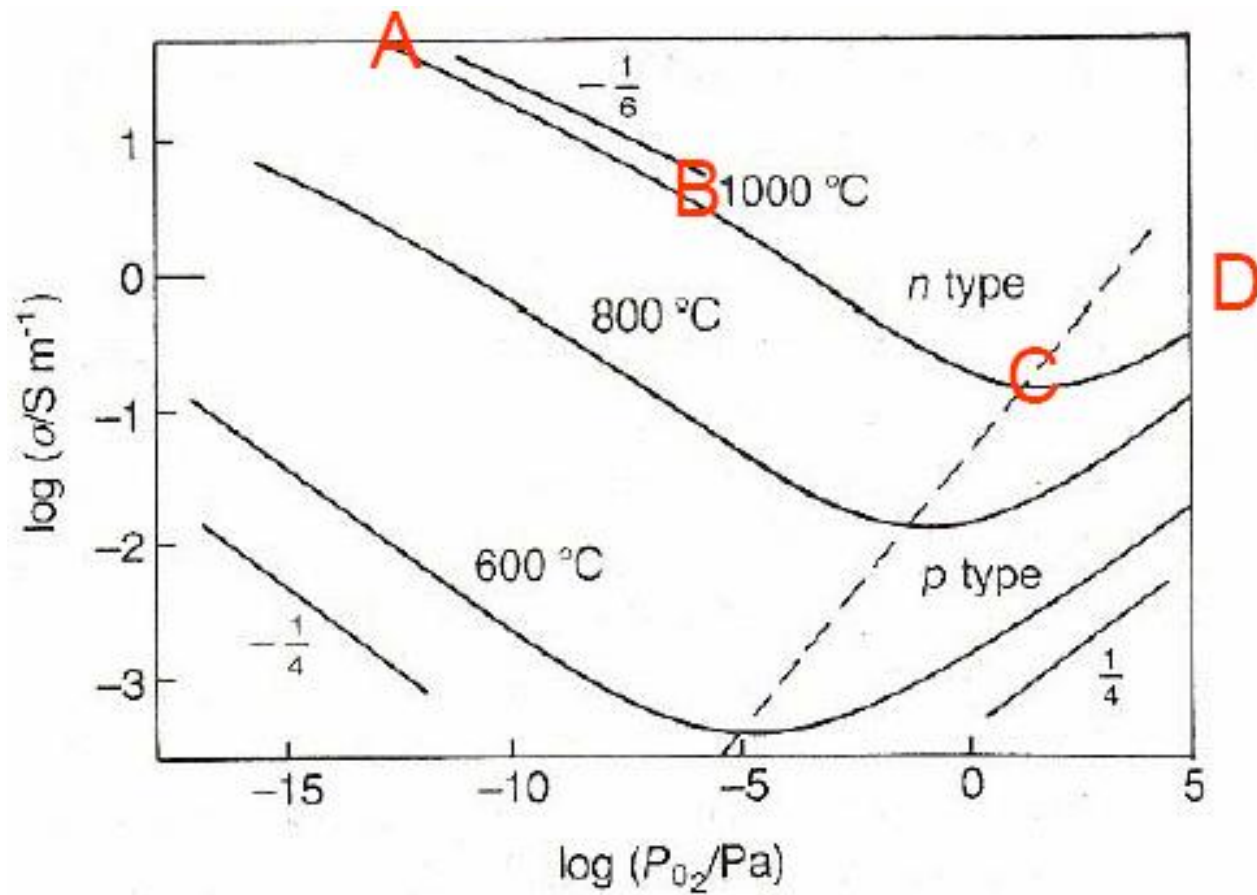
Electronic Conductor

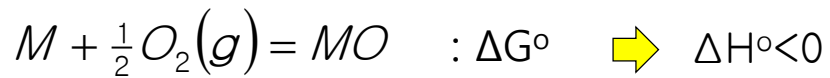
When  $\Delta H_s^\circ < \Delta H_i^\circ \Rightarrow K_s \gg K_i$



Ionic Conductor

## Electronic Conduction ( $\text{BaTiO}_3$ : the effect of $P_{\text{O}_2}$ )



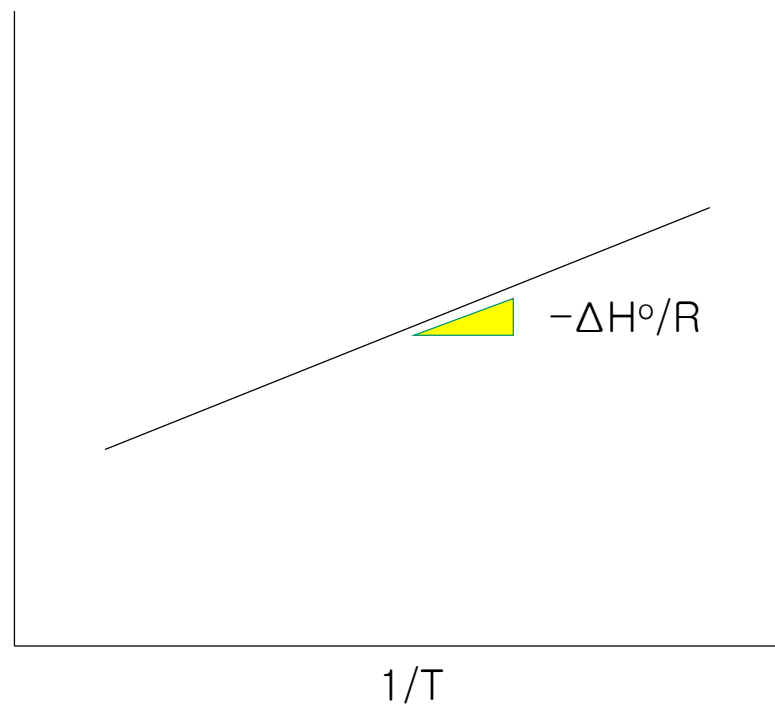


$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -RT \ln \left( \frac{1}{P_{O_2}^{1/2}} \right)$$

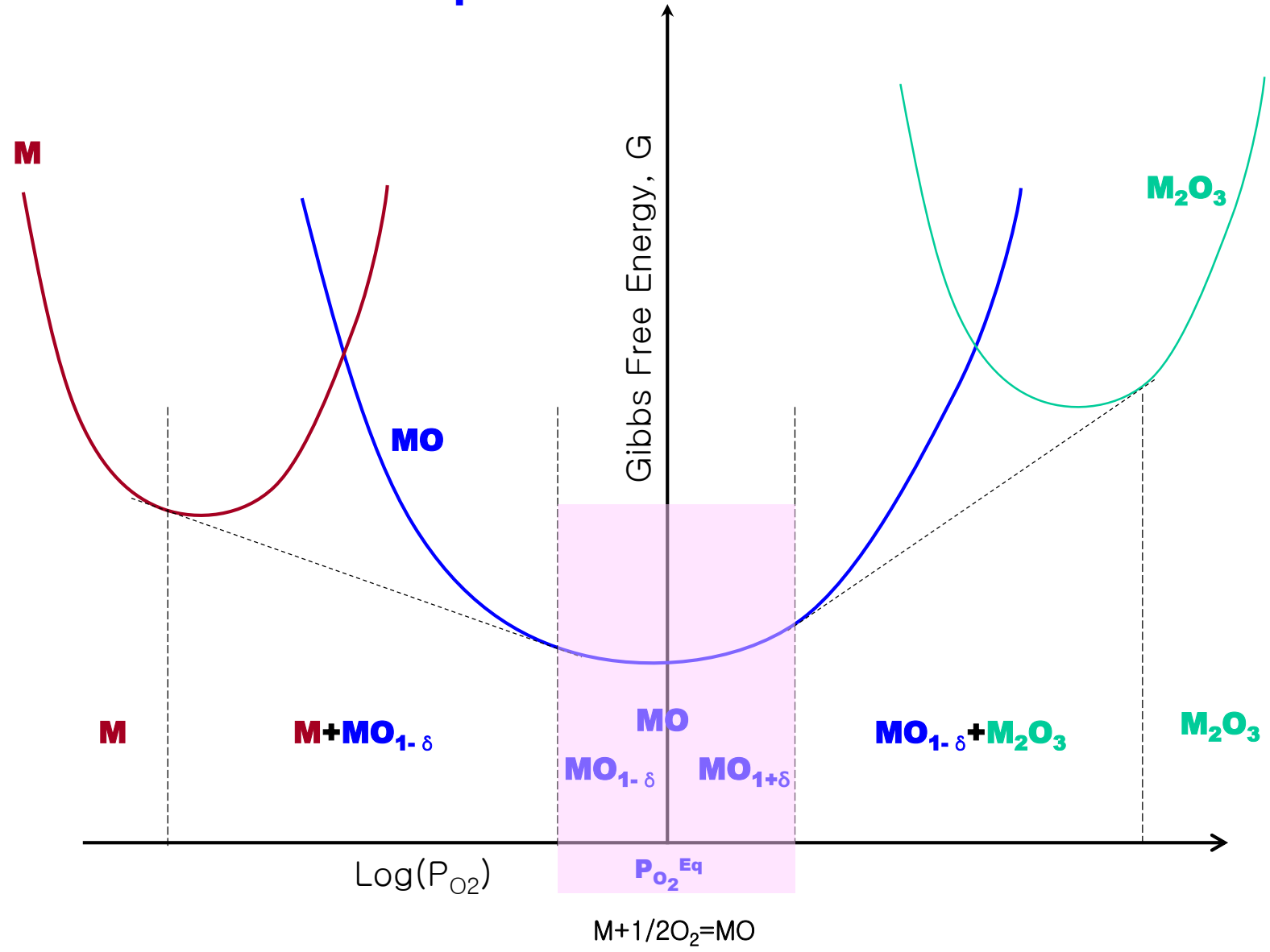
$$\ln \left( \frac{1}{P_{O_2}^{1/2}} \right) =$$

ln K

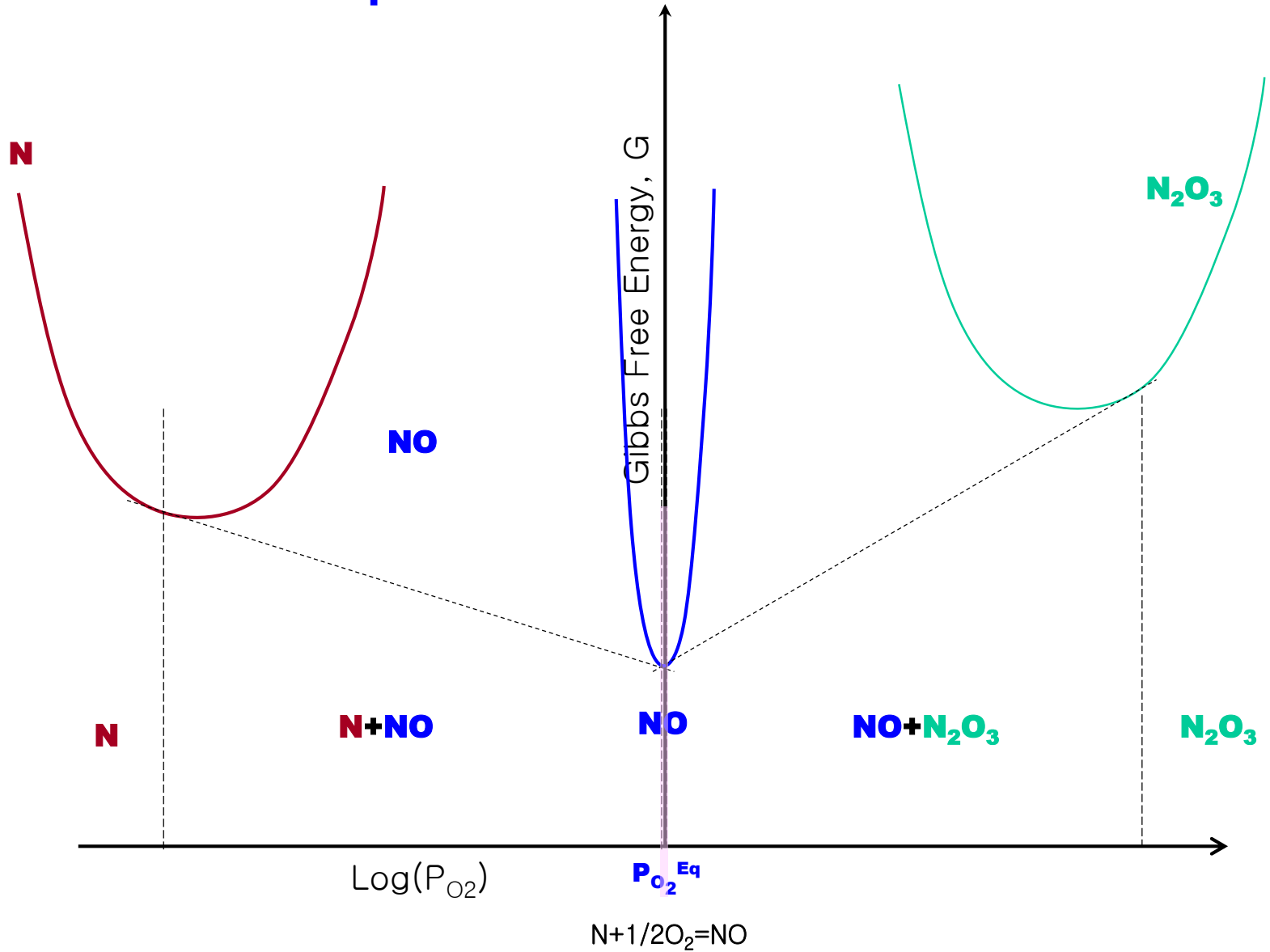


$P_{O_2}^{Eq}$  increases with T

# Non-stoichiometric Compound

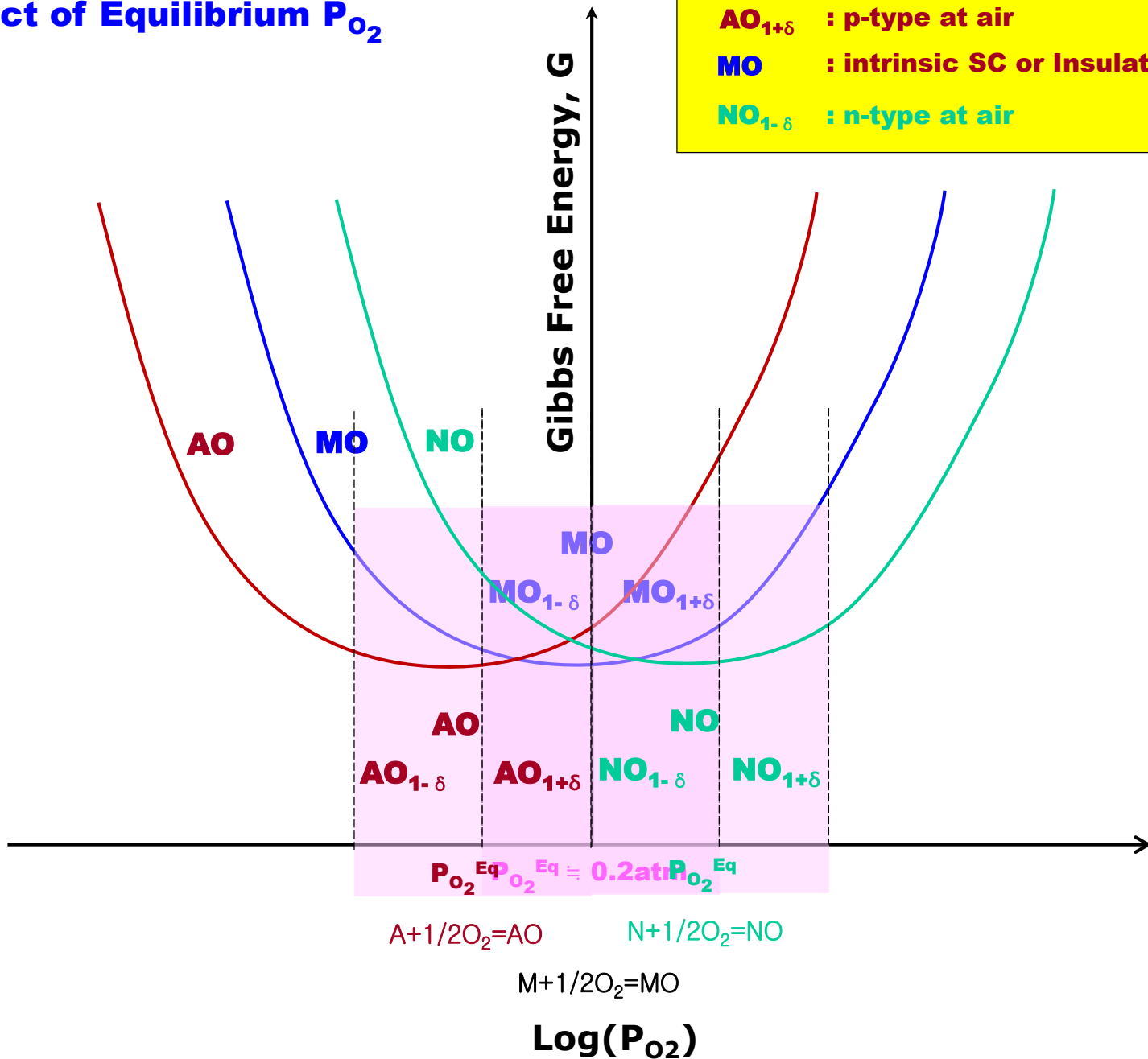


# Stoichiometric Compound



# Effect of Equilibrium $P_{O_2}$

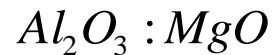
**$AO_{1+\delta}$**  : p-type at air  
**MO** : intrinsic SC or Insulator at air  
 **$NO_{1-\delta}$**  : n-type at air



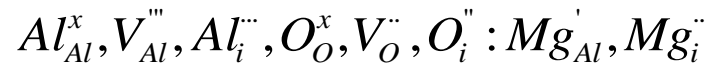
## \*-2. Extrinsic: 13-4.3 Impurities in Nonstoichiometric Compound

Not real crystalline compound is pure; additional elements are always incorporated to some extent.

Assume that an alumina crystal is doped with magnesium oxide (MgO) : Magnesium oxide is widely used as a sintering aid in the consolidation of alumina powders.

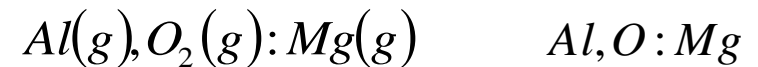
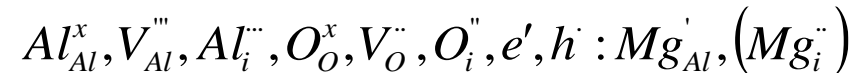


- (1) List the entities that may exist in the crystal of concern



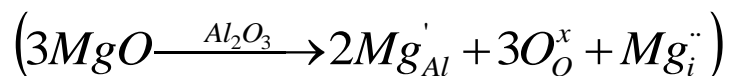
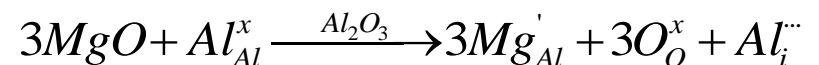
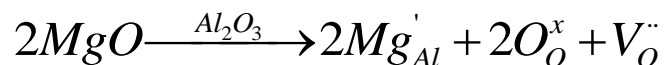
- (2) Determine the number of independent defect reactions

$$[C^{\alpha} + C^{\beta} - E - 2] = [9(10) + 3 - 3 - 2] = 7(8)$$



- (3) Construction of balanced defect chemistry equation

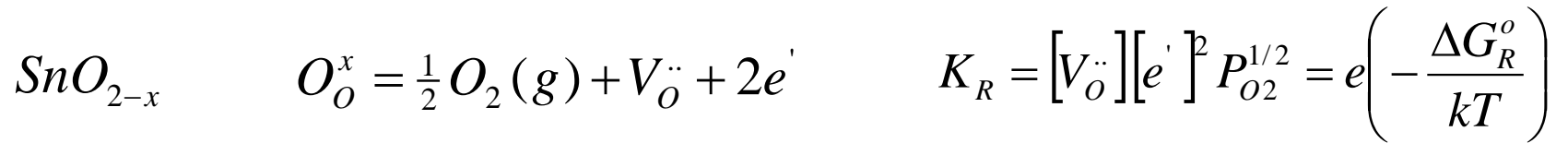
① Mass Conservation + ② Site Ratio Conservation + ③ Charge Neutrality



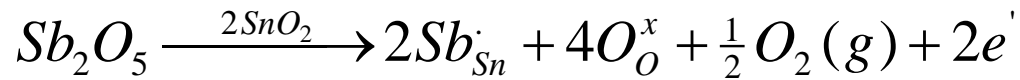
Most undoped ceramic materials contain very significant concentrations of impurities. Impurity additions can completely alter the equilibrium distribution of defects.

The thermodynamic treatment of defect chemistry presented here provides a foundation for understanding physical phenomena such as ionic conductivity, diffusion, oxide layer growth, and dielectric and optical behavior in crystalline compounds.

# SnO<sub>2</sub>

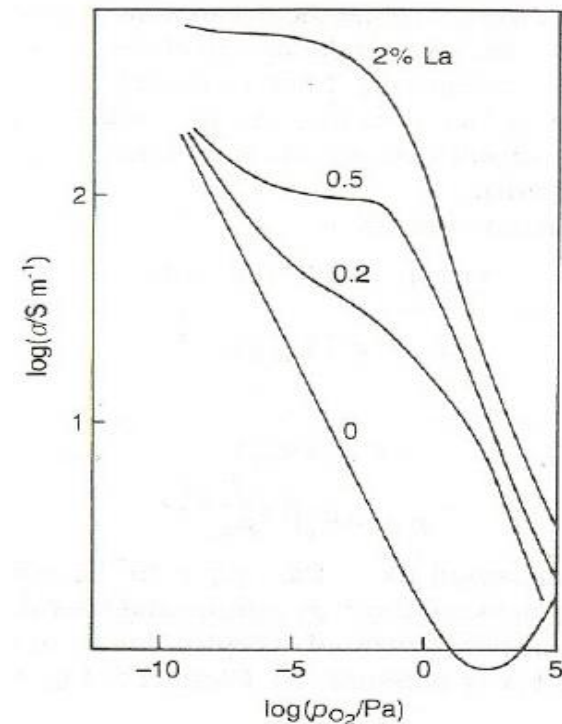
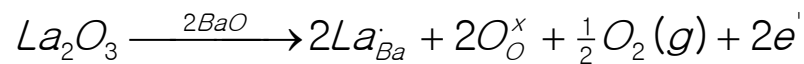
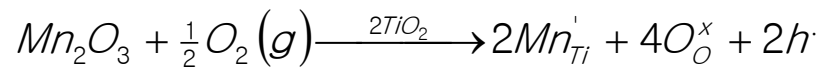


: n-type semiconductor due to oxygen deficiency



: increase conductivity of n-type semiconductor SnO<sub>2</sub>

# BaTiO<sub>3</sub>



# Chapter 15 : Electrochemistry

**Ionization energy** of an element = the difference in energy between an atom of that element in its vapor state and an ion of the same element.

When that element is present as a component in a solution, its ionization energy may be greatly reduced as a result of its interactions with the surrounding solvent molecules.

A salt dissolved in water dissociates to a greater or lesser extent to form cations and anions.

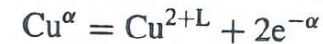
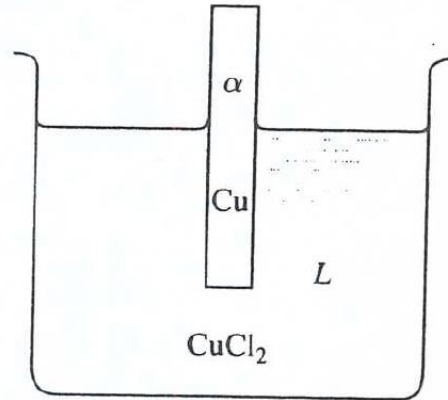
The resulting solution is called an **electrolyte** because it transports a charge when subjected to an electric field.

Many other so called polar solvent such as acetone or glycerol also form electrolyte solutions.

Solid electrolyte, in which a charge current is carried by diffusion of the ions in the system, also exist and find useful applications.

Because the measurement of an electrical potential require a close circuit, the minimum configuration of a system that can be devised in which an electric potential can be measured is the **galvanic cell**. Such a system consists of at least four phases; two electrodes inserted into an electrolyte and externally connected by a wire. [Fig. 15.1]

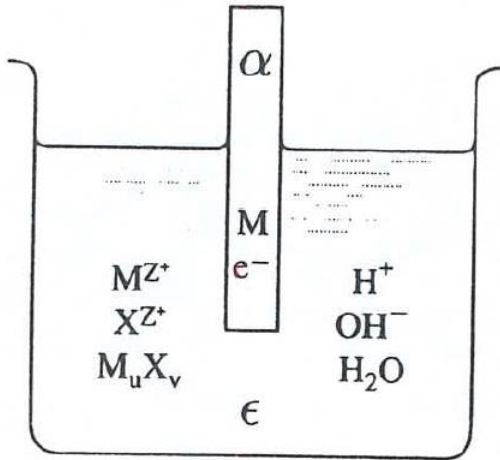
## 15-2 Equilibrium in Two Phase Systems involving an Electrolyte



If the concentration of  $\text{CuCl}_2$  in the electrolyte is dilute, copper atoms dissolve from the rod and form cupric ions in the solution; copper atoms oxidized; rod=(-) & electrolyte=(+)



If the electrolyte is sufficiently concentrated, cupric ions plate out on the copper rod; cupric ions reduced; rod=(+) & electrolyte=(-)



$$dS'_{sys}{}^{\alpha} = \frac{1}{T^{\alpha}} dU'^{\alpha} + \frac{P^{\alpha}}{T^{\alpha}} dV'^{\alpha} - \frac{1}{T^{\alpha}} [\mu_M^{\alpha} dn_M^{\alpha} + \mu_e^{\alpha} dn_e^{\alpha}]$$

$$dS'_{sys}{}^{\epsilon} = \frac{1}{T^{\epsilon}} dU'^{\epsilon} + \frac{P^{\epsilon}}{T^{\epsilon}} dV'^{\epsilon} - \frac{1}{T^{\epsilon}} [\mu_{M^{z+}}^{\epsilon} dn_{M^{z+}}^{\epsilon}]$$

$$dS'_{sys} = dS'^{\alpha} + dS'^{\epsilon}$$

### Isolation constraints:

$$dm_M = dn_M^{\alpha} + dn_{M^{z+}}^{\epsilon} = 0 \rightarrow dn_{M^{z+}}^{\epsilon} = -dn_M^{\alpha}$$

$$q^{\alpha} = -N_o e n_e^{\alpha} = -F n_e^{\alpha} \rightarrow dq^{\alpha} = -F dn_e^{\alpha}$$

$$q^{\epsilon} = N_o z^+ e n_{M^{z+}}^{\epsilon} = z^+ F n_{M^{z+}}^{\epsilon} \rightarrow dq^{\epsilon} = z^+ F dn_{M^{z+}}^{\epsilon}$$

$$dq_{tot} = dq^{\alpha} + dq^{\epsilon} = 0 \rightarrow -F dn_e^{\alpha} + z^+ F dn_{M^{z+}}^{\epsilon} = 0 \rightarrow dn_e^{\alpha} = z^+ dn_{M^{z+}}^{\epsilon}$$

$$\rightarrow dn_e^{\alpha} = -z^+ dn_M^{\alpha}$$

$$dV'_{sys} = dV'^{\alpha} + dV'^{\epsilon} = 0 \rightarrow dV'^{\epsilon} = -dV'^{\alpha}$$

$$dE'_{tot} = dU'^{\alpha} + dU'^{\epsilon} + \varphi^{\alpha} dq^{\alpha} + \varphi^{\epsilon} dq^{\epsilon}$$

$$dE'_{tot} = dU'^{\alpha} + dU'^{\epsilon} + \varphi^{\alpha}(-Fdn_e^{\alpha}) + \varphi^{\epsilon}(z^+Fdn_{Mz^+}^{\epsilon})$$

$$dE'_{tot} = dU'^{\alpha} + dU'^{\epsilon} + \varphi^{\alpha}(z^+Fdn_M^{\alpha}) + \varphi^{\epsilon}(-z^+Fdn_M^{\alpha})$$

$$dE'_{tot} = dU'^{\alpha} + dU'^{\epsilon} + z^+F\{\varphi^{\alpha} - \varphi^{\epsilon}\}dn_M^{\alpha}$$

$$dE'_{tot,iso} = dU'^{\alpha} + dU'^{\epsilon} + z^+F\{\varphi^{\alpha} - \varphi^{\epsilon}\}dn_M^{\alpha} = 0$$

$$dU'^{\epsilon} = -[dU'^{\alpha} + z^+F\{\varphi^{\alpha} - \varphi^{\epsilon}\}dn_M^{\alpha}]$$

$$dq^{\alpha} = -Fdn_e^{\alpha}$$

$$dq^{\epsilon} = z^+Fdn_{Mz^+}^{\epsilon}$$

$$dn_e^{\alpha} = -z^+dn_M^{\alpha}$$

$$dn_{Mz^+}^{\epsilon} = -dn_M^{\alpha}$$

$$dS'_{sys} = \frac{1}{T^\alpha} dU'^\alpha + \frac{P^\alpha}{T^\alpha} dV'^\alpha - \frac{1}{T^\alpha} [\mu_M^\alpha dn_M^\alpha + \mu_e^\alpha dn_e^\alpha]$$

$$dS'_{sys} = \frac{1}{T^\epsilon} dU'^\epsilon + \frac{P^\epsilon}{T^\epsilon} dV'^\epsilon - \frac{1}{T^\epsilon} [\mu_{M^{z+}}^\epsilon dn_{M^{z+}}^\epsilon]$$

$$dn_e^\alpha = -z^+ dn_M^\alpha$$

$$dU'^\epsilon = -[dU'^\alpha + z^+ F\{\varphi^\alpha - \varphi^\epsilon\} dn_M^\alpha]$$

$$dV'^\epsilon = -dV'^\alpha$$

$$dn_{M^{z+}}^\epsilon = -dn_M^\alpha$$

$$dS'_{sys,iso} = dS'^\alpha + dS'^\epsilon$$

$$= \frac{1}{T^\alpha} dU'^\alpha + \frac{P^\alpha}{T^\alpha} dV'^\alpha - \frac{1}{T^\alpha} [\mu_M^\alpha dn_M^\alpha + \mu_e^\alpha (-z^+ dn_M^\alpha)]$$

$$- \frac{1}{T^\epsilon} [dU'^\alpha + z^+ F\{\varphi^\alpha - \varphi^\epsilon\} dn_M^\alpha] - \frac{P^\epsilon}{T^\epsilon} dV'^\alpha + \frac{1}{T^\epsilon} [\mu_{M^{z+}}^\epsilon dn_{M^{z+}}^\alpha]$$

$$= \left( \frac{1}{T^\alpha} - \frac{1}{T^\epsilon} \right) dU'^\alpha + \left( \frac{P^\alpha}{T^\alpha} - \frac{P^\epsilon}{T^\epsilon} \right) dV'^\alpha - \frac{1}{T^\alpha} [\mu_M^\alpha - z^+ \mu_e^\alpha] dn_M^\alpha + \frac{1}{T^\epsilon} [\mu_{M^{z+}}^\epsilon - z^+ F\{\varphi^\alpha - \varphi^\epsilon\}] dn_M^\alpha = 0$$

$T^\alpha = T^\epsilon$  : **Thermal Equilibrium**

$P^\alpha = P^\epsilon$  : **Mechanical Equilibrium**

$$- \frac{1}{T^\alpha} \{ [\mu_M^\alpha - z^+ \mu_e^\alpha] - [\mu_{M^{z+}}^\epsilon - z^+ F\{\varphi^\alpha - \varphi^\epsilon\}] \} dn_M^\alpha = 0$$

$$[\mu_M^\alpha - z^+ \mu_e^\alpha] - [\mu_{M^{z+}}^\epsilon - z^+ F\{\varphi^\alpha - \varphi^\epsilon\}] = 0$$

$$[\mu_M^\alpha - (z^+ \mu_e^\alpha + \mu_{M^{z+}}^\epsilon)] + z^+ F\{\varphi^\alpha - \varphi^\epsilon\} = 0 : \text{Electrochemical Equilibrium}$$

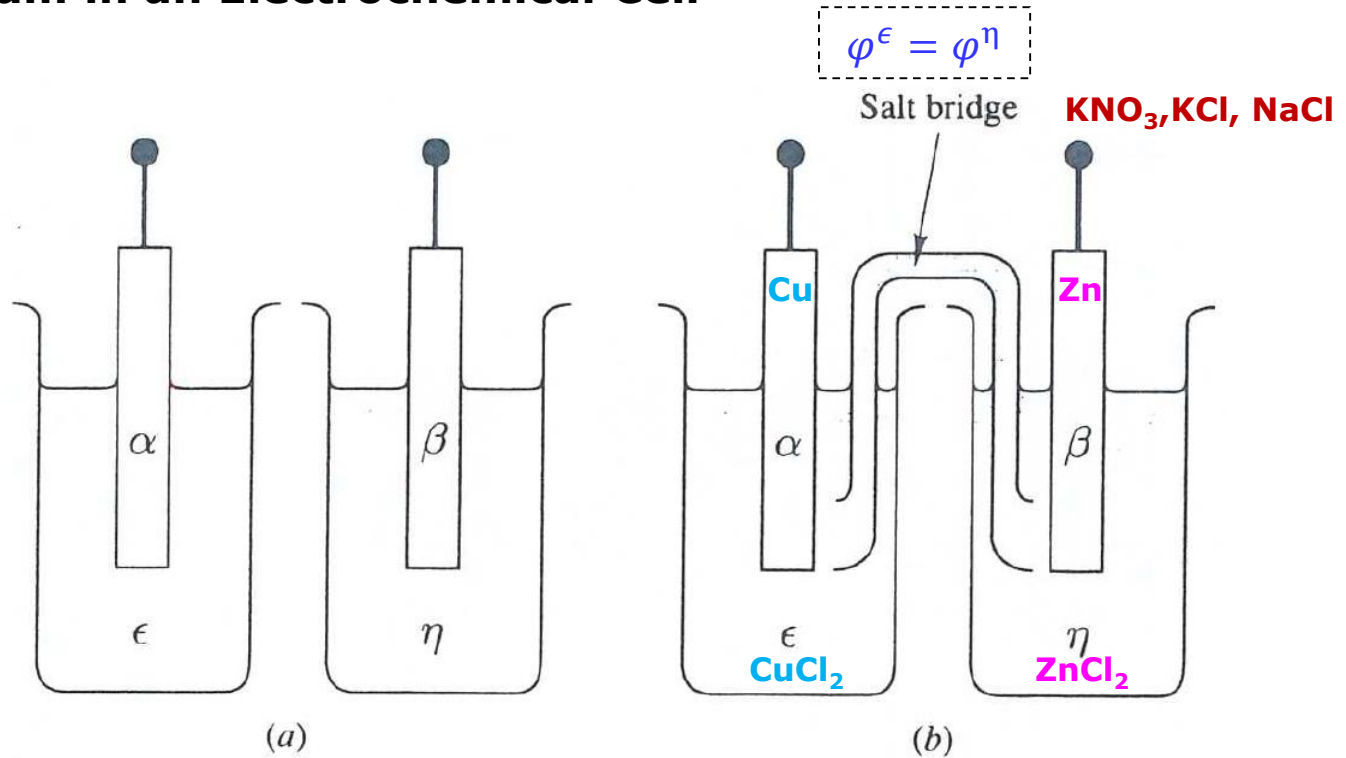
$$[\mu_M^\alpha - (z^+ \mu_e^\alpha + \mu_{M^{z+}}^\epsilon)] = -z^+ F\{\varphi^\alpha - \varphi^\epsilon\}$$

$$A \equiv [\mu_M^\alpha - (z^+ \mu_e^\alpha + \mu_{M^{z+}}^\epsilon)] : (M^{z+})^\epsilon + z^+ e^- = M^\alpha \text{ Reduction}$$

**Electrochemical Equilibrium Condition (in a Half-cell)**

$$(M^{z+})^\epsilon + z^+ e^- = M^\alpha \Rightarrow A = -z^+ F\{\varphi^\alpha - \varphi^\epsilon\}$$

## 15-3 Equilibrium in an Electrochemical Cell



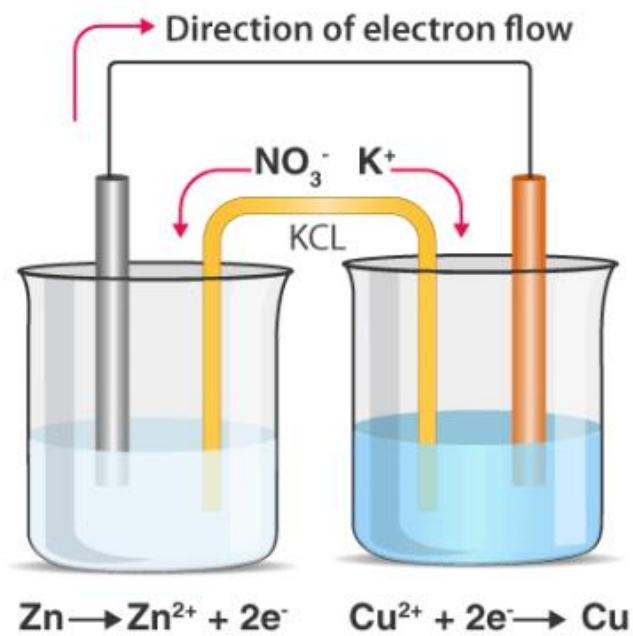
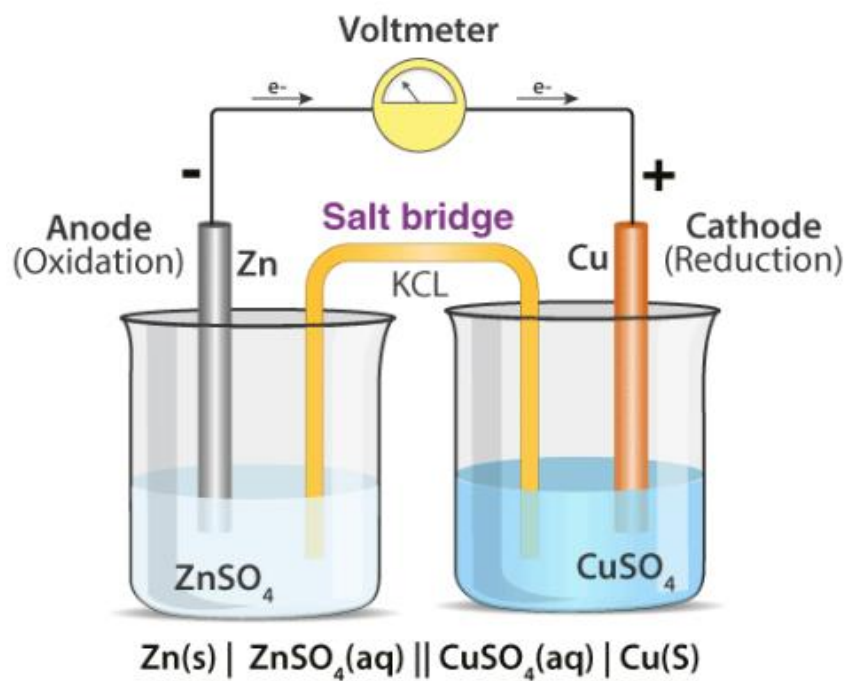
### Electrochemical Equilibrium Condition

$$(M^{Z+})^\epsilon + z^+ e^- = M^\alpha \quad \Rightarrow \quad A = -z^+ F \{ \varphi^\alpha - \varphi^\epsilon \}$$

$$- \left[ \begin{array}{l} (Cu^{2+})^\epsilon + 2(e^-)^\alpha = Cu^\alpha \quad \left[ \mu_{Cu}^\alpha - (2\mu_e^\alpha + \mu_{Cu^{2+}}^\epsilon) \right] = -2F \{ \varphi^\alpha - \varphi^\epsilon \} \\ (Zn^{2+})^\eta + 2(e^-)^\beta = Zn^\beta \quad \left[ \mu_{Zn}^\beta - (2\mu_e^\beta + \mu_{Zn^{2+}}^\eta) \right] = -2F \{ \varphi^\beta - \varphi^\eta \} \end{array} \right.$$

$$\left[ \mu_{Zn}^\beta - (2\mu_e^\beta + \mu_{Zn^{2+}}^\eta) \right] - \left[ \mu_{Cu}^\alpha - (2\mu_e^\alpha + \mu_{Cu^{2+}}^\epsilon) \right] = -2F \{ \varphi^\beta - \varphi^\alpha \}$$

## Working of a Salt Bridge



$$\left[ \mu_{Zn}^{\beta} - (2\mu_e^{\beta} + \mu_{Zn^{2+}}^{\eta}) \right] - \left[ \mu_{Cu}^{\alpha} - (2\mu_e^{\alpha} + \mu_{Cu^{2+}}^{\epsilon}) \right] = -2F\{\varphi^{\beta} - \varphi^{\alpha}\} \quad \mu_e^{\alpha} = \mu_e^{\beta}$$

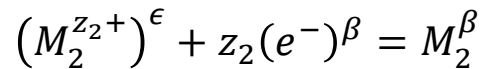
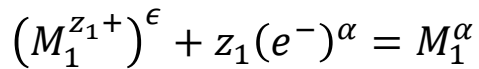
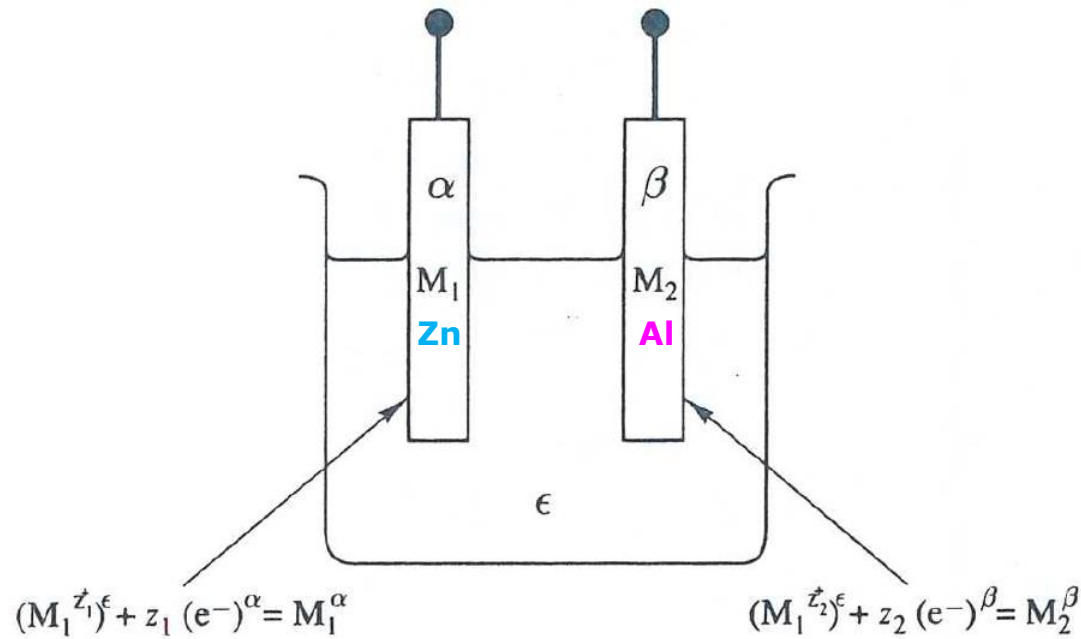
$$\left[ \mu_{Zn}^{\beta} - \mu_{Zn^{2+}}^{\eta} \right] - \left[ \mu_{Cu}^{\alpha} - \mu_{Cu^{2+}}^{\epsilon} \right] = -2F\{\varphi^{\beta} - \varphi^{\alpha}\}$$

$$\left[ \mu_{Zn}^{\beta} + \mu_{Cu^{2+}}^{\epsilon} \right] - \left[ \mu_{Cu}^{\alpha} + \mu_{Zn^{2+}}^{\eta} \right] = -2F\{\varphi^{\beta} - \varphi^{\alpha}\} \quad : \quad Cu^{\alpha} + (Zn^{2+})^{\eta} = Zn^{\beta} + (Cu^{2+})^{\epsilon}$$

### 15-3-1 Conditions for Equilibrium in a General Galvanic Cell

Left Electrode | Electrolyte1 | | Electrolyte2 | Right Electrode





$$A^\alpha = \left[ \mu_{M_1}^\alpha - \left( z_1 \mu_e^\alpha + \mu_{M_1^{z_1+}}^\epsilon \right) \right] = -z_1 F \{ \varphi^\alpha - \varphi^\epsilon \} \quad *(z_2/z_1)$$

$$A^\beta = \left[ \mu_{M_2}^\beta - \left( z_2 \mu_e^\beta + \mu_{M_2^{z_2+}}^\epsilon \right) \right] = -z_2 F \{ \varphi^\beta - \varphi^\epsilon \}$$

$$A^\beta - \frac{z_2}{z_1} A^\alpha = \left[ \mu_{M_2}^\beta - \left( z_2 \mu_e^\beta + \mu_{M_2^{z_2+}}^\epsilon \right) \right] - \frac{z_2}{z_1} \left[ \mu_{M_1}^\alpha - \left( z_1 \mu_e^\alpha + \mu_{M_1^{z_1+}}^\epsilon \right) \right] = -z_2 F \{ \varphi^\beta - \varphi^\epsilon \} + \frac{z_2}{z_1} z_1 F \{ \varphi^\alpha - \varphi^\epsilon \}$$

$$A^\beta - \frac{z_2}{z_1} A^\alpha = \left[ \mu_{M_2}^\beta - \left( z_2 \mu_e^\beta + \mu_{M_2^{z_2+}}^\epsilon \right) \right] - \frac{z_2}{z_1} \left[ \mu_{M_1}^\alpha - \left( z_1 \mu_e^\alpha + \mu_{M_1^{z_1+}}^\epsilon \right) \right] = -z_2 F \{ \varphi^\beta - \varphi^\alpha \}$$

$$= \left[ \mu_{M_2}^\beta - \left( \mu_{M_2^{z_2+}}^\epsilon \right) \right] - \frac{z_2}{z_1} \left[ \mu_{M_1}^\alpha - \left( \mu_{M_1^{z_1+}}^\epsilon \right) \right] = -z_2 F \{ \varphi^\beta - \varphi^\alpha \} \quad \mu_e^\alpha = \mu_e^\beta$$

$$A_{cell} = \left[ \mu_{M_2}^\beta + \frac{z_2}{z_1} \mu_{M_1^{z_1+}}^\epsilon \right] - \left[ \mu_{M_2^{z_2+}}^\epsilon + \frac{z_2}{z_1} \mu_{M_1}^\alpha \right] = -z_2 F \{ \varphi^\beta - \varphi^\alpha \}$$

$$\left( M_2^{z_2+} \right)^\epsilon + \frac{z_2}{z_1} M_1^\alpha = M_2^\beta + \frac{z_2}{z_1} \left( M_1^{z_1+} \right)^\epsilon$$

**Suppose  $\alpha = M_1 = \text{Zn}$  and  $\beta = M_2 = \text{Al}$ ,**  $(\text{Al}^{3+})^\epsilon + \frac{3}{2} \text{Zn}^\alpha = \text{Al}^\beta + \frac{3}{2} (\text{Zn}^{2+})^\epsilon$

$$A_{cell} = \left[ \mu_{\text{Al}}^\beta + \frac{3}{2} \mu_{\text{Zn}^{2+}}^\epsilon \right] - \left[ \mu_{\text{Al}^{3+}}^\epsilon + \frac{3}{2} \mu_{\text{Zn}}^\alpha \right] = -3F \{ \varphi^\beta - \varphi^\alpha \}$$

$$A \equiv \Delta G^{\circ} + RT \ln Q$$

$$A_{cell} = \Delta G_{cell}^{\circ} + RT \ln Q_{cell} = -zF \varepsilon_{cell}$$

$$\varepsilon_{cell} \equiv \{\varphi^{\beta} - \varphi^{\alpha}\}$$

If  $Q_{cell} = 1$        $\Delta G_{cell}^{\circ} = -zF \varepsilon_{cell}^{\circ}$        $\varepsilon_{cell}^{\circ}$  : std. electrode potential  
||

The two electrodes are pure and the two electrolytes are prepared with a molarity that yields an activity of 1.

$$A_{cell} = -zF \varepsilon_{cell}^{\circ} + RT \ln Q_{cell} = -zF \varepsilon_{cell}$$

$$\varepsilon_{cell} = \varepsilon_{cell}^{\circ} - \frac{RT}{zF} \ln Q_{cell}$$

**Nernst equation**

$$\varepsilon = \varepsilon^{\circ} - \frac{0.05915}{z} \log Q [V]$$

$$\frac{RT}{F} * 2.303 = 0.05915$$

### 15-3-3 The Standard Hydrogen Electrode

$$\varepsilon^{\alpha\beta} = \varphi^{\beta} - \varphi^{\alpha} = (\varphi^{\beta} - \varphi^{std}) - (\varphi^{\alpha} - \varphi^{std})$$

$$\varphi^{\alpha} - \varphi^{std} = (\varphi^{\beta} - \varphi^{std}) - (\varphi^{\beta} - \varphi^{\alpha})$$

$$\varepsilon^{\beta} \equiv \varphi^{\beta} - \varphi^{std} = \varphi^{\beta} - 0 = \varphi^{\beta}$$

: Half cell potential  
/ Single electrode potential

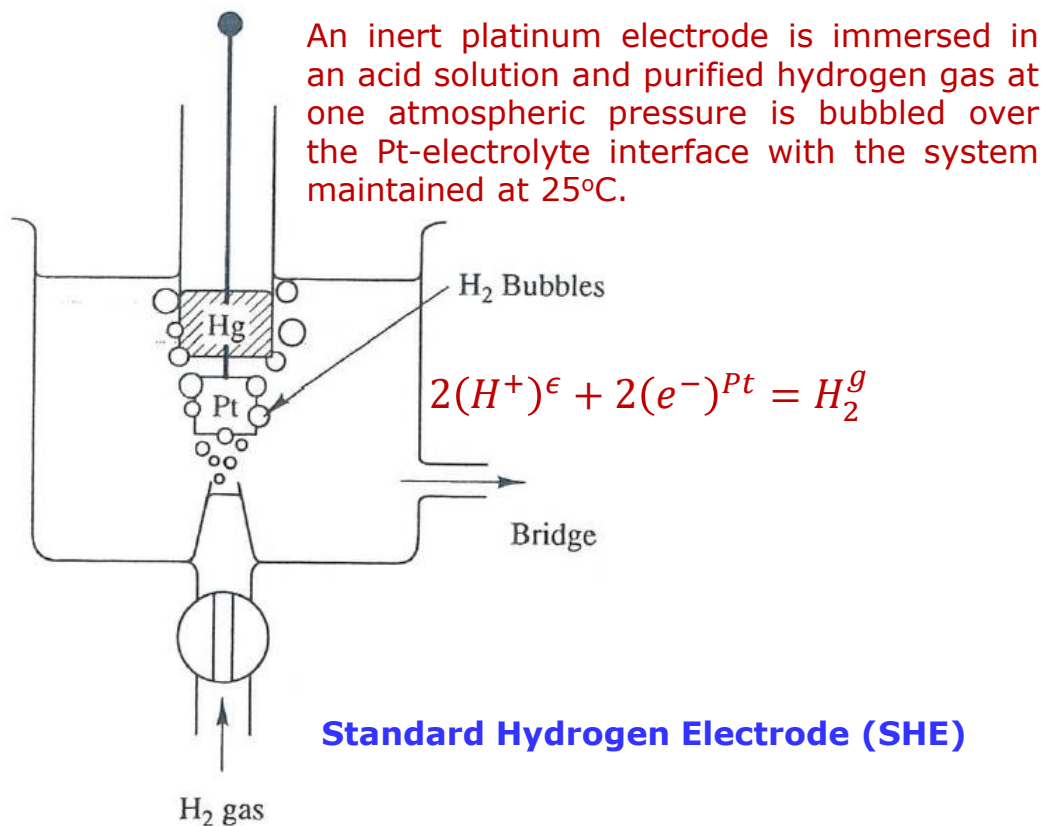
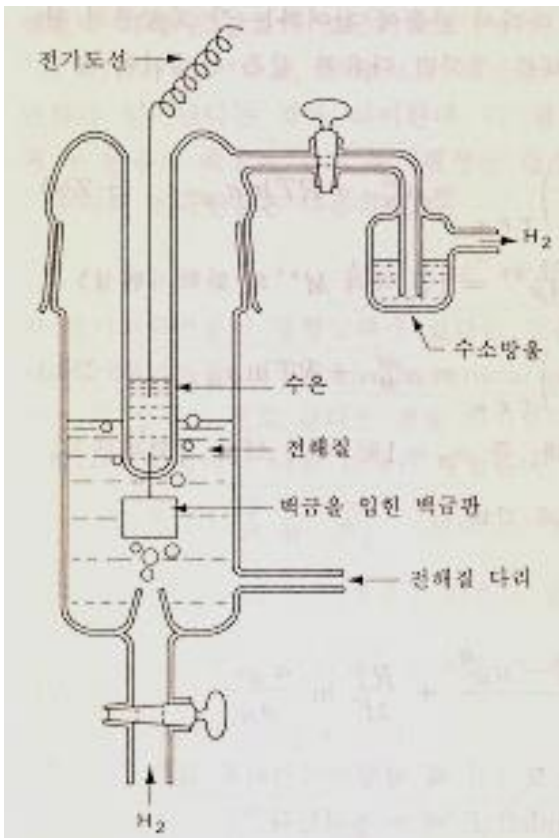


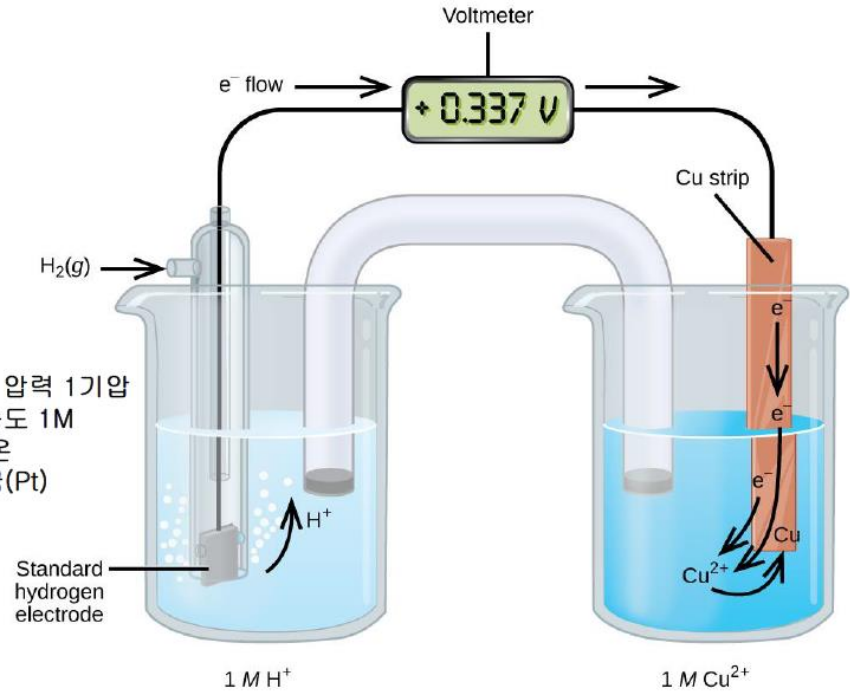
TABLE 15.3

Selected values from the electromotive series

Reduction reaction	emf(volts)
$Ca^+ + e^- = Ca$	-3.80
$Na^+ + e^- = Na$	-2.71
$Al^{+++} + 3e^- = Al$	-1.662
$Fe^{++} + 2e^- = Fe$	-0.447
$Ni^{++} + 2e^- = Ni$	-0.257
$Fe^{+++} + 3e^- = Fe$	-0.037
$2H^+ + 2e^- = H_2$	0.00000
$Cu^{++} + e^- = Cu^+$	0.153
$Cu^+ + e^- = Cu$	0.521
$Fe^{+++} + e^- = Fe^{++}$	0.771
$O_2 + 4H^+ + 4e^- = 2H_2O$	1.229
$Au^+ + e^- = Au$	1.692
$Ag^{++} + e^- = Ag^+$	1.980



수소가스 압력 1기압  
 전해질 농도 1M  
 온도: 실온  
 전극: 백금(Pt)



전극 반응	표준 전극 전위(V)	전극 반응	표준 전극 전위(V)
$\text{Li}^+/\text{Li}$	-3,045	$\text{MnO}_2/\text{MnOOH}(a_{\text{OH}^-}=1)$	0,15
$\text{Na}^+/\text{Na}$	-2,714	$\text{Cu}^{2+}/\text{Cu}$	0,347
$\text{Mg}^{2+}/\text{Mg}$	-2,363	$\text{Ag}_2\text{O}/\text{Ag}(a_{\text{OH}^-}=1)$	0,345
$\text{Al}^{3+}/\text{Al}$	-1,662	$\text{O}_2/\text{OH}^-(a_{\text{OH}^-}=1)$	0,401
$\text{ZnO}_2^{2-}/\text{Zn}(a_{\text{OH}^-}=1)$	-1,215	$\text{NiOOH}/(\text{NiOH})_2(a_{\text{OH}^-}=1)$	0,49
$\text{H}_2/\text{OH}^-(a_{\text{OH}^-}=1)$	-0,828	$\text{Fe}^{3+}/\text{Fe}^{2+}$	0,771
$\text{Cd}(\text{OH})_2/\text{Cd}(a_{\text{OH}^-}=1)$	-0,825	$\text{Ag}^+/\text{Ag}$	0,7991
$\text{Zn}^{2+}/\text{Zn}$	-0,763	$\text{Br}_2/\text{Br}^-$	1,087
$\text{Fe}^{2+}/\text{Fe}$	-0,440	$\text{O}_2/\text{H}_2\text{O}(a_{\text{OH}^-}=1)$	1,229
$\text{Cr}^{3+}/\text{Cr}^{2+}$	-0,408	$\text{Cl}_2/\text{Cl}^-$	1,3595
$\text{Cd}^{2+}/\text{Cd}$	-0,403	$\text{Ce}^{4+}/\text{Ce}^{3+}$	1,61
$\text{PbSO}_4/\text{Pb}$	-0,3588	$\text{PbO}_2/\text{PbSO}_4$	1,685
$\text{Ni}^{2+}/\text{Ni}$	-0,250	$\text{F}_2/\text{F}^-$	2,87

$$A_{cell} = -zF \varepsilon_{cell}^0 + RT \ln Q_{cell} = -zF \varepsilon_{cell}$$

$$\lim_{Q \rightarrow K} A_{cell} = -zF \varepsilon_{cell}^0 + RT \ln Q_{cell} = 0$$

$$-RT \ln K = -zF \varepsilon^0$$

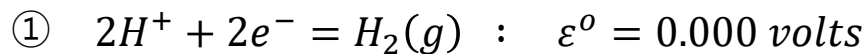
$$\varepsilon^0 = \frac{RT}{zF} \ln K$$

$\varepsilon^0 (+)$   $\rightarrow K > 1 \rightarrow$  resistant to dissolution  $\rightarrow$  noble elements

$\varepsilon^0 (-)$   $\rightarrow K < 1 \rightarrow$  reactants dominate at Eq.  $\rightarrow$  reactive elements

## 15-4 Pourbaix Diagram

### 15-4-1 The Stability of Water : $\text{H}_2\text{O}$ , $\text{H}^+$ , $\text{e}^-$ , $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$



For this half cell reaction,

$$\log Q = \log \left[ \frac{a_{\text{H}_2}^g}{a_{\text{H}^+}^2 a_{\text{e}^-}^2} \right] = \log \left[ \frac{a_{\text{H}_2}^g}{a_{\text{H}^+}^2} \right] = \log P_{\text{H}_2} - 2 \log a_{\text{H}^+}$$

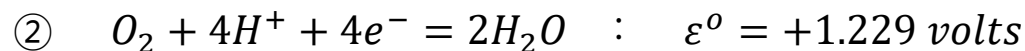
$$\log Q = \log P_{\text{H}_2} + 2\text{pH}$$

$$\varepsilon = 0.000 - \frac{0.05915}{2} [\log P_{\text{H}_2} + 2\text{pH}]$$

$$\varepsilon = \varepsilon^0 - \frac{0.05915}{z} \log Q \text{ [V]}$$

Let  $0.05915 = b$

$$\varepsilon = -b\text{pH} - \frac{b}{2} \log P_{\text{H}_2}$$



For this half cell reaction,

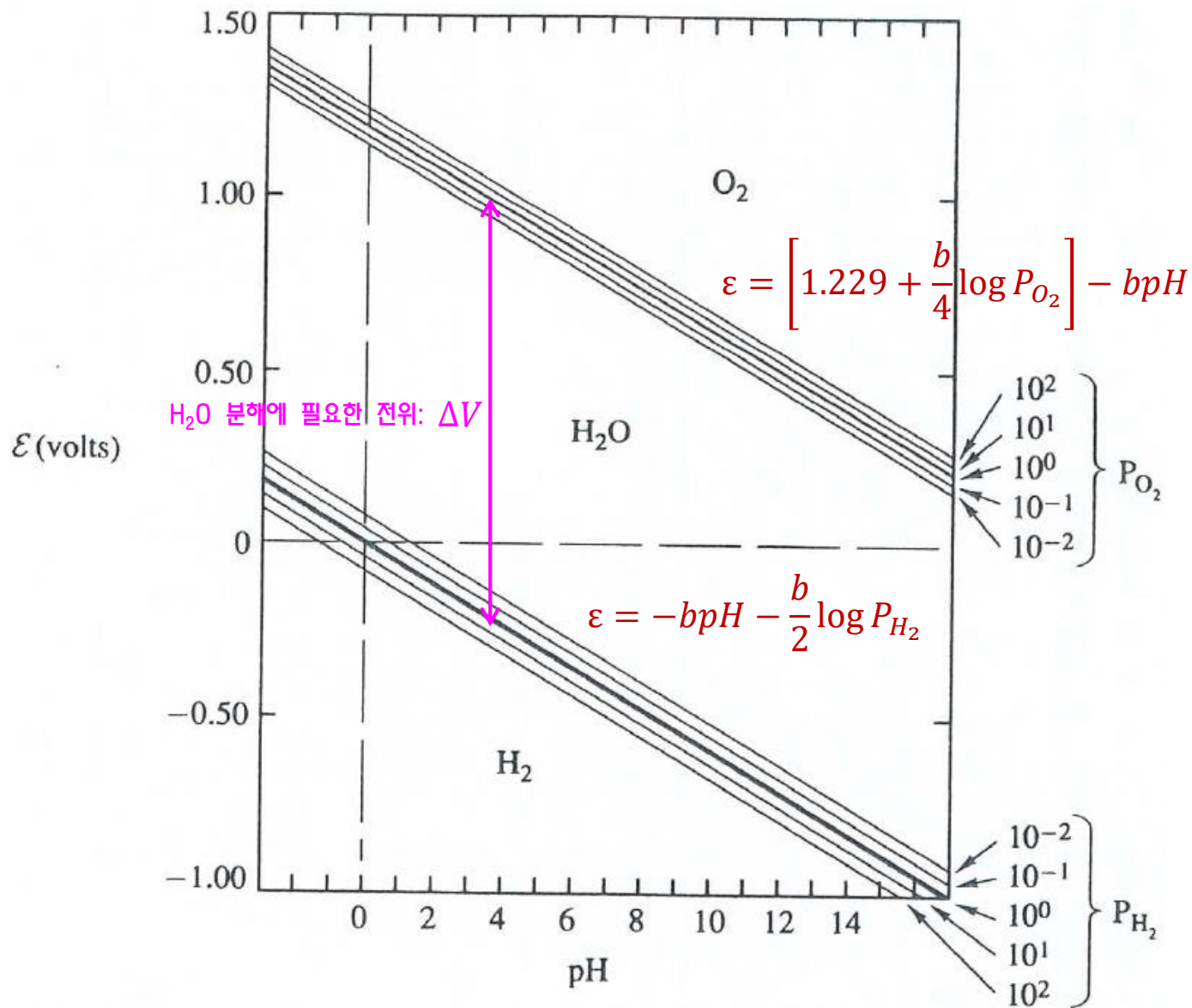
$$\log Q = \log \left[ \frac{a_{H_2O}^2}{a_{O_2}^g a_{H^+}^4 a_{e^-}^4} \right] = \log \left[ \frac{1}{P_{O_2} a_{H^+}^4} \right] = -\log P_{O_2} - 4 \log a_{H^+}$$

$$\log Q = -\log P_{O_2} + 4pH$$

$$\varepsilon = +1.229 - \frac{0.05915}{4} [-\log P_{O_2} + 4pH]$$

Let  $0.05915 = b$

$$\varepsilon = \left[ 1.229 + \frac{b}{4} \log P_{O_2} \right] - b pH$$



## 15-4-2 Pourbaix Diagram for Copper

### Copper-Water System

① Components: 7

*solid components: Cu, CuO, Cu<sub>2</sub>O*  
*ionic species: Cu<sup>+</sup>, Cu<sup>++</sup>, HCuO<sub>2</sub><sup>-</sup>, CuO<sub>2</sub><sup>-</sup>*  
*others: H<sup>+</sup>, H<sub>2</sub>O, e<sup>-</sup>*

② Elements: 3

*Cu, H, O*

③ Independent Reactions = C-E = 10-3 = 7

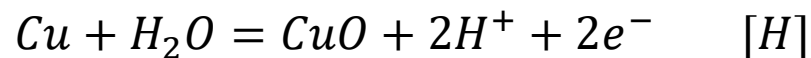
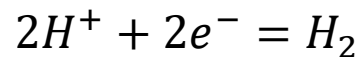
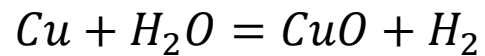
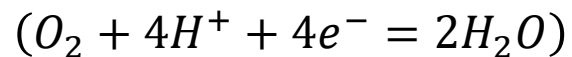
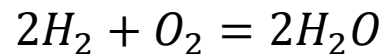
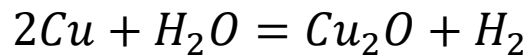
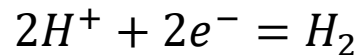
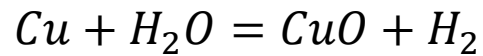
④ The number of reactions must be considered: 21

$${}_rC_2 = \frac{7!}{2!5!} = 21$$

TABLE 15.4

Reactions considered in computing the Pourbaix Diagram for pure copper

$\text{Cu}^{++} + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H}^+$	[A]
$\text{Cu}^{++} + 2\text{H}_2\text{O} = \text{CuO}_2^{--} + 4\text{H}^+$	[B]
$\text{HCuO}_2^- = \text{CuO}_2^{--} + \text{H}^+$	[C]
$\text{Cu}^+ = \text{Cu}^{++} + \text{e}^-$	[D]
$\text{Cu}^+ + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H} + \text{e}^-$	[E]
$\text{Cu}^+ + 2\text{H}_2\text{O} = \text{CuO}_2^{--} + 4\text{H}^+ + \text{e}^-$	[F]
$\text{Cu} + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	[G]
$\text{Cu} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+ + 2\text{e}^-$	[H]
$\text{Cu}_2\text{O} + \text{H}_2\text{O} = 2\text{CuO} + 2\text{H}^+ + 2\text{e}^-$	[I]
$2\text{Cu}^+ + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+$	[J]
$\text{Cu}^{++} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+$	[K]
$\text{CuO} + \text{H}_2\text{O} = \text{HCuO}_2^- + \text{H}^+$	[L]
$\text{CuO} + \text{H}_2\text{O} = \text{CuO}_2^{--} + 2\text{H}^+$	[M]
$\text{Cu} = \text{Cu}^+ + \text{e}^-$	[N]
$\text{Cu} = \text{Cu}^{++} + 2\text{e}^-$	[O]
$\text{Cu} + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H}^+ + 2\text{e}^-$	[P]
$\text{Cu} + 2\text{H}_2\text{O} = \text{CuO}_2^{--} + 4\text{H}^+ + 2\text{e}^-$	[Q]
$\text{Cu}_2\text{O} + 2\text{H}^+ = 2\text{Cu}^{++} + \text{H}_2\text{O} + 2\text{e}^-$	[R]
$\text{Cu}_2\text{O} + 3\text{H}_2\text{O} = 2\text{HCuO}_2^- + 4\text{H}^+ + 2\text{e}^-$	[S]
$\text{Cu}_2\text{O} + 3\text{H}_2\text{O} = 2\text{CuO}_2^{--} + 6\text{H}^+ + 2\text{e}^-$	[T]
$\text{Cu}^+ + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+ + \text{e}^-$	[U]



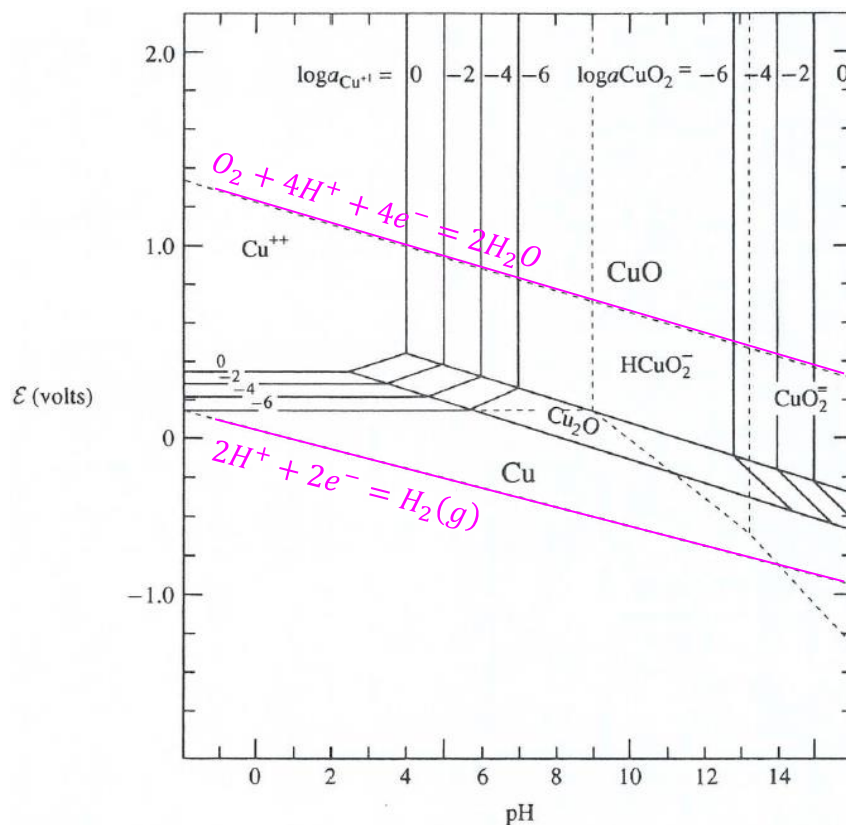
**TABLE 15.4**  
**Reactions considered in computing**  
**the Pourbaix Diagram for pure**  
**copper**

$\text{Cu}^{++} + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H}^+$	[A]
$\text{Cu}^{++} + 2\text{H}_2\text{O} = \text{CuO}_2^{--} + 4\text{H}^+$	[B]
$\text{HCuO}_2^- = \text{CuO}_2^{--} + \text{H}^+$	[C]
$\text{Cu}^+ = \text{Cu}^{++} + \text{e}^-$	[D]
$\text{Cu}^+ + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H} + \text{e}^-$	[E]
$\text{Cu}^+ + 2\text{H}_2\text{O} = \text{CuO}_2^{--} + 4\text{H}^+ + \text{e}^-$	[F]
$\text{Cu} + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	[G]
$\text{Cu} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+ + 2\text{e}^-$	[H]
$\text{Cu}_2\text{O} + \text{H}_2\text{O} = 2\text{CuO} + 2\text{H}^+ + 2\text{e}^-$	[I]
$2\text{Cu}^+ + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+$	[J]
$\text{Cu}^{++} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+$	[K]
$\text{CuO} + \text{H}_2\text{O} = \text{HCuO}_2^- + \text{H}^+$	[L]
$\text{CuO} + \text{H}_2\text{O} = \text{CuO}_2^{--} + 2\text{H}^+$	[M]
$\text{Cu} = \text{Cu}^+ + \text{e}^-$	[N]
$\text{Cu} = \text{Cu}^{++} + 2\text{e}^-$	[O]
$\text{Cu} + 2\text{H}_2\text{O} = \text{HCuO}_2^- + 3\text{H}^+ + 2\text{e}^-$	[P]
$\text{Cu} + 2\text{H}_2\text{O} = \text{CuO}_2^{--} + 4\text{H}^+ + 2\text{e}^-$	[Q]
$\text{Cu}_2\text{O} + 2\text{H}^+ = 2\text{Cu}^{++} + \text{H}_2\text{O} + 2\text{e}^-$	[R]
$\text{Cu}_2\text{O} + 3\text{H}_2\text{O} = 2\text{HCuO}_2^- + 4\text{H}^+ + 2\text{e}^-$	[S]
$\text{Cu}_2\text{O} + 3\text{H}_2\text{O} = 2\text{CuO}_2^{--} + 6\text{H}^+ + 2\text{e}^-$	[T]
$\text{Cu}^+ + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+ + \text{e}^-$	[U]

Group I = Reactions in which no electrons are transferred to the electrode: [A],[B],[C],[J],[K],[L], and [M] ⇒ Vertical lines at a fixed pH

Group II = Reactions in which do not dependent upon the hydrogen ions: [D],[N], and [O] ⇒ Horizontal lines

Group III = Reactions in which both electrons and hydrogen ions involve: ⇒ Lines of a slope  $n \cdot b$



For the half cell reaction, [K]  $Cu^{2+} + H_2O = CuO + 2H^+$

$$\varepsilon = \varepsilon_o - \frac{b}{2} \log Q$$

$$\log Q = \log \left[ \frac{a_{CuO} a_{H^+}^2}{a_{H_2O} a_{Cu^{2+}}} \right] = \log \left[ \frac{a_{H^+}^2}{a_{Cu^{2+}}} \right] = 2 \log a_{H^+} - \log a_{Cu^{2+}}$$

$$\varepsilon = \varepsilon_o - \frac{b}{2} [2 \log a_{H^+} - \log a_{Cu^{2+}}] = 0$$

$$\varepsilon = \varepsilon_o + b pH + \frac{b}{2} \log a_{Cu^{2+}} = 0$$

$$b pH = -\frac{1}{b} \varepsilon_o - \frac{1}{2} \log a_{Cu^{2+}}$$

For the half cell reaction, [M]  $CuO + H_2O = CuO_2^{2-} + 2H^+$

$$\varepsilon = \varepsilon_o - \frac{b}{2} \log Q$$

$$\log Q = \log \left[ \frac{a_{CuO_2^{2-}} a_{H^+}^2}{a_{H_2O} a_{CuO}} \right] = \log \left[ \frac{a_{CuO_2^{2-}} a_{H^+}^2}{1} \right] = \log a_{CuO_2^{2-}} + 2 \log a_{H^+}$$

$$\varepsilon = \varepsilon_o - \frac{b}{2} [2 \log a_{H^+} + \log a_{CuO_2^{2-}}] = 0$$

$$\varepsilon = \varepsilon_o + bpH - \frac{b}{2} \log a_{CuO_2^{2-}} = 0$$

$$bpH = -\frac{1}{b} \varepsilon_o + \frac{1}{2} \log a_{CuO_2^{2-}}$$

For the half cell reaction, [-H]  $CuO + 2H^+ + 2e^- = Cu + H_2O$

$$\varepsilon = \varepsilon_o - \frac{b}{2} \log Q$$

$$\log Q = \log \left[ \frac{a_{Cu} a_{H_2O}}{a_{CuO} a_{H^+}^2 a_{e^-}^2} \right] = \log \left[ \frac{1}{a_{H^+}^2} \right] = -2 \log a_{H^+}$$

$$\varepsilon = \varepsilon_o + \frac{b}{2} [2 \log a_{H^+}]$$

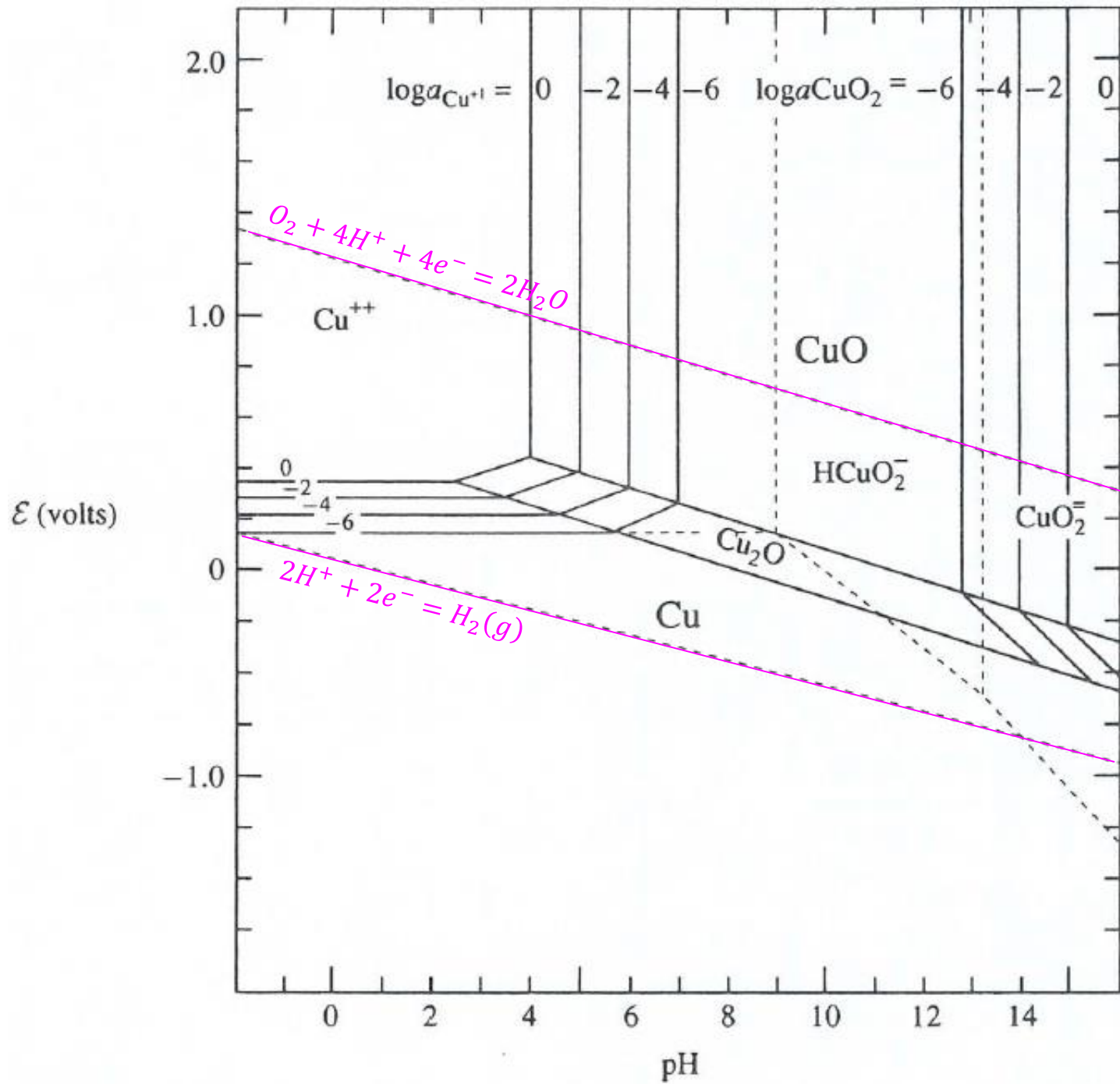
$$\varepsilon = \varepsilon_o - b pH$$

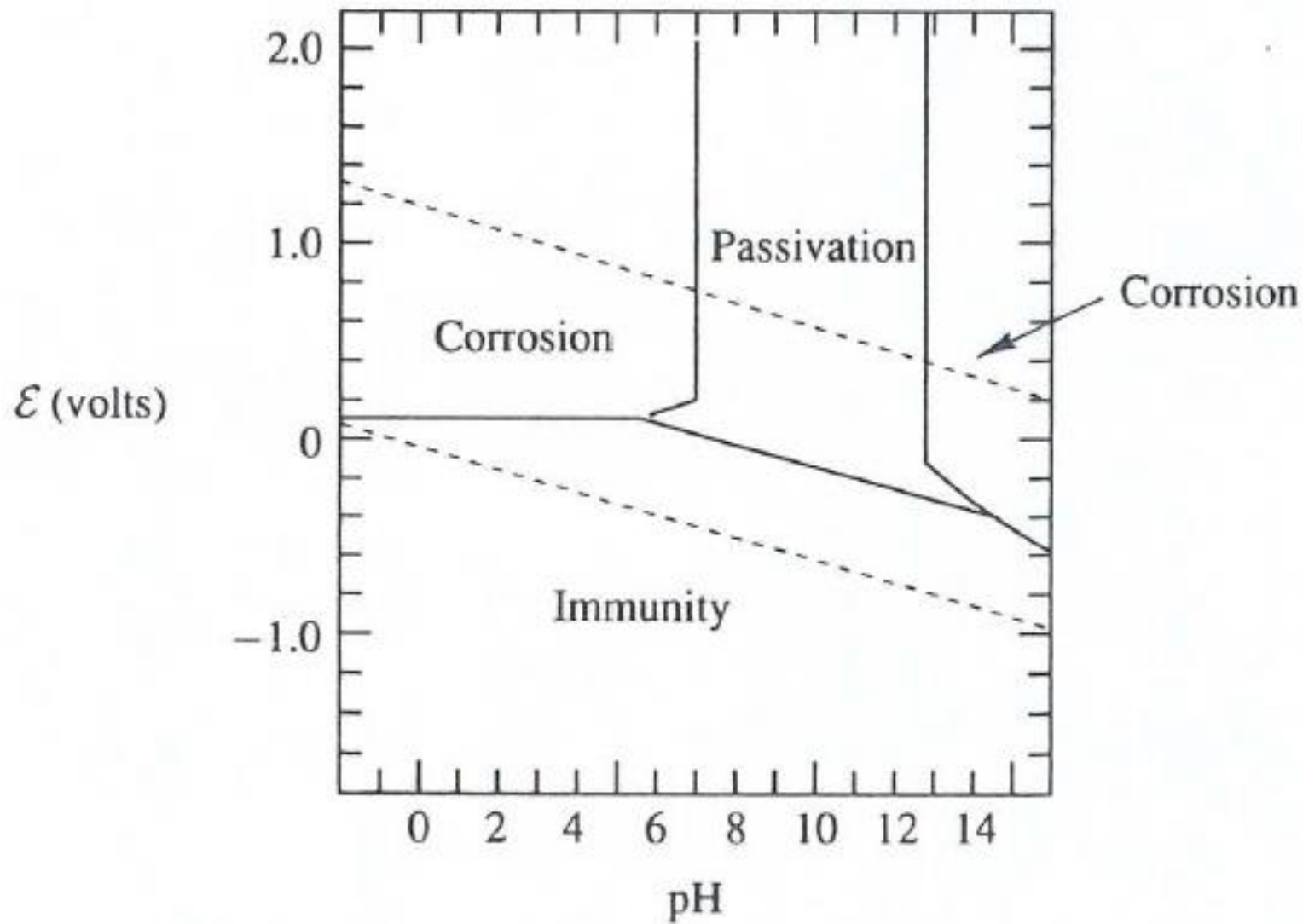
For the half cell reaction, [-O]  $Cu^{2+} + 2e^{-} = Cu$

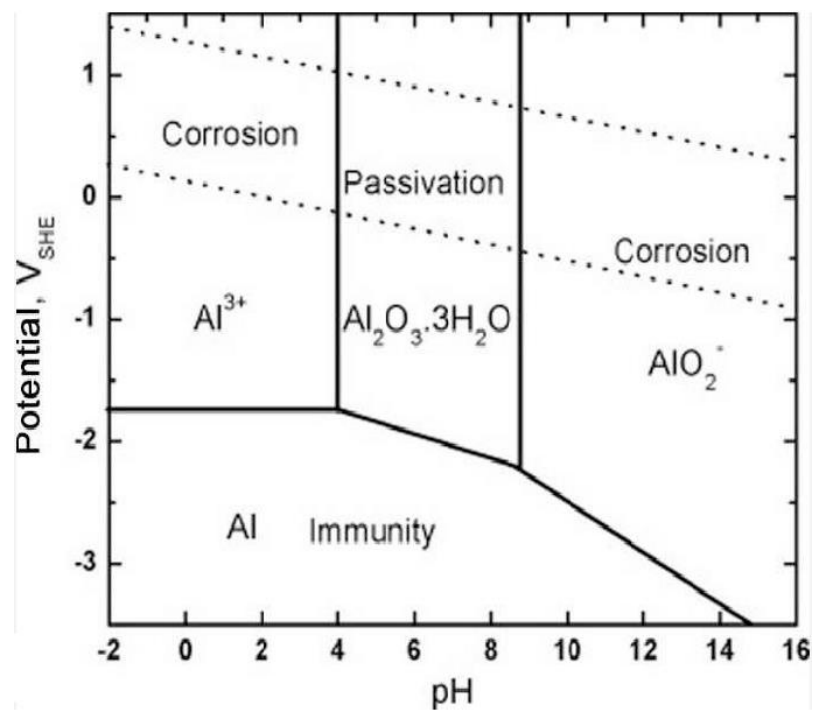
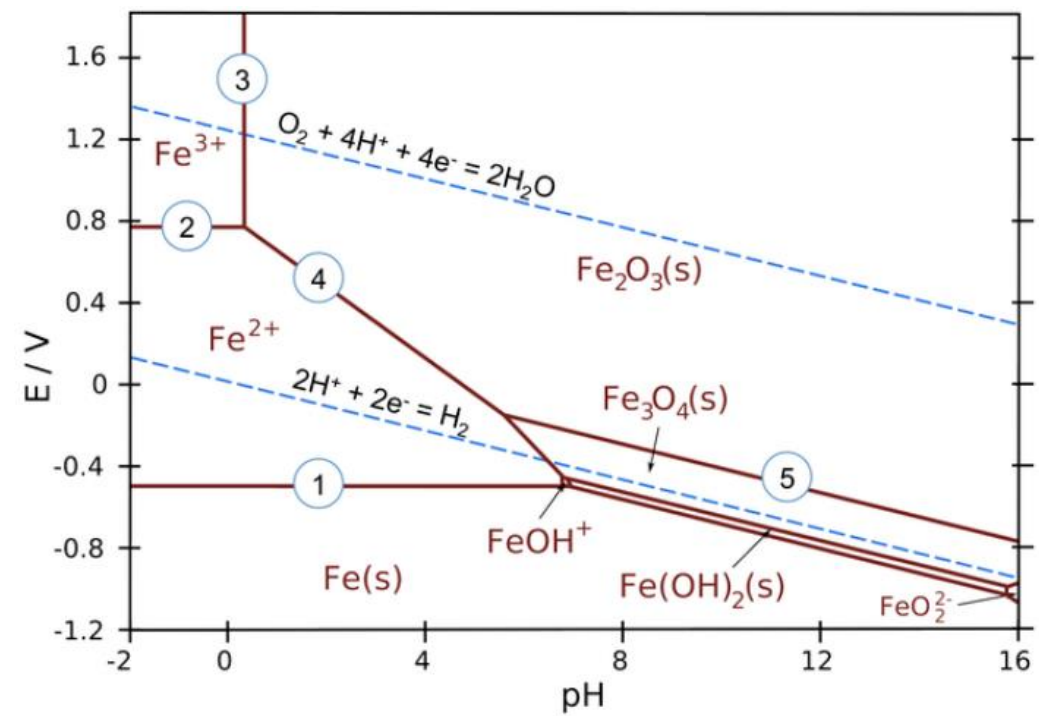
$$\varepsilon = \varepsilon_o - \frac{b}{2} \log Q$$

$$\log Q = \log \left[ \frac{a_{Cu}}{a_{Cu^{2+}} a_{e^{-}}^2} \right] = \log \left[ \frac{1}{a_{Cu^{2+}}} \right] = -\log a_{Cu^{2+}}$$

$$\varepsilon = \varepsilon_o + \frac{b}{2} [\log a_{Cu^{2+}}]$$







**ATLAS OF  
ELECTROCHEMICAL  
EQUILIBRIA  
IN AQUEOUS SOLUTIONS**

**BY**

**MARCEL POURBAIX**

Translated from the French by

**JAMES A. FRANKLIN**

(except Sections I, III 5 and III 6, which were originally written in English)

**NATIONAL ASSOCIATION of CORROSION ENGINEERS**

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**CEBELCOR**

**Brussels**



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Version 10 Modules  
All modules included as standard

1. Sim - Process simulation

2. LCA Evaluation

3. Mass Balance

4. Reaction Equations

5. Heat and Material Balances

6. Heat Loss Calculator

7. Equilibrium Calculations

8. Exergy Balance

9. Eh-pH Diagrams - Pourbaix

10. H, S, Cp and Ellingham Diagrams

11. Tpp Diagram-Stability diagrams

12. Lpp Diagrams-Stability diagrams

13. Water - Steam tables, etc.

14. H, S, Cp Estimates

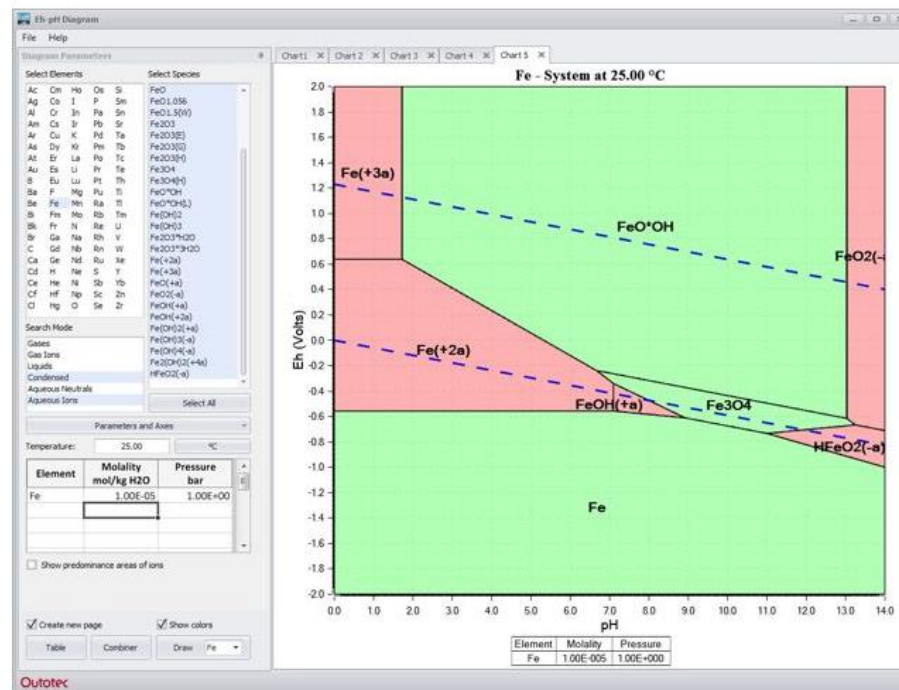
15. Benson Estimation

16. Species Converter

## EH-PH DIAGRAMS – POURBAIX

[Eh-pH User Manual](#)

Knowledge of the stabilities of ionic and non-ionic species in water solutions is critical to understanding problems of corrosion, dissolution, I



HSC Eh-Ph Diagrams

With this calculation option you can easily draw simple diagrams with only an element and H<sub>2</sub>O, as well as more complicated diagrams with  
The dotted cyan lines indicate the stability area of water. The stability regions of ions can be outlined with blue lines, if necessary. The conc