MSE-204 Thermodynamics for Materials Science

L4. THERMODYNAMICS OF GASES

IDEAL GAS | MIXTURES OF IDEAL GASES | REAL GASES | IDEAL MIXTURES OF REAL GASES

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REMINDER FROM LAST WEEK

$pV = nRT$

$\Rightarrow$ implies $\mu = \mu^*(T) + RT \ln \frac{p}{p^*} = \mu^* + RT \ln p$

ideal mixture of ideal gases

$\Delta_{mix} U = 0$ $\Delta_{mix} H = 0$

$\Delta_{mix} G = RT \sum_i n_i \ln x_i$

$\Delta S_{mix} = -R \sum_i n_i \ln x_i$

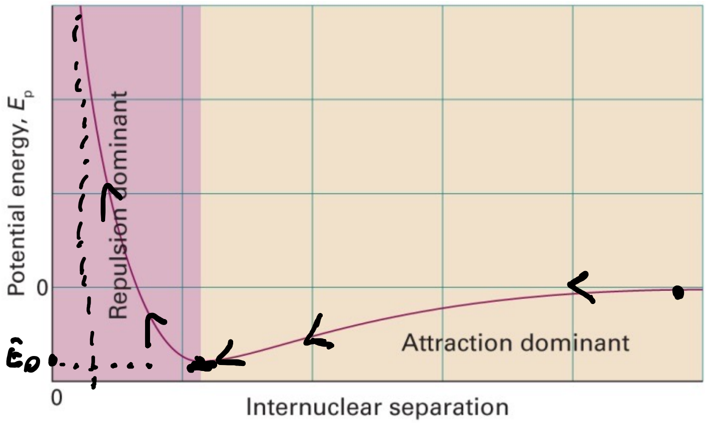
$\mu_i = \mu_i^*(T) + RT \ln p + \underline{RT \ln x_i}$

$= \mu_i^*(T) + RT \ln p_i$

REAL GASES

We can now start studying real gases. **The molecules of these gases have interactions with each other and occupy a finite volume.** Thus, they do not follow the equation of state of the simple form.

The simplest type of interaction that we can think of is a Lennard-Jones interaction (6-12 potential):



$$V(r) = -\frac{C_1}{r^6} + \frac{C_2}{r^{12}}$$

$$E_0 < k_B T$$

EQUATIONS OF STATE FOR REAL GASES

$$pV = nRT$$

$$p\frac{V}{n} = RT \rightarrow pv = RT \quad p = \frac{RT}{v}$$

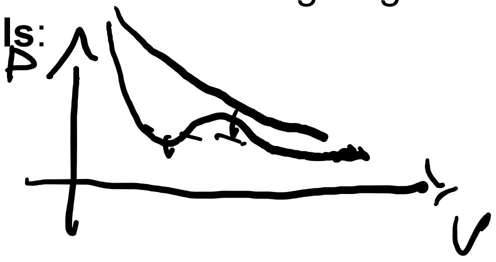
Up to an atmosphere of pressure or more the behavior of most gases can be represented with fairly good accuracy by introducing into the equation of state an adjustable parameter B :

$$\rightarrow \quad p(v - B) = RT \quad \leftarrow \quad \| \qquad \frac{1}{v} = \rho = \frac{n}{V}$$

The quantity B has the dimensions of a volume, is usually negative at low temperatures but changes sign at high temperatures. Thus it cannot be interpreted as being proportional to the volume occupied by the molecules.

Larger deviations from the gas law can be represented by means of an equation containing a greater number of adjustable constants. A typical "two-parameter" equation is that of **van der Waals**:

$$\rightarrow \left(p + \frac{a}{v^2}\right)(v - b) = RT$$



Where the term $\frac{a}{v^2}$ is regarded as an "internal pressure" arising from the attractive forces between the molecules.

Large deviations from the ideal gas law can also be represented by means of the power series:

$$p = \frac{RT}{v}\left(1 + B/v + C/v^2 + \cdots\right) = RT\rho\left(1 + B\rho + C\rho^2 + \cdots\right) = RT\rho + BRT\rho^2 + CRT\rho^3$$

Where B and C are called the second and third viral coefficients respectively and are in general functions of temperature. Alternatively, the volume may be expressed as a power series in the pressure.

THE FUGACITY OF A REAL GAS

We saw that the ideal gas, by definition, is one whose chemical potential, at constant temperature, is a linear function of the logarithm of its pressure.

In the case of gases which are not ideal, it is convenient to define a kind of pressure, called the fugacity, to which the chemical potential of the gas bears the same linear relationship.

Let μ be the chemical potential of the pure gas at temperature T and pressure p. The fugacity f of the gas is defined by the following relations in which **μ^0 is a function of T only**:

$\mu = \mu^* + RT \ln f$ ideal case $\mu = \mu^* + RT \ln p$

$$\mu = \mu^0 + RT\ln f \quad \text{when} \quad \frac{f}{p} \to 1 \quad \text{as} \quad p \to 0$$

This limiting relation makes the fugacity equal to the pressure under conditions where the gas obeys the ideal gas law.

IDEAL MIXTURES OF REAL GASES

The mixture of ideal gases has been defined as:

$\mu_i = \mu_i^*(T) + RT \ln f + RT \ln x_i$

$\mu_i^0(T,p)$

$$\boxed{\mu_i = \mu_i^0(T) + RT \ln p + RT \ln x_i}$$

where μ_i^0 is a function of temperature only. The chemical potential is thus a linear function of the logarithm of the total pressure, and this is why the mixture obeys the ideal gas law.

IDEAL GAS / IDEAL MIXTURE

$\mu_i = \mu_i^*(T) + RT \ln p + RT \ln x_i$

A much less restrictive model of a gas mixture is one that obeys the equation:

$$\boxed{\mu_i = \mu_i^*(T, p) + RT \ln x_i}$$

$\mu_i = \mu_i^\ominus(T,p) + RT \ln x_i$

REAL GASES / IDEAL MIXTURE

$\mu_i = \mu_i^0(T,p) + RT \ln x_i$

where $\boldsymbol{\mu_i^*}$ **is both a function of temperature and pressure**. In this case, only the dependence on composition is made explicit – **the chemical potential of $\boldsymbol{i}$ depends only on its own mole fraction $\boldsymbol{x_i}$ and not on the mole fractions of any other component, at constant total pressure and temperature. This relationship defines the ideal mixture of real gases**.

THERMODYNAMIC FUNCTIONS OF IDEAL MIXTURES OF REAL GASES

Such mixtures also have **the property of having a zero volume change of mixing, zero internal energy of mixing, and a zero enthalpy of mixing at constant temperature and pressure.**

By differentiation:

after before

before ✓ mixing

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = \left(\frac{\partial \mu_i^*}{\partial p}\right)_T$$

$$\frac{\partial\left(\overbrace{\mu_i^* + RT\ln f}\right)}{\partial p} = \frac{\partial \mu^\circ}{\partial p}$$

$$\frac{\partial\left(\mu_i^\circ + \overset{0}{\boxed{RT\ln x_i}}\right)}{\partial p} = \frac{\partial \mu_i^\circ}{\partial p}$$

$$\bar{V}_i = V_i$$

$$\Delta_{mix} V = 0$$

$$\Delta_{mix} U = 0 \qquad \Delta_{mix} H = 0$$

$$\left.\begin{aligned} \Delta_{mix} G &= RT\sum_i n_i \ln x_i \\ \Delta_{mix} S &= -R\sum_i n_i \ln x_i \end{aligned}\right]$$

THE FUGACITIES OF THE IDEAL MIXTURES OF REAL GASES

The definition of the ideal mixture of real gases has an important consequence to the fugacities in the mixture. It can be shown that:

$$\mu_i = \mu_0(p,T) + RT\ln x_i \,.$$
$$= \mu^*(T) + RT\ln f \,.$$

$$\boxed{RT\ln\frac{f_i}{x_i} = \mu_i^* - \mu_i^0}$$

The right-hand side is independent of composition, and therefore the ratio $\frac{f_i}{x_i}$ must remain unchanged as x_i is brought up to unity:

$$\frac{f_i}{x_i} = f_i' \quad or \quad \boxed{f_i = x_i f_i'}$$

where f_i' is the fugacity of pure component i at the same temperature and total pressure as the mixture. This is known as the **Lewis and Randall's rule**, i.e. **the fugacity of each constituent is equal to its mole fraction multiplied by the fugacity which it would exhibit as a pure gas, at the same temperature and the same total pressure**.

Thus, the problem of knowing the fugacity of a component of a mixture is reduced to knowing the fugacity of the same gas in its pure state.

THE ACTIVITY AND ACTIVITY COEFFICIENT OF IDEAL MIXTURES

Experimental measurements of the thermodynamic behavior of solutions are not aimed at the determination of chemical potentials, although this quantity lies at the core of the description of such systems. Common practice measures another property, the activity of component i, which is defined in terms of the chemical potential by the equation:

$$\underline{\mu_i^* - \mu_i^0} = \Delta\mu_i = \boxed{RT \ln a_i}$$

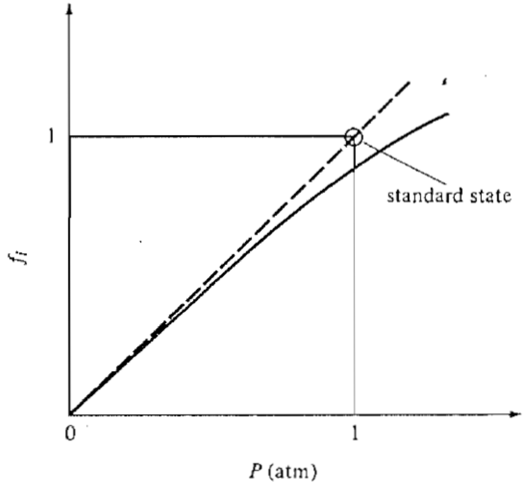
a_i is the activity of i in a solution **at a given temperature, pressure and composition**. **Activity is a unitless quantity**, as is the mole fraction of component i.

Another convenient measure of solution behavior, called the **activity coefficient of component i, γ_i**, is defined as:

$$a_i = \gamma_i x_i \qquad \& \qquad \mu_i^* - \mu_i^0 = \Delta\mu_i = RT \ln \gamma_i x_i$$

If $\gamma_i = 1$, the activity of component i is equal to its mole fraction and the behavior of i, in terms of its chemical potential is determined completely by its composition. If $\gamma_i > 1$, $a_i > \gamma_i$ and in the evaluation of chemical potential, component i acts as if the solution contains more i than the mole fraction suggests.

NOTE ON IDEALITY AND ITS DEVIATION [FUGACITY FUNCTION]



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NO CHEMICAL REACTION

L6. INTRODUCTION TO PHASES OF NON-REACTING SYSTEMS

DEFINITION OF PHASE | FUNDAMENTAL RELATIONS OF MULTIPHASE SYSTEMS | CONDITIONS OF EQUILIBRIUM | ROLE OF CHEMICAL POTENTIAL | PHASE RULE

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DEFINITION OF PHASE

In real systems, we often find different materials and within these materials we can find different parts of the same materials coexisting. For example, a glass of water with ice cubes. In materials, this kind of coexistence is quite common.

A phase is a part of a system that on a macroscopic scale can be considered as homogeneous.

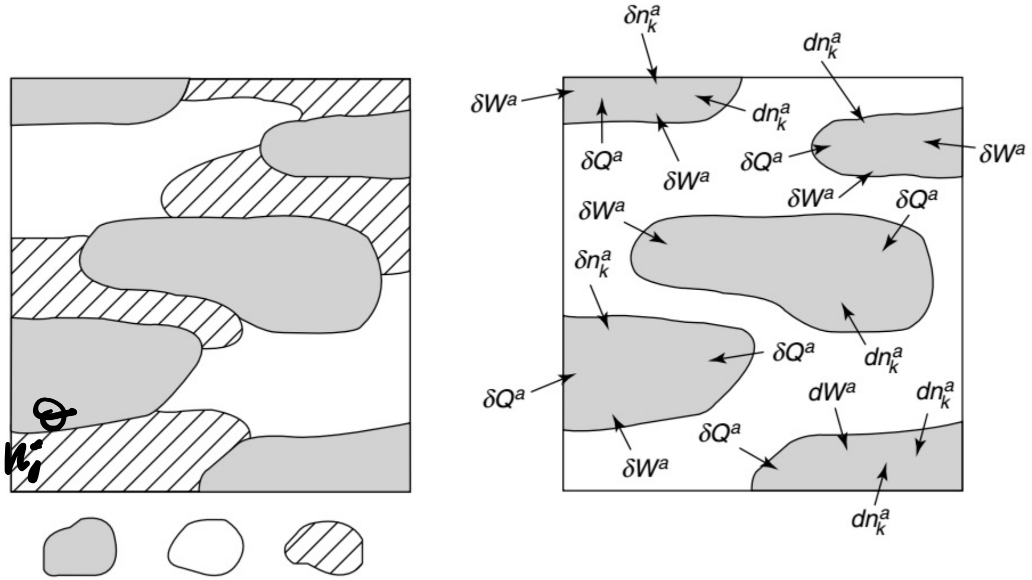
does not need to be continuous

but there need to be a way to define boundaries between phases

FUNDAMENTAL RELATIONS OF MULTIPHASE, CLOSED, NON-REACTING SYSTEMS

What we now need to study is what are the conditions of the multiple phases to coexist and to be at equilibrium.

Let us consider a heterogeneous closed system consisting of the homogeneous phases $\alpha, \beta, \ldots$. Each phase contains n_i^θ mole of component i.



multiple components $i = 1, 2, \ldots n$

multiple phases $\theta = \alpha, \beta, \gamma, \delta, \ldots \varphi$

$$dU^\theta = T^\theta dS^\theta - p^\theta dV^\theta + \sum_i \mu_i^\theta dn_i^\theta$$

For the whole system

$$U = \sum_\theta U^\theta \qquad S = \sum_\theta S^\theta \qquad V = \sum_\theta V^\theta \qquad n_i = \sum_\theta n_i^\theta \qquad dn_i = \sum_\theta dn_i^\theta = 0$$

At equilibrium $dU = \sum_\theta dU^\theta = 0$ $\quad dS = \sum_\theta dS^\theta = 0$ $\quad dV = \sum_\theta dV^\theta = 0$

TEMPERATURE CONDITIONS FOR EQUILIBRIUM

A possible process can be characterized by the following variations in entropy, volume and composition of the phases:

$$\underline{dV^\theta = 0} \quad \forall \theta \qquad \underline{dn_i^\theta = 0 \quad \forall \theta} \qquad dS^\theta = 0 \quad \forall \theta \text{ from } \gamma \text{ onward}$$

$$dS^\alpha \qquad dS^\beta \qquad dS = 0 \rightarrow \underbrace{dS^\alpha + dS^\beta = 0}_{\boxed{dS^\beta = -dS^\alpha}}$$

$$dU = 0 = dU^\alpha + dU^\beta = T^\alpha dS^\alpha - \cancel{P\, dV^\alpha} + \cancel{\sum_i \mu_i^\alpha dn_i^\alpha} + T^\beta dS^\beta \cancel{- P\, dV^\beta} + \cancel{\sum_i \mu_i^\beta dn_i^\beta}$$

$$= T^\alpha dS^\alpha + T^\beta dS^\beta = (T^\alpha - T^\beta)\, dS^\alpha = 0$$

$$T^\alpha = T^\beta = T^\gamma = T^\delta = \dots = T$$

Thermal Equilibrium

PRESSURE CONDITIONS FOR EQUILIBRIUM

$$dS^\theta = 0 \quad \forall\theta \qquad dn_i^\theta = 0 \quad \forall\theta \qquad \underline{dV^\theta = 0} \quad \forall\theta \text{ from } t \text{ onward}$$

$$dV^\alpha \quad dV^\beta \qquad dV = 0 \qquad \left[\underline{dV^\alpha = -dV^\beta}\right]$$

$$dU = -p^\alpha dV^\alpha - p^\beta dV^\beta = 0$$

$$(p^\beta - p^\alpha)\, dV^\alpha = 0$$

$$p^\alpha = p^\beta = p^\gamma = p^\delta = \dots = P$$

Mechanical equilibrium

CONDITIONS ON THE CHEMICAL POTENTIALS FOR EQUILIBRIUM

$$dS^\theta = 0 \quad \forall\theta \qquad dV^\theta = 0 \quad \forall\theta \qquad dn_i^\theta = 0 \ \forall\theta$$ from r onward

$$dn_i^\alpha \qquad dn_i^\beta \qquad dn_i = 0$$

$$\underline{dn_i^\beta = -dn_i^\alpha}$$

$$dU = \mu_i^\alpha \, dn_i^\alpha + \mu_i^\beta \, dn_i^\beta = 0$$

$$(\mu_i^\alpha - \mu_i^\beta) \, dn_i^\alpha = 0$$

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \mu_i^\theta = \dots = \mu_i \quad \forall i$$

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots \quad \forall i \ \forall\theta$$

SPONTANEOUS TRANSFER OF A SPECIE FROM ONE PHASE TO ANOTHER

We will now consider a system that can only exchange volume work with its environment. It comprises of two phases and the various species can freely exchange from one phase to another. They do so at constant pressure and temperature.

$$dG^{\vartheta} = -S^{\vartheta} dT + \cancel{p}V^{\vartheta} dp + \sum_i \mu_i^{\vartheta} dn_i^{\vartheta} \qquad dG < 0$$

α, β

$$dG^{\alpha\to\beta} = dG^{\beta} + dG^{\alpha} =$$

$$= -S^{\alpha}\cancel{dT} + V^{\alpha}\cancel{dp} + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \left[-S^{\beta}\cancel{dT} + V^{\beta}\cancel{dp} + \sum_i \mu_i^{\beta} dn_i^{\beta}\right] =$$

$dT = 0$ $\quad dp = 0$ $\quad dn_i$ for $i = 2, \dots$

dn_1

$$= \mu_1^{\alpha} dn_i^{\alpha} - \mu_i^{\beta} dn_i^{\beta} =$$

$$= \underbrace{(\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\beta}} \Rightarrow 0$$

GIBBS PHASE RULE (FOR NON-REACTING SYSTEMS)

We need to establish a rule, which will allow us to determine the number of intensive variables that can be independently modified. This modification will induce a change in all the other intensive variables in such a way that a new state of equilibrium will be reached.

multicomponent $i = 1, 2, 3, \ldots n$

$T^\theta, p^\theta, \mu_i \ \forall i$ n+2 variable

$\theta = \alpha, \beta, \gamma \ldots q$

variable

$q(n+2)$

multi phase

conditions

$q(n+2)$

1) $\forall\theta \quad \sum x_i^\theta = 1$ $\quad -q$

2) thermal equilibrium $T = T^\alpha = T^\beta = T^\gamma = \ldots$ $\quad -(q-1)$

3) mechanical equilibrium $p = p^\alpha = p^\beta = p^\gamma$ $\quad -(q-1)$

4) chemical equilibrium $\quad -n(q-1)$

$\cancel{q}n + 2\cancel{q} - \cancel{q} - \cancel{q} + 1 - q + 1 - \cancel{q}n + n =$

$$\boxed{n + 2 - q = F}$$

PHASE EQUILIBRIA OF A PURE SUBSTANCE

Let’s apply the Gibbs phase rule to single component coexistence of phases.

MSE-204 Thermodynamics for Materials Science

L7.1 SINGLE COMPONENT PHASE DIAGRAMS

ENTROPY ACCORDING TO BOLTZMANN | PHASE EQUILIBRIA BETWEEN GASES, LIQUIDS, AND SOLIDS

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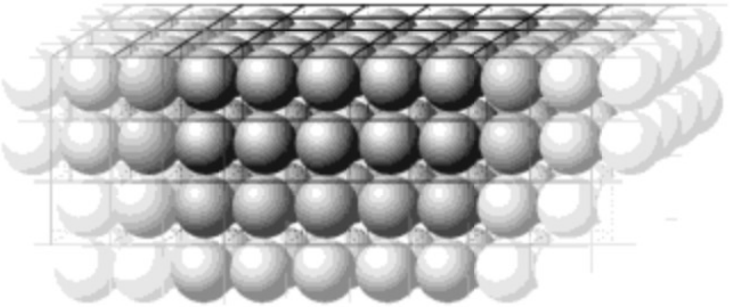
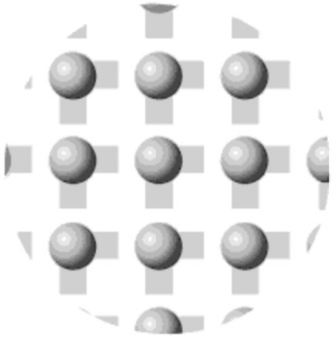
WHY DO LIQUIDS BOIL? | LET'S DEFINE THE SYSTEM

LATTICE MODEL FOR THE DESCRIPTION OF THE THERMODYNAMIC BEHAVIOR OF LIQUIDS/SOLIDS

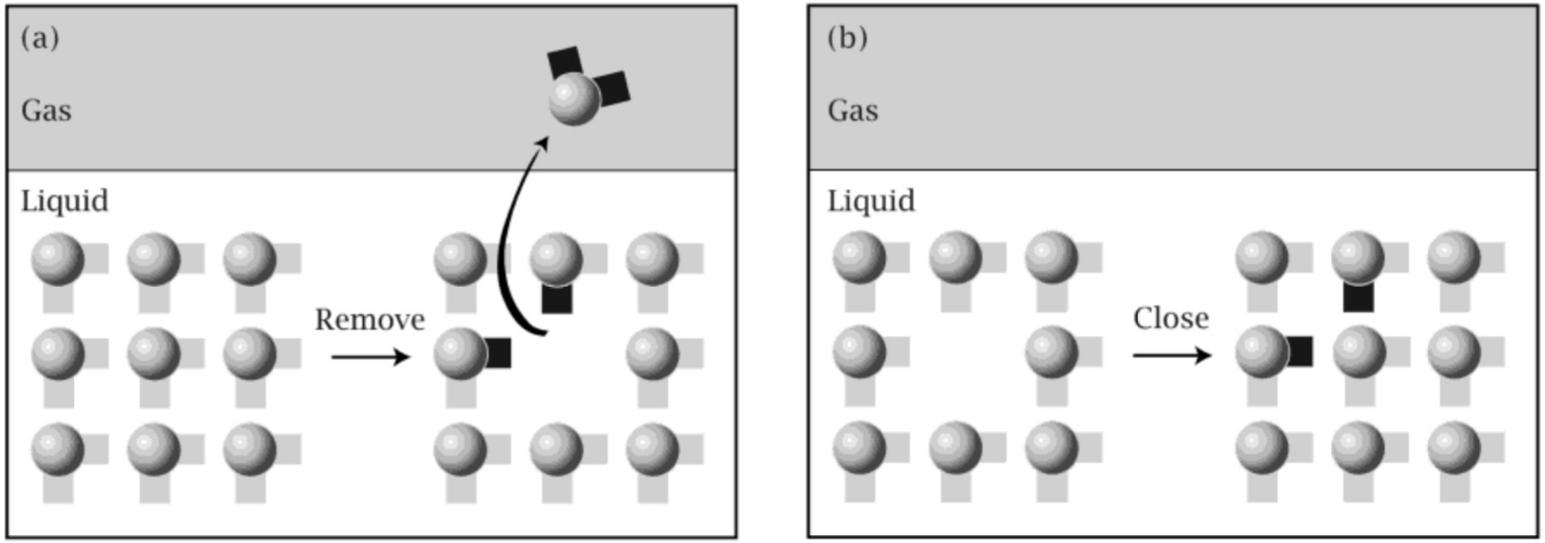
We model a liquid (or a solid) as if its particles occupied a crystalline lattice, with every site occupied by one particle. For practical reasons the lattice is considered to be infinite. The main insight represented by the lattice model is that the most important energetic interactions for holding liquids together are the short-range interactions of its particle with its nearest neighbors, and that the number of nearest neighbors has a relatively well-defined average.





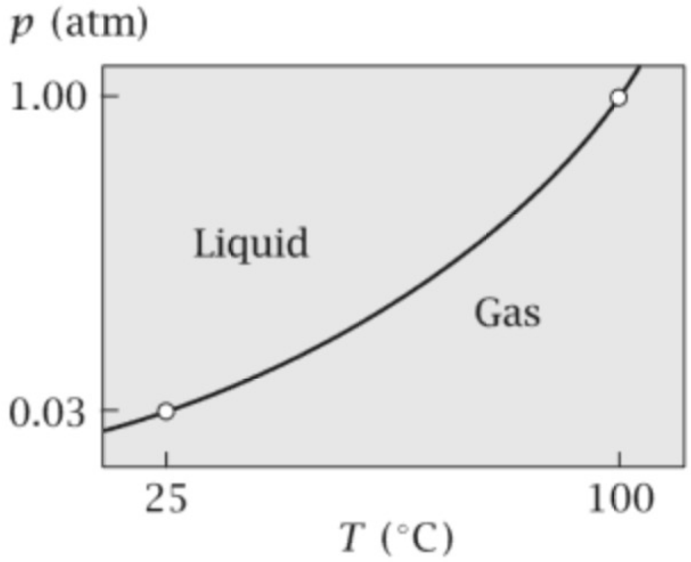
CAVITIES IN LIQUIDS AND SOLIDS

Does it matter whether an atom/molecule leaves from the surface or the bulk?

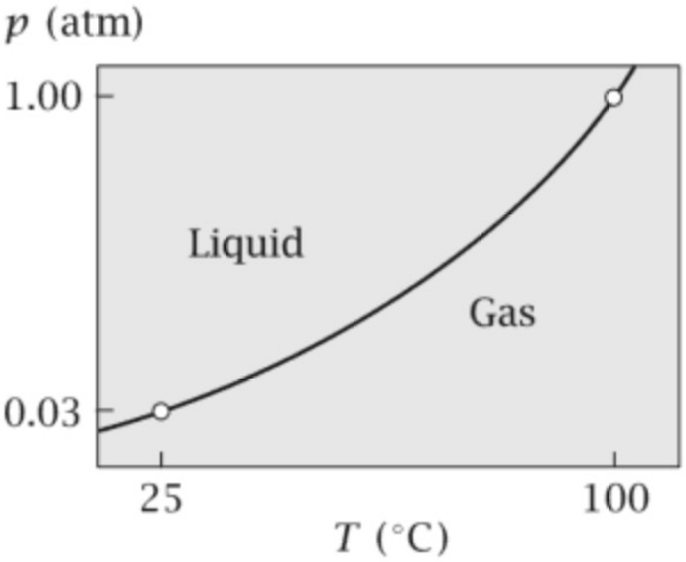


EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE

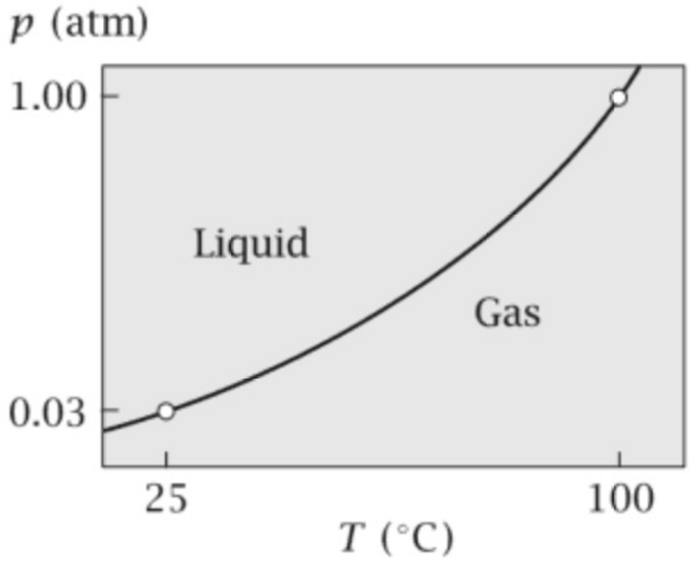
Each line on a phase diagram (also called a phase boundary) represents a set of (p,T) points at which two phases are equally stable. We can mathematically calculate these coexistence lines and then we can construct a phase diagram.



EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE: THE CLAPEYRON EQUATION | CONTINUED



EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE: THE CLAUSIUS CLAPEYRON EQUATION | CONTINUED



Example of Two Phase Equilibria

The Refrigerator

In a refrigerator, a “working fluid” is pumped around a system of tubes and undergoes repeated thermodynamic cycles of vaporization and condensation.

Their operation is based on two principles:

a. That boiling stores energy by breaking noncovalent bonds and condensation gets that energy back, and

b. That a fluid can be boiled at a low temperature and re-condensed at a high temperature by controlling the pressure