# Physical Chemistry 1

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❑ Provide the lecture materials

❑ There will be two exams

       1. Midterm exam (End of October)

       2. Final exam (Mid of December)

# PHYSICAL CHEMISTRY

THIRD EDITION

THOMAS ENGEL    PHILIP REID

| Syllabus and Weekly plan | | |
|---|---|---|
| Week | Topic | Class Type |
| 1 | Chapter 1. General Introduction of the course & Fundamental Concepts of Thermodynamics | lecture |
| 2 | Chapter 2. Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics | lecture |
| 3 | Chapter 2. Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics | lecture |
| 4 | Chapter 3. The Importance of State Functions: Internal Energy and Enthalpy | lecture |
| 5 | Chapter 4. Thermochemistry | lecture |
| 6 | Chapter 4. Thermochemistry | lecture |
| 7 | Chapter 5. Entropy and the Second and Third Laws of Thermodynamics | lecture |
| 8 | Mid-term exam | lecture/mid-term exam (written) |
| 9 | Chapter 5. Entropy and the Second and Third Laws of Thermodynamics | lecture |
| 10 | Chapter 6. Chemical Equilibrium | lecture |
| 11 | Chapter 6. Chemical Equilibrium | lecture |
| 12 | Chapter 6. Chemical Equilibrium | lecture |
| 13 | Chapter 7. The Properties of Real Gases | lecture |
| 14 | Chapter 8. Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases | lecture |
| 15 | Chapter 8. Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases | lecture |
| 16 | Final exam | final exam (written) |

# Chapter 1
## Fundamental Concepts of Thermodynamics

# Physical Chemistry, 3$^{rd}$ Edition

Thomas Engel, Philip Reid

# Legend and Abbreviations
# to be used in the lecture note

( ) or eq=equation ; [ ]=section ; #=the number of

amt=amount ; app=appendix ; bnd(r)y=boundary ; bt(w)n=between ;

cf =confer ; comp=component ; conc (or $C$)=concentration ; $CP$=chemical potential ;

eos=eq of state ; EP=Example Problem ; eqm=equilibrium ; ext=external ;
ER= Engel & Reid ; GWC= Gilbert W. Castellan
id=ideal ; indep=independent ; LN=lecture note ; P=product(s)

qlty=quality ; qnty=quantity ; R=reactant(s) ; rx or rxn=reaction ; $T$, $V$, $P$

rev=reversible ; irrev=irreversible ; $\rho$ (rho)=density

soln=solution ; solv=solvent ; std st=standard state ; surrs=surroundings ;

sys=system ; TD=thermodynamic(s) ; ttbk =textbook ; vble=variable ;

vdW=van der Waals ; w/=with ; w/o=without ; wrt =with respect to

Numerator 분자; denominator 분모; rectangular parallelepided(cuboid)직육면체

abscissa (x-axis)가로축 ; ordinate (y-axis)세로축   ※ 약자는 변수만 *italics*로

※ superscript(상첨자 )약속: * 순물질 ; ° 표준상태 (1 bar)

# Physical Chemistry?

- Ph**y**sical ch**e**mistry is the branch of chemistry which applies the methods and theories of physics to chemical problems.

- It involves more theory and more mathematics than the other branches of chemistry.

수정

보강

# Objectives

- Basic concepts in thermodynamics (열역학)
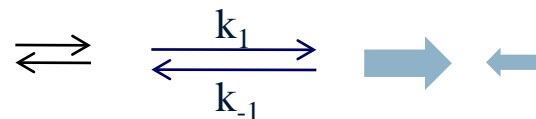- Derivation and discussion of the usefulness of equations of state (상태방정식)

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$$\approx \Delta {}^{\circ}C \pm \longleftrightarrow \equiv \eth \propto đ\, \partial\, {}^{\circ} \text{※} \neq {}^{\circ} \because \xi\, \zeta \rightleftharpoons \alpha \times -\infty \sqrt{\ } \phi\, {}^{\circ}\ E\, {}^{\circ}\ \tilde{N} -$$

$$E\, {}^{\circ} \ll \gg \nabla \geq \leq \Theta\, \uparrow \downarrow \frac{1}{2}\pi \cdot \ddagger\, \Box\, \circ\, \bullet\ \Delta G_R{}^{\circ}\ \Delta U_R{}^{\circ}\ \Delta G_f{}^{\circ}\ \sigma$$

$$\alpha A\ +\ \beta B \rightleftharpoons \gamma C\ +\ \delta D$$

오타 in p. →  ☞ Fig.7.6, LN p.6.15 ☜   $\rightleftharpoons$   $\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$

# Chapter Outline (pp.1-16)

1.  What is thermodynamics and why is it useful?
2.  The macroscopic (bulk) variables : $V$, $P$, and $T$  ← *observable*
3.  Basic definitions needed to describe thermodynamic systems: system & surr$^{\underline{s}}$ ; eqm & 0th law of TD
4.  Equations of state (eos, 상태방정식) and the ideal gas law (이상기체법칙)
5.  A brief introduction to real gases

   **< 열역학 >**
*   화학적 또는 물리적 과정에서의  열과 다른 에너지와의 관계를 거시적 관점에서 취급하는 학문
   - 어떤 형태의 에너지가 다른 형태의 에너지로의 전환
   - 에너지 변화의 예측
   - 평형의 위치(자발변화 방향) or 평형조성

# 1.1 What is Thermodynamics and Why is it Useful?

- Thermodynamics describes a system of interest in terms of its <u>bulk properties</u>, such as $P$, $\rho$, $V$, and $T$. (*or* macroscopic vbles)

## Usefulness

- high yield of $NH_3$ at lower $T$ & higher $P$ (Ch.6), pp139-144
- efficiencies of engines (Ch.5) : fuel cell & internal combustion engine
- Gibbs energy & cell potential (Ch.11) : $\Delta G_R^\circ = -n\, F\, E_{cell}^\circ$
- extent of reaction, or position of eqm, can't be altered by catalyst. (Ch.6)

Ch.5.  TD 2$^{nd}$ law
Ch.6.  Chemical eqm  *(cf) urea fertilizer, 尿素肥料, $(NH_2)_2CO$
Ch.11. Electrochemistry

# 1.2 The Macroscopic Variables : $V$, $P$, and $T$ ☞ [16.1]

Microscopic model

- → **Gas kinetic theory** (Ch.16) provides a central concept of translational motion of gas particles (병진운동).

- A gas molecule is envisioned as traveling through space w/ a velocity, $v$ that can be decomposed into 3 Cartesian components: $v_x$, $v_y$, and $v_z$ as in Fig.1.1.

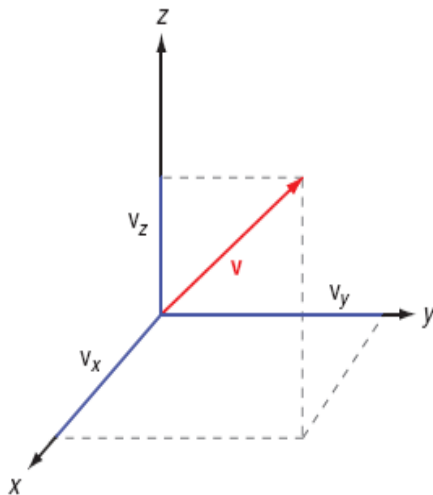By René Descartes = Renatus Cartesius, "Cogito, ergo sum.", 1637.



$-mv_x$

$mv_x$

$v$

Area = $A$

$\Delta x = v_x \Delta t$

*Fig*.1.2 *Collision btn a gas particle and a wall*.

*Fig*.1.1 *Cartesian coord. of velocity*.
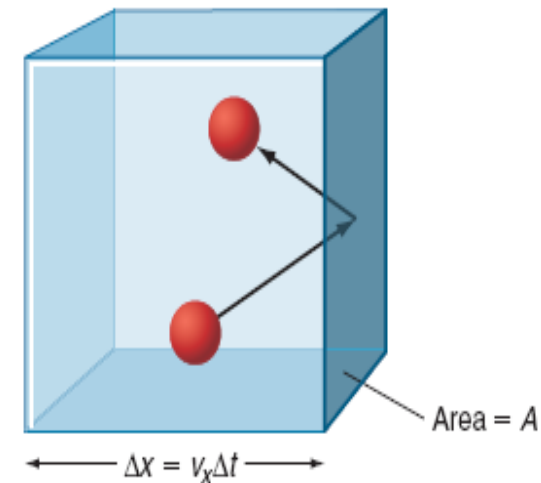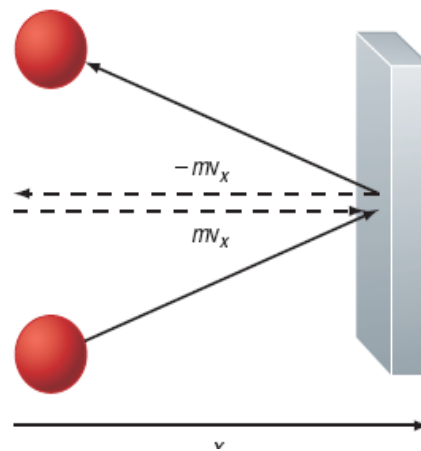
*Fig*.1.3 *# collisions w/wall per unit time*.

# 1.2 The Macroscopic Variables : $V$, $P$, and $T$

- The square of the velocity magnitude, $v^2$ is given by,

$$v^2 = v \bullet v = v_x^2 + v_y^2 + v_z^2 \quad \sim \text{Pythagorean theorem} \tag{1.1}$$

$$v_x^2 = v_y^2 = v_z^2 = \frac{1}{3}v^2 \quad (\alpha)$$

- The particle kinetic energy is $\frac{1}{2}mv^2$ such that

$$\varepsilon_{Tr} = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \varepsilon_{Tr,x} + \varepsilon_{Tr,y} + \varepsilon_{Tr,z} \tag{1.2}$$

where the subscript $Tr$ indicates that the energy corresponds to the translational motion of the particle.

- Pressure arises from the collisions of gas particles w/ the walls of the container as can be seen in Fig.1.2.

$$P = \frac{F}{A} \;;\; P_i = \frac{ma_i}{A} = \frac{m}{A}\left(\frac{dv_i}{dt}\right) = \frac{1}{A}\left(\frac{dmv_i}{dt}\right) = \frac{1}{A}\left(\frac{dp_i}{dt}\right) \tag{1.3}$$

$A$ = area of the wall ($m^2$)
$F$ = force ($ma : kg\ m\ s^{-2}$)
$p_i$ = particle's linear momentum in the $i$ direction ($mv : kg\ m\ s^{-1}$)
(선형 운동량)

# 1.2 The Macroscopic Variables : *V*, *P*, and *T*

☞ Ch.16. *Assumptions for id gas* (LN p.16.4)

- Therefore, the total momentum change that gives rise to the pressure is given by

$(cf)$ GWC pp.52-54 for derivation

$$\Delta p_{Total} = \frac{\Delta p}{molecule} \times (\#colliding\ molecules) \qquad (1.4)$$

← From Fig.1.2

- From Fig.1.3, the collisional volume element (충돌부피요소) is

$$V = A(\Delta x),\ where\ \ \Delta x = v_x \Delta t \ \text{~이 안에 있는 분자들은} \ \varDelta t \ \text{동안} A \text{면에 충돌함} \qquad (1.5, 1.6)$$

- #particles that strike the wall of the container in a given period of time, $N_{collision}$ is then

$$N_{coll} = \tilde{N}(Av_x \Delta t)\left(\frac{1}{2}\right) = \frac{nN_A}{V}(Av_x \Delta t)\left(\frac{1}{2}\right);\ \tilde{N} = number\ density \ \text{(수밀도)} \qquad (1.7)$$

~ $v_x$ is (+) or (-), but only (+) counts!

- Substituting (1.7) into (1.4):

$$\Delta p_{x,Total} = (2mv_x)(N_{coll}) = (2mv_x)\left(\frac{nN_A}{V}\frac{Av_x \Delta t}{2}\right) = \frac{nN_A}{V}Am\Delta t\langle v_x^2 \rangle \qquad (1.8)$$

수정

where $\langle v_x^2 \rangle$ denotes the average value of $v_x^2$.

# 1.2 The Macroscopic Variables : $V$, $P$, and $T$

※ Note the difference in subscripts of vbles btn ttbk & LN in this page !

- From (1.3) and (1.8):

$$F_x \equiv \left( \frac{\Delta p_{x,total}}{\Delta t} \right) = \frac{nN_A}{V} Am\langle v_x^2 \rangle \quad \Rightarrow P_x = \frac{F_x}{A} = \frac{nN_A}{V} m\langle v_x^2 \rangle \qquad (1.9)$$

- In Ch.15, the avg translational energy for an individual particle in one dimension

$$\frac{U_T}{N_A} \equiv \varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z = \frac{3kT}{2} \quad \Rightarrow \quad \varepsilon_x \equiv \frac{m\langle v_x^2 \rangle}{2} = \frac{k_B T}{2} \quad \Rightarrow \quad m\langle v_x^2 \rangle = k_B T \qquad (1.10)$$

$$\text{(15.20), p.376} \downarrow$$

where $k_B$ is the Boltzmann constant and is equal to $R/N_A$.

- $P_x = P_y = P_z = P$ due to random motions of gas molecules.

- Substituting (1.10) into (1.9), we have

$$P_x = P = \frac{nN_A}{V} k_B T = \frac{nRT}{V} : ideal \ gas \ law \qquad (1.11)$$

# 1.2 The Macroscopic Variables : $V$, $P$, and $T$

### ※ Note the similarity btn Celsius scale and centigrade scale.

- T $\propto \varepsilon_x$ from (1.10), degree of hotness. A **thermometer** is an **i**nstrument that can measure relative hotness or coldness.

- Emp**i**rical t**e**mperature, $t$, is linearly related to the value of the thermom**e**tric property (온도측정성질), $x$.

  *(예)* 수은 온도계나 알코올 온도계의 경우 : $x$ =그들의 부피

edited
$$T(x) = a + bx$$  ☞ LN p.1-27     (1.12)

- $x$는 T의 단일(s**i**ngle-v**a**lued), 연속(cont**i**nuous), 단조(monot**o**nic) 함수여야 함, intensive p.

  unit : ℃, ℉, K, R, where $℃ = \dfrac{5}{9}(℉ - 32)$ and $R = ℉ + 460$ ♥ -40℃ = -40℉

- **Celsius scale** is det**e**rmined by one fixed r**e**ference point at which ice, liquid water, and gaseous water are in eqm: triple point ≡ 0.01 ℃. ☞ [8.2] $P_{tp}$ = 610.6 $Pa$

- The **TD temperature scale** or **absolute temperature scale**

# 1.3 Basic Definitions Needed to Describe Thermodynamic Systems *Q: What kind of system is our planet ?*

- A **system** (계) consists of all the materials involved in the process under study. =part of universe that we single out for study
- An **open system** (열린계) can exchange matter with the surroundings (주위). If not, a **closed system** (닫힌계).
- A **diathermal system** (투열계) can exchange energy with the surroundings. If not, an **adiabatic system** (단열계).
- **Isolated systems** (고립계) exchange neither matter nor energy with the surroundings. (=닫힌계+단열계)
- The interface between the system and its surroundings is called the **boundary** (경계),
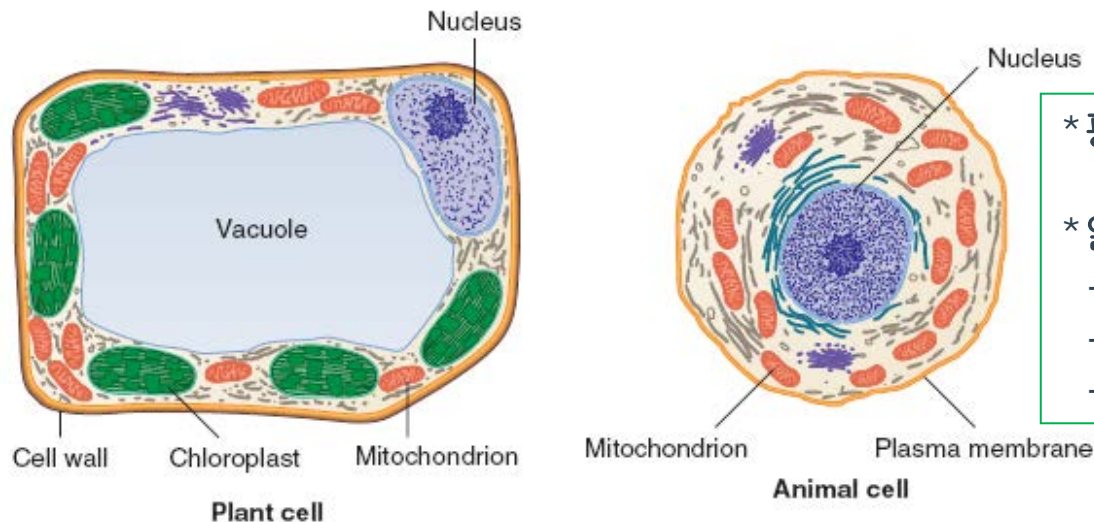
  *(예)* sys: oceans → bndy: 해저바닥 및 해수표면
  sys: liquid in a beaker → bndy: 비커 내벽과 액체표면

- TD eqm = eqm wrt sys vbles ($P$, $T$, $C$)  ☞ LN p.1.14

# 1.3 Basic Definitions Needed to Describe Thermodynamic Systems

- The **zeroth law of thermodynamics** states that two systems (A&B) that are separately in thermal equilibrium with a third system (C) are also in thermal equilibrium with one another. A=C & B=C, then A=B

- The 3rd system (C) can be a thermometer.

15/03/8



Nucleus

Vacuole

Cell wall    Chloroplast    Mitochondrion

**Plant cell**

Nucleus

Mitochondrion    Plasma membrane

**Animal cell**

*평형조건: $dX/dt$=0 & **same** $X$

*열역학적/열적/기계적
 -TD eqm: wrt $T,P,C$
 -Thermal eqm: wrt $T$
 -Mechanical eqm: wrt $P$

*Fig*.1.6 *Typical plant and animal cells* (*open and diathermal*).

# 1.4 Equations of State and the Ideal Gas Law
※ Anders Celcius (1701-1744) & Daniel Fahrenheit (1686-1736)

- **Ideal gas law** (이상기체법칙)= an equation of state:

$$PV = Nk_BT = nRT$$

~ empirical law

$k_B =$ **Boltzmann constant**
$R$ = **ideal gas constant**
$N$ = number of molecules
$n$ = number of moles of the gas

(1.18)

*intensive (세기: $P, T$) & extensive (크기: $n, V$) vbles

- It  can be also be written in terms of <u>intensive vbles</u>:

$$P = \frac{n}{V}RT = \rho_m RT = CRT \; ; \; \rho_m, C = \text{molarity } (mol/L)$$

(1.13)

$\rho_m$= molar density≡ #moles/volume= molarity

3/6-2,3,4

- For an ideal gas mixture, the total pressure $P$ is given

$$P = \sum_i \frac{n_i RT}{V} = \sum P_i = P_1 + P_2 + P_3 + ...$$

~ Dalton's  1st law

(1.20)

where $P_i$ : partial pressure (분압) of component $i$.

# 1.4 Equations of State and the Ideal Gas Law

$$\frac{P_i}{P} = \frac{\dfrac{n_i RT}{V}}{\displaystyle\sum_i \dfrac{n_i RT}{V}} = \frac{\dfrac{n_i RT}{V}}{\dfrac{nRT}{V}} = \frac{n_i}{n} = x_i :$$

$n = \Sigma n_i$ : total # moles
$x_i$=mole fraction (몰분율)     (1.21)
~ Dalton's 2nd law

- Pressure units related to Pascal as shown.

**TABLE 1.1   UNITS OF PRESSURE AND CONVERSION FACTORS**

| Unit of Pressure | Symbol | Numerical Value |
| --- | --- | --- |
| Pascal : *SI* unit | Pa | $1\ \text{N m}^{-2} = 1\ \text{kg m}^{-1}\ \text{s}^{-2}$ |
| Atmosphere | atm | $1\ \text{atm} = 101{,}325\ \text{Pa (exactly)}$ |
| Bar | bar | $1\ \text{bar} = 10^5\ \text{Pa}$ |
| Torr or millimeters of Hg | Torr | $1\ \text{Torr} = 101{,}325/760 = 133.32\ \text{Pa}$ |
| Pounds per square inch | psi | $1\ \text{psi} = 6{,}894.8\ \text{Pa}$ |

# 1.4 Equations of State and the Ideal Gas Law

- Values of the gas constant $R$ with different combinations of units are shown in Table 1.2.
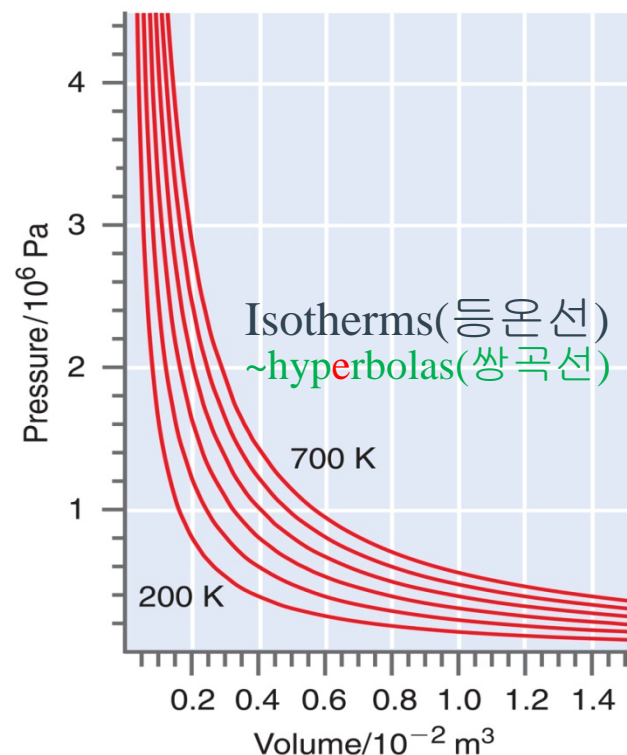
**TABLE 1.2   THE IDEAL GAS CONSTANT, $R$, IN VARIOUS UNITS**

$R = 8.314 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1}$    : *SI* unit

$R = 8.314 \, \text{Pa} \, \text{m}^3 \, \text{K}^{-1} \, \text{mol}^{-1}$   : *SI* unit

$R = 8.314 \times 10^{-2} \, \text{L} \, \text{bar} \, \text{K}^{-1} \, \text{mol}^{-1}$

$R = 8.206 \times 10^{-2} \, \text{L} \, \text{atm} \, \text{K}^{-1} \, \text{mol}^{-1}$

$R = 62.36 \, \text{L} \, \text{Torr} \, \text{K}^{-1} \, \text{mol}^{-1}$

Isotherms(등온선)
~hyperbolas(쌍곡선)

700 K

200 K

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- $PV = \alpha T = \text{constant at constant T}$    (1.17)

*Fig*.1.8. *Plots of* $PV = \alpha T$.

# Example Problem 1.1

Starting out on a trip into the mountains, you inflate the tires on your automobile to a recommended pressure of $3.21 \times 10^5$ *Pa* on a day when the temperature is -5.00 *°C*. You drive to the beach, where the temperature is 28.0 *°C*.

a. What is the final pressure in the tires?

b. Derive a formula for the final pressure assuming more realistically that the volume of the tire increases with increasing internal pressure as $V_f = V_i\left(1 + \gamma\left[P_f - P_i\right]\right)$.

※ **units**는 *italics*로

# Solution

a. Because the number of moles is constant,

$$nR = \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} ; \quad P_f = \frac{P_i V_i T_f}{V_f T_i} ; \text{ tire volume remains constant}$$

$$P_f = \frac{P_i T_f}{T_i} = 3.21 \times 10^5 \times \frac{(273.15 + 28.0)}{(273.15 - 5.00)} = 3.60 \times 10^5 \, Pa$$

b. $\dfrac{P_i V_i}{T_i} = \dfrac{P_f V_i \left[1 + \gamma (P_f - P_i)\right]}{T_f}$ ; $P_f^2 T_i \, \gamma + P_f T_i (1 - P_i \gamma) - P_i T_f = 0$

$$P_f = \frac{-T_i (1 - P_i \gamma) \pm \sqrt{T_i^2 (1 - P_i \gamma)^2 + 4 T_i T_f \gamma P_i}}{2 T_i \gamma}$$

(음의 부호는 제외, quadratic formula) (cf)quartic eqn

# Example Problem 1.2

Consider the composite system, which is held at 298 *K*, shown in the following figure. Assuming ideal gas behavior, calculate the total pressure and the partial pressure of each component if the barriers separating the compartments are removed. Assume that the volume of the barriers is negligible.



| He | Ne | Xe |
| --- | --- | --- |
| 2.00 L | 3.00 L | 1.00 L |
| 1.50 bar | 2.50 bar | 1.00 bar |
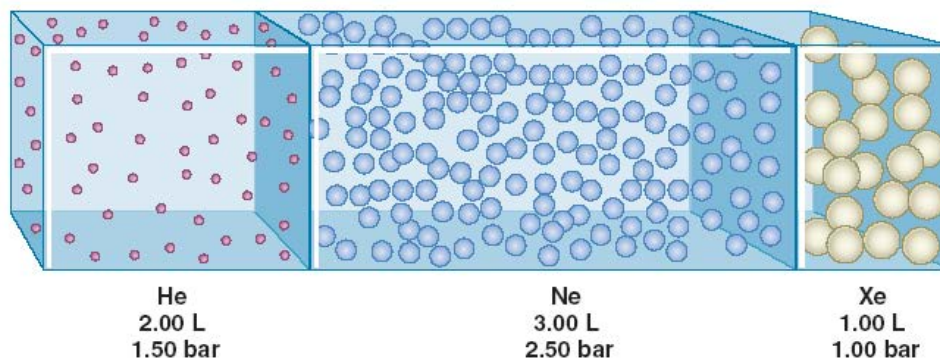
# Solution

The number of moles of *He*, *Ne*, and *Xe* is given by

$$n_{He} = \frac{PV}{RT} = \frac{1.5 \times 2}{8.314 \times 10^{-2} \times 298} = 0.121 \, mol$$

$$n_{Ne} = \frac{PV}{RT} = \frac{2.5 \times 3}{8.314 \times 10^{-2} \times 298} = 0.303 \, mol$$

$$n_{Xe} = \frac{PV}{RT} = \frac{1 \times 1}{8.314 \times 10^{-2} \times 298} = 0.0403 \, mol$$

$$n = n_{He} + n_{Ne} + n_{Xe} = 0.464 \, mol$$

The mole fractions are

$$x_{He} = \frac{n_{He}}{n} = \frac{0.121}{0.464} = 0.261$$

$$x_{Ne} = \frac{n_{Ne}}{n} = \frac{0.303}{0.464} = 0.653$$

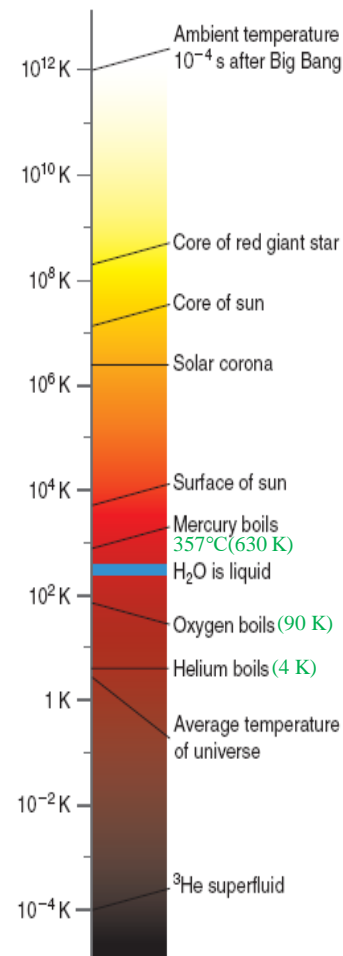$$x_{Xe} = \frac{n_{Xe}}{n} = \frac{0.0403}{0.464} = 0.0860$$

Ambient temperature
$10^{-4}$ s after Big Bang

$10^{12}$ K

$10^{10}$ K

Core of red giant star

$10^8$ K

Core of sun

Solar corona

$10^6$ K

Surface of sun

$10^4$ K

Mercury boils
357°C (630 K)

H$_2$O is liquid

$10^2$ K

Oxygen boils (90 K)

Helium boils (4 K)

1 K

Average temperature
of universe

$10^{-2}$ K

$^3$He superfluid

$10^{-4}$ K

*Fig*.1.4  log *T*.

# Solution

The total pressure is given by

$$P = \frac{\left(n_{He} + n_{Ne} + n_{Xe}\right)RT}{V} = \frac{0.464 \times 8.3145 \times 10^{-2} \times 298}{6} = 1.92 \, bar$$

The partial pressures are given by

$$P_{He} = x_{He}P = 0.261 \times 1.92 = 0.501 \, bar$$

$$P_{Ne} = x_{Ne}P = 0.653 \times 1.92 = 1.25 \, bar$$

$$P_{Xe} = x_{Xe}P = 0.0860 \times 1.92 = 0.165 \, bar$$

※ Summary : Dalton's law of partial pressure

$$P = \sum P_i \leftarrow 1st \, law \; ; P_i = x_iP \leftarrow 2nd \, law$$

# 1.5 A Brief Introduction to Real Gases

- Two <u>problem**a**tic</u> ass**u**mptions for id gas: ☞ Ch.16

a) Atoms or molecules of an id gas do not interact with one another (no IMF),

b) Atoms or molecules can be treated as point masses.

- **van der Waals** eos (in more detail in Ch.7)

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \qquad (1.22)$$

※ $a$, $b$ in Table 7.4, App.B, p.565.

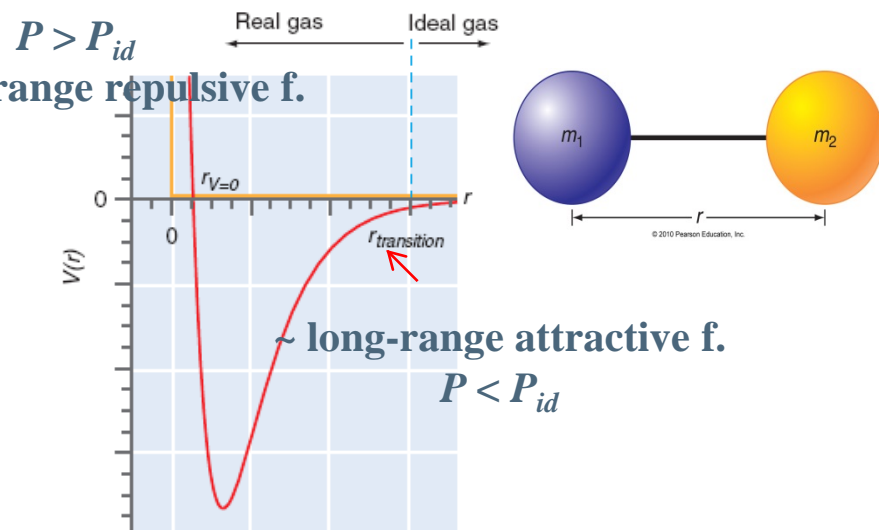♥ $a$, $b$, and $r_{transition}$ are all material-dependent!!

$P > P_{id}$
~ **short-range repulsive f.**

Real gas    Ideal gas

$r_{V=0}$

$r_{transition}$

$V(r)$

~ **long-range attractive f.**
$P < P_{id}$

$m_1$    $m_2$

$r$

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Fig.1.10 Potential energy btn two molecules as a function of their separation.

# Example Problem 1.3

Van der Waals parameters are generally tabulated with either of two sets of units:

a : *Pa m$^6$ mol$^{-2}$* or *bar dm$^6$ mol$^{-2}$*

b : *m$^3$ mol$^{-1}$* or *dm$^3$ mol$^{-1}$*

Determine the conversion factor to convert one system of units to the other. Note that 1 *dm³* = (0.1*m*)³ = (10 *cm*)³ = 10³ *cm³* = 1 *L.*

-----------------------------------------------------------------

## Solution

Thus we have

$$Pa\, m^6\, mol^{-2} \times \frac{bar}{10^5\, Pa} \times \left(\frac{10^3\, dm^3}{m^3}\right)^2 = 10\, bar\, dm^6\, mol^{-2}$$

$$m^3\, mol^{-1} \times \frac{10^3\, dm^3}{m^3} = 10^3\, dm^3\, mol^{-1}$$

# Example Problem 1.4

a. Calculate the pressure exerted by $N_2$ at 300 $K$ for molar volumes of 250 and 0.100 $L$ using the ideal gas and the vdW eos. The values of parameters $a$ and $b$ for $N_2$ are 1.370 *bar dm$^6$ mol$^{-2}$* and 0.0387 *dm$^3$ mol$^{-1}$*, respectively.

b. Compare the results of your calculations at the two molar volumes. If P calculated using the vdW equation of state is greater than those calculated with the ideal gas law, we can conclude that the repulsive interaction of the $N_2$ molecules outweighs the attractive interaction for the calculated value of the density. A similar statement can be made regarding the attractive interaction. Is the attractive or repulsive interaction greater for $N_2$ at 300 $K$ and $V_m$= 0.100 $L$?

# Solution

a. The pressures calculated from the ideal gas eos are

$$P = \frac{RT}{V_m} = \frac{8.314 \times 10^{-2} \times 300}{250} = 9.98 \times 10^{-2} \, bar$$

$$P = \frac{RT}{V_m} = \frac{8.314 \times 10^{-2} \times 300}{0.100} = 249 \, bar$$

The pressures calculated from the vdW eos are

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$= \frac{1 \times 8.314 \times 10^{-2} \times 300}{250 - 1 \times 0.0387} - \frac{(1)^2 \times 1.370}{(250)^2} = 9.98 \times 10^{-2} \, bar$$

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$= \frac{1 \times 8.314 \times 10^{-2} \times 300}{0.1 - 1 \times 0.0387} - \frac{(1)^2 \times 1.370}{(0.1)^2} = 270 \, bar$$

# Solution

b. Note that the vdW result is identical with that for the ideal gas law for $V_m$=250 $L$, and that the result calculated for $V_m$=0.100 $L$ deviates from the ideal gas law result. Because $P^{real} > P^{ideal}$, we conclude that the repulsive interaction is more important than the attractive interaction for this specific value of molar volume and temperature.

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<PS #1>

1.1 Derive the ideal gas law using Boyle's law, Charles's law (or Gay-Lussac) and Avogadro's law.

1.2 Calculate the value of $R$ (gas constant) in two SI units.

♥ Carolus Linnaeus modified the Celsius temperature scale into the form that we use today in 1745. The scale had been invented by his compatriot, Anders Celsius, who had said 0°C was the boiling point of water and 100°C was water's freezing point. Linnaeus realized that it would be more useful if these values were reversed and persuaded the rest of the scientific world to follow his example. (종속과목강문계)
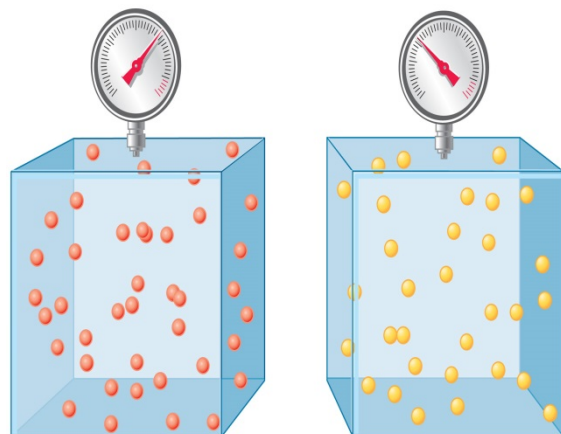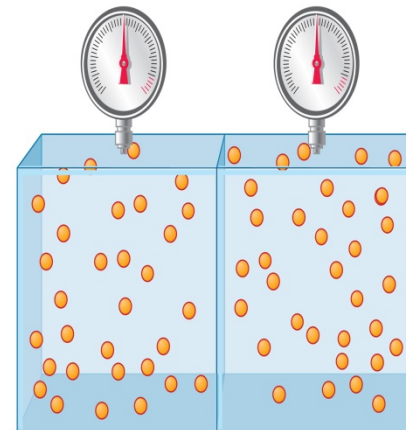
(a) Two w/ same molar density, $\rho_m$
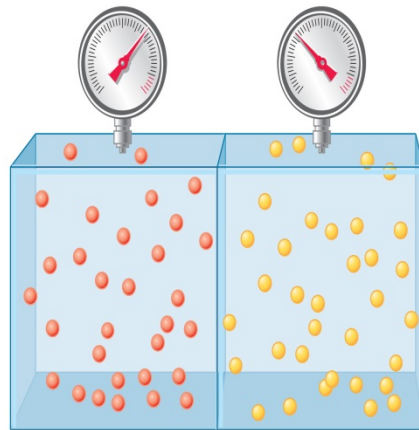
(b) Walls in contact: adiabatic
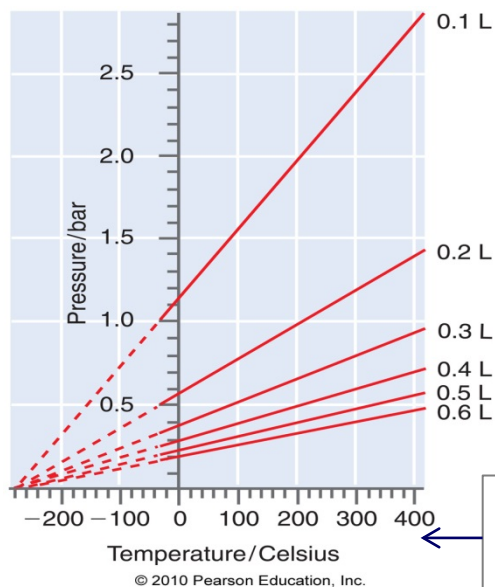
(c) Walls in contact: diathermal

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Fig.1.7. (a) Two separated systems w/ rigid and adiabatic walls. (b) Two systems w/ adiabatic walls in intimate contact. (b) Two systems w/ diathermal walls in intimate contact. Two pressures become equal.



Fig.1.5

*Gas-indep. T values are obtained only below P ~ 0.01 atm.*

$P=CRT \rightarrow T=P/(CR)$   (1.14)
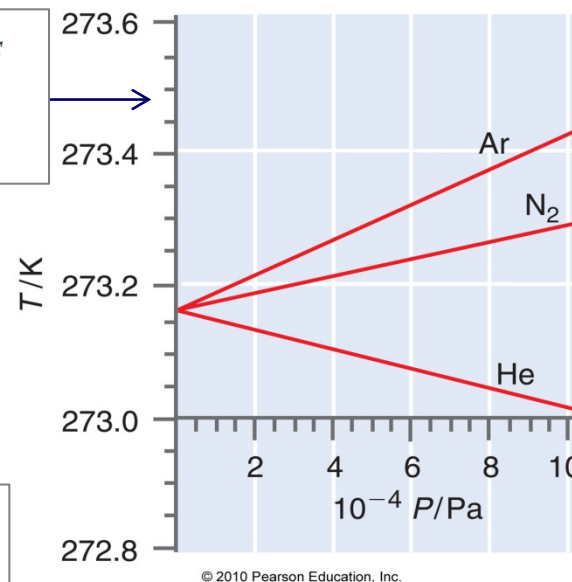$P\rightarrow 0$ as $T\rightarrow 0$  or  $P\rightarrow 0$ as $T\rightarrow 0$



Fig.1.9

Thank you