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etc.

Review of Previous

Non-ideal Solution: 非理想溶液
Activity coefficient: 活度系数
Gibbs-Duhem Relation：Gibbs-Duhem关系式
Dilute Solution：稀溶液
Colligative Properties：依数性
Osmotic Pressure：渗透压
Regular Solution：规则溶液

稀溶液及其依数性

- Dilute solution/稀溶液

溶剂符合Raoult定量，即理想溶液

溶质符合Henry定量，非理想，活度系数为常数

Raoult’s law and Henry’s law

Raoult’s law

1887年，经验定律，

$$P_A = P_A^* x_A \Rightarrow a_A = x_A$$

“溶液中溶剂的蒸气压P_A等于同一温度下纯溶剂的蒸气压P^*_A与溶液中溶剂的摩尔分数x_A的乘积”

Henry’s law

1803年，经验定律

$$x_B = k'_{x,B} P_B \Rightarrow P_B = k_{x,B} x_B \not\rightarrow \gamma_B = 1$$

$$k_{x,B} \,?\, P_B^*$$

“在一定温度下微溶气体在溶液中的平衡组成与该气体的平衡气相分压成正比”

Dilute Solution and Colligative Properties (2)

The vapor pressure of the solvent is reduced.

The *boiling point* of the solvent is elevated.

The *freezing point* of the solvent is lowered.

The solvent will display an *osmotic pressure*.

Colligative properties

依数性：？

Dilute Solution and Colligative Properties (3)

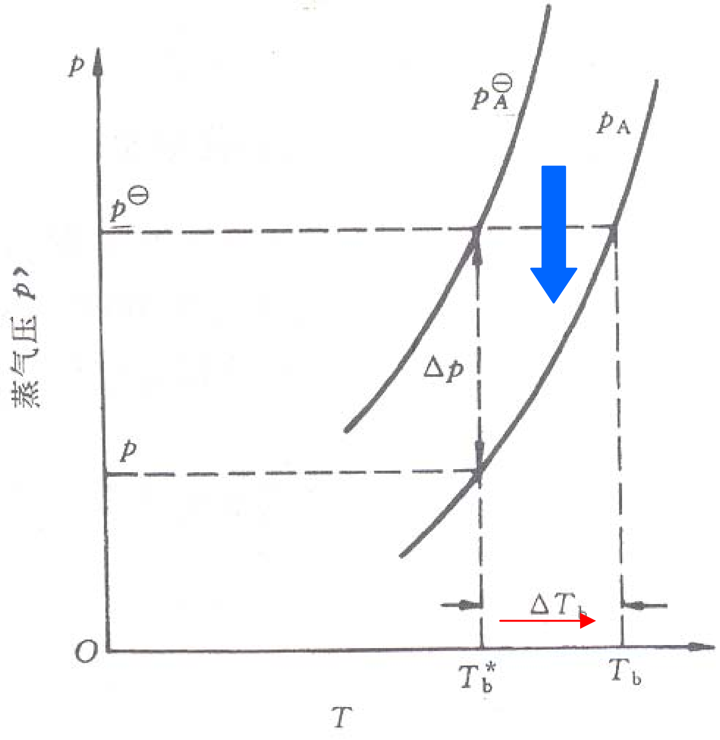


图 5－6　稀溶液中溶液的沸点升高

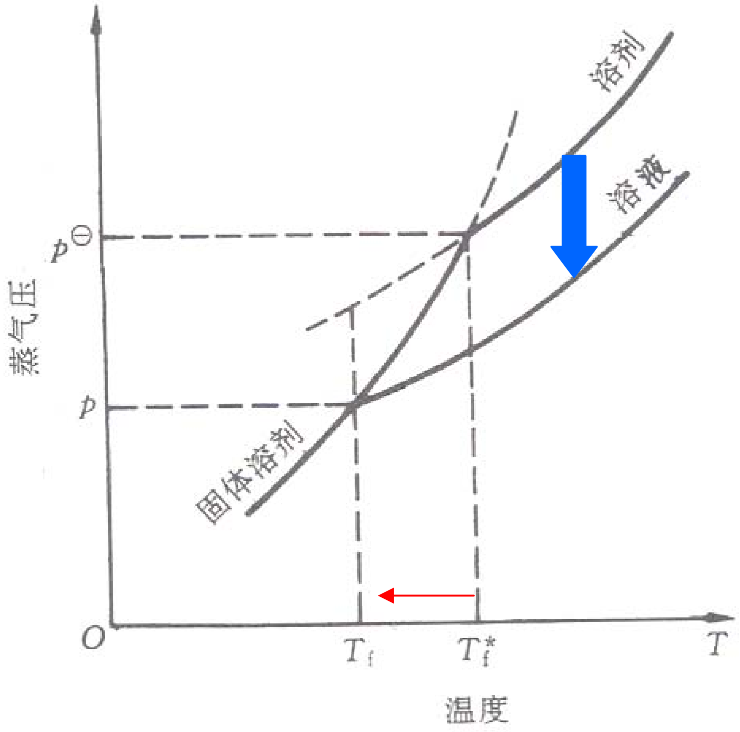


图 5－7　稀溶液的凝固点下降

Osmotic Pressure (1)

$$\mu_A - \mu_A^\circ = RT \ln x_A$$ Raoult's law

$$\mu_A - \mu_A^\circ = RT\,\underline{\ln(1 - x_B)} = -RTx_B$$

$$\mu_A - \mu_A^\circ = \int_{P+\Pi}^{P} \underline{V}_A\, dP = -\underline{V}_A \Pi$$

$$\boxed{\Pi = RT \frac{x_B}{\underline{V}_A}}$$

半透膜！

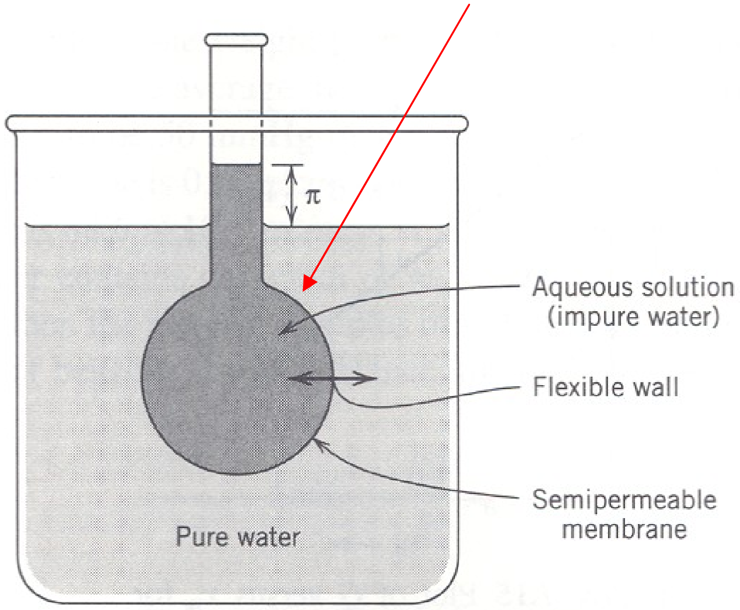


Figure 7.14 Osmotic pressure.

规则溶液

- 非理想溶液

$$\ln \gamma_A = \frac{\omega}{RT} x_B^2 = \frac{\omega}{RT}\left(1 - x_A\right)^2$$

$$\Updownarrow$$

$$\underline{G}^{xs}_M = \underline{H}^{xs}_M = \omega x_A x_B$$

$$\underline{S}^{xs}{}_M = 0$$

Regular Solution Atomistic Interpretation (3)

For the regular solution: $\underline{S}_M = 0$ $\quad \underline{G}^{xs}_M = \underline{H}^{xs}_M = \omega x_A x_B$

$$\overline{H}^{xs}_B = \underline{H}^{xs}_M + x_A\left(\frac{\partial \underline{H}^{xs}_M}{\partial x_B}\right)_T \qquad \overline{H}^{xs}_B = \omega x_A x_B + x_A\left(\frac{\partial\left(\omega x_A x_B\right)}{\partial x_B}\right)_T$$

$$\overline{H}^{xs}_B = \omega x_A x_B + x_A\omega\left(x_A - x_B\right)$$

$$\overline{H}^{xs}_B = \omega x_A^2 \qquad \overline{G}^{xs}_B = RT\ln\gamma_B$$

$$\ln\gamma_B = \frac{\omega}{RT}x_A^2$$

Justify the algebraic form c
in a regular solution.

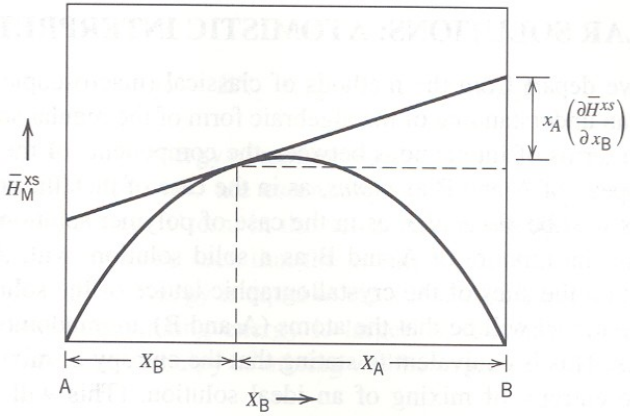


Figure 7.13 Plot of excess enthalpy of mixing versus composition for a nonideal solution.

Regular Solution: Atomistic Interpretation (1)

A,B二元完全无序分布
只考虑最近邻原子间的相互作用

N_A个A原子与N_B个B原子混合形成规则溶液

Random distribution
Z: coordination number
E_{AA}: bonding energy

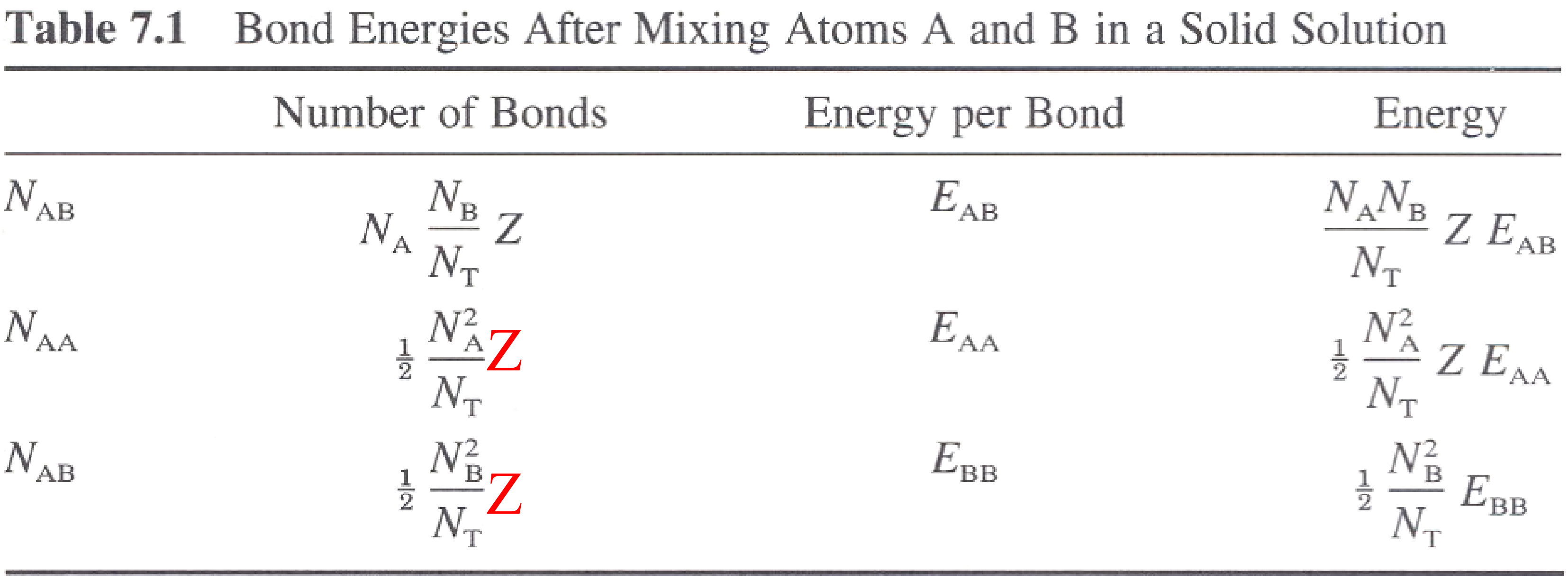


Table 7.1 Bond Energies After Mixing Atoms A and B in a Solid Solution

	Number of Bonds	Energy per Bond	Energy
N_{AB}	$N_A \frac{N_B}{N_T} Z$	E_{AB}	$\frac{N_A N_B}{N_T} Z E_{AB}$
N_{AA}	$\frac{1}{2} \frac{N_A^2}{N_T} Z$	E_{AA}	$\frac{1}{2} \frac{N_A^2}{N_T} Z E_{AA}$
N_{AB}	$\frac{1}{2} \frac{N_B^2}{N_T} Z$	E_{BB}	$\frac{1}{2} \frac{N_B^2}{N_T} E_{BB}$

Nomenclature

Phase: 相

Component: 组元

Degrees of freedom: 自由度

Phase rule: 相律

Phase diagram: 相图

One-component system：单元系

Phase

Phase: a homogeneous, physically distinct, and mechanically separable portion of matter present in a nonhomogeneous physical chemical system.

<*Webster's Dictionary*>

Phase (Britannica) 1

in thermodynamics, chemically and physically uniform or homogeneous quantity of matter that can be separated mechanically from a nonhomogeneous mixture and that may consist of a single substance or of a mixture of substances. The three fundamental phases of matter are solid, liquid, and gas (vapour), but others are considered to exist, including crystalline, glassy, amorphous, and plasma phases.

Phase (Britannica) 2

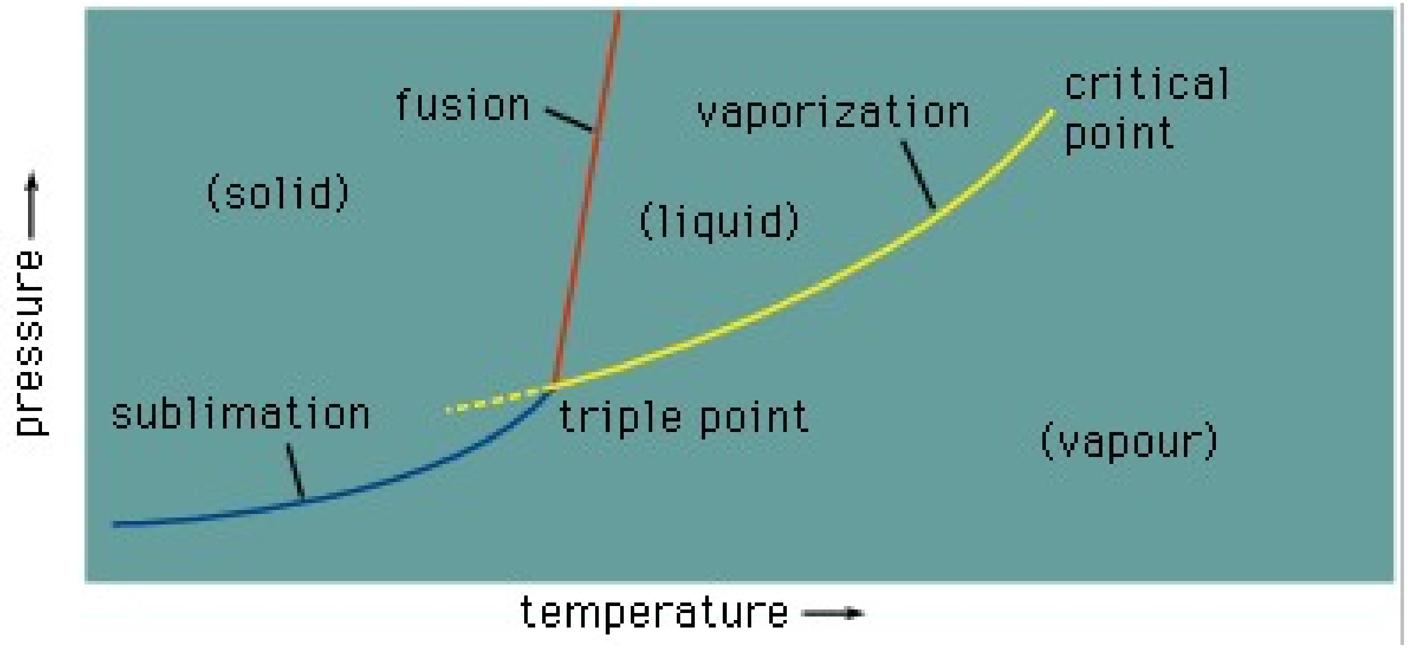
Matter is considered to form one homogeneous phase if its atomic or molecular dispersion is uniform; e.g., a glass of water containing dissolved salt, sugar, and a dye constitutes only a single liquid phase. If hundreds of grains of sand were added, all the grains together would constitute only a single additional (solid) phase.

The different phases of a pure substance bear a fixed relationship to one another in terms of temperature and pressure. Thus, if the pressure on some liquids is raised, they will freeze at a higher temperature. This relationship is extremely important in industrial as well as scientific work.

Phase diagram (Britannica) 1

graph showing the limiting conditions for solid, liquid, and gaseous phases of a single substance or of a mixture of substances while undergoing changes in pressure and temperature or in some other combination of variables, such as solubility and temperature.

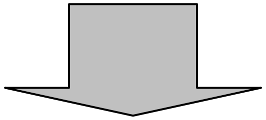
Phase diagram (Britannica) 2



The Figure shows a typical phase diagram for a one-component system (i.e., one consisting of a single pure substance), the curves having been obtained from measurements made at various pressures and temperatures.

Phase Rule

Thermodynamic stability of coexisting elements, compounds, and solution



Equilibrium structure
How many phases

所有多相平衡系统都遵循的普遍规律！

描述平衡系统中相数、组分数以及影响系统状态的独立可变因素（如温度、压力、组成等）的总数（称为自由度数）之间的关系。

8.1 Phase 1

何谓相：物理、化学性质相同的均匀部分

相与相之间有明确界面，越过界面，性质突变

- 气相，无论多少，1相
- 液相，纯、溶液（均匀），1相

  多种液体混合，溶解度，1，2，3，…
- 固相，纯或原子/分子状态相互混合成固溶体，1相

  一般体系中，多一种固体便多一个相

8.1 Phase 2

冰、水

冰、盐水溶液

冰、盐水溶液、盐粒

冰、盐水溶液、平衡气相

独立组元/组分数

- 物种 chemical species N

体系中每个可以单独分离出来并能独立存在的化学均匀物质

例子：食盐水 NaCl + H_2O

N=2

$$\boxed{C = N - R}$$

•独立组元，构成平衡体系所需的最少物种

R，物种之间存在的独立关系数

例子：N_2,H_2,NH_3

•彼此无关

•化学平衡

•化学平衡 ＋ N_2:H_2起始浓度比＝1：3

限制条件3仅限于同一相中的物质，且不包括一相中各组元的摩尔分数之和为1这一条件

$$\boxed{N_2 + 3H_2 = 2NH_3}$$

Degrees of Freedom

- 在一定范围内独立变动而不致破坏多相平衡的强度因素（温度、压力和组成等）的数目
- 不考虑相的数量，表面及表面能

液态水

水与水汽

水、水汽和冰

Why？

8.3 Specifying a System

Intensive properties

VAR: total number of variables to be specified

$$\boxed{VAR = P(C-1)+2}$$

Not take account of following situations:

- Amount of each phase
- Surfaces or surface energy

8.4 Equilibrium Conditions

Equilibrium conditions:

The chemical potential (partial molar Gibbs free energy) of a component must be the same throughout the system.

Intensive properties

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \mu_i^4 = \ldots = \mu_i^p$$

No significant potential and kinetic energy differences in the system

μ_i^p the chemical potential of component i in phase P

The total number of relationship

$$\boxed{REL = C(P-1)}$$

8.5 Gibbs Phase Rule

Degrees of freedom available in the system (F):

VAR: the number of variables required to specify the system
REL: the number of relationships required by the equilibrium condition

$$F = VAR - REL$$

$$F = P(C-1) + 2 - C(P-1)$$

$$\boxed{F = C - P + 2}$$

n

F: the number of system variables that we may freely vary, or arbitrarily fix
C: components
P: phase

8.7 Example 1

Decomposition of calcium carbonate into calcium oxide and carbon dioxide:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Three chemical species and one relationship among them
Components: 2=3-1
Three phases, P=3

$$\boxed{F = C - P + 2 = 2 - 3 + 2 = 1}$$

Temperature is fixed, then pressure is fixed.

!限制条件仅限于同一相中的物质

8.7 Example 2

Decomposition of calcium carbonate into calcium oxide and carbon dioxide
Nitrogen is added to the system:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Four chemical species and one relationship among them
Components: 3
Three phases, P=3

$$\boxed{F = C - P + 2 = 3 - 3 + 2 = 2}$$

<u>The temperature and the total pressure can each be varied independently.</u>

8.7 Example 3

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

Three chemical species and one relationship among them
Components: 2
Two phases, P=2

$$\boxed{F = C - P + 2 = 2 - 2 + 2 = 2}$$

<u>The temperature and the total pressure can each be varied independently.</u>

例子

? 求下列平衡系统的相数、组分数和自由度数

- 密闭容器中有Na_2SO_4饱和溶液（没有充满）和少许过量的Na_2SO_4晶体
- 上述系统中Na_2SO_4溶液没有饱和
- ZnS在纯氧中焙烧成ZnO，平衡系统中发生三个独立化学反应：

$$ZnS(s)+\frac{3}{2}O_2(g)=ZnO(s)+SO_2(g)$$

$$ZnS(s)+2O_2(g)=ZnSO_4(s)$$

$$SO_2(g)+\frac{1}{2}O_2(g)=SO_3(g)$$

例子2

? 求下列平衡系统的相数、组分数和自由度数

- NH_4Cl(s)部分分解为NH_3(g)及HCl(g)，达成平衡；
- $NaHCO_3$(s)部分分解为Na_2CO_3(s)、H_2O(g)及CO_2(g)，达成平衡；
- 在1atm压力下，$CHCl_3$溶于水与$CHCl_3$，两个溶液平衡；

解释：

- 纯物质在一定压力下，熔点为定值；
- 在一定压力的CO_2气体中加热$CaCO_3$固体，则$CaCO_3$固体可在一定温度范围内不分解。

8.6 One-component System

Degrees of freedom available in the system (F):

$$\boxed{F = C - P + 2}$$

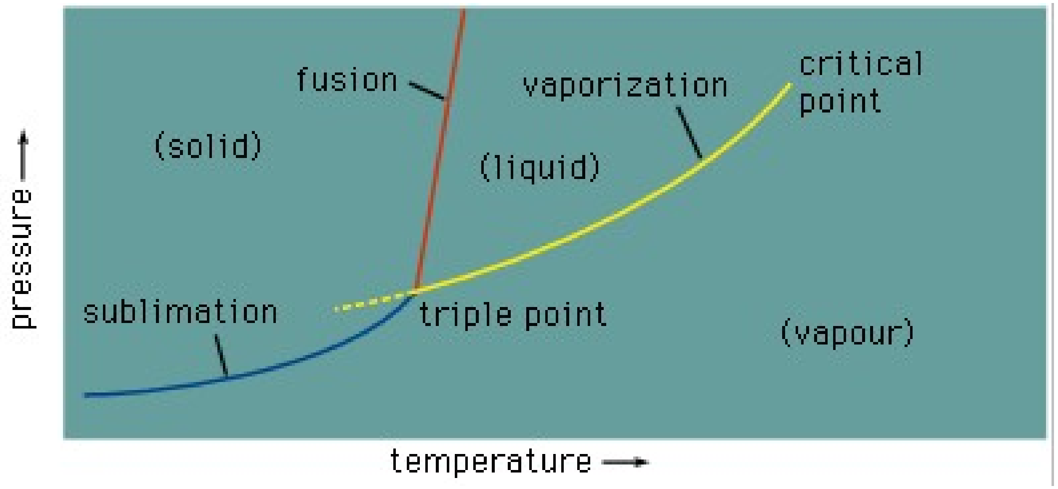
F: the number of system variables that we may freely vary, or arbitrarily fix
C: components
P: phase

$$\boxed{C = 1} \quad \boxed{\begin{array}{l} P = 1, F = 2 \\ P = 2, F = 1 \\ P = 3, F = 0 \end{array}}$$

Phase diagram

Minimum of P and F: 1,0

Maximum of F: 2



单元系的复相平衡

Clausius-Clapeyron方程

$$G_m^\alpha = G_m^\beta$$

$$G_m^\alpha + dG_m^\alpha = G_m^\beta + dG_m^\beta$$

$$\boxed{dG_m^\alpha = dG_m^\beta}$$

$$dG = -SdT + VdP$$

$$\Delta H = \Delta S T, \quad reversible$$

$$\frac{dP}{dT} = \frac{\Delta_\alpha^\beta \underline{H}}{T\Delta_\alpha^\beta \underline{V}}$$

气液或气固平衡

$$\Delta_\alpha^\beta \underline{V} = \underline{V}^g - \underline{V}^l \approx \underline{V}^g = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta_\alpha^\beta \underline{H}}{RT^2} P$$

P与T成指数关系

$$\boxed{P = A\exp\left(-\frac{\Delta_\alpha^\beta \underline{H}}{RT}\right)}$$

单元系的复相平衡2

Clausius-Clapeyron方程

$$\frac{dP}{dT}=\frac{\Delta_{\alpha}^{\beta}\underline{H}}{T\Delta_{\alpha}^{\beta}\underline{V}}$$

液固平衡

$$P_2-P_1=\frac{\Delta_{\alpha}^{\beta}\underline{H}}{\Delta_{\alpha}^{\beta}\underline{V}}\ln\frac{T_2}{T_1}$$

$$\ln(1+x)\approx x,\quad x<<1$$

$$\ln\frac{T_2}{T_1}=\ln(1+\frac{T_2-T_1}{T_1})\approx\frac{\Delta T}{T_1}$$

$$\boxed{\Delta P=\frac{\Delta H}{\Delta V}\frac{\Delta T}{T_1}=K\cdot\Delta T}$$

ΔP与ΔT成直线关系

单元系的复相平衡3

$$\boxed{\Delta P = \frac{\Delta_\alpha^\beta \underline{H}}{\Delta_\alpha^\beta \underline{V}} \frac{\Delta T}{T_1} = K \cdot \Delta T}$$

ΔP与ΔT成直线关系

$$l \rightarrow s \qquad \Delta H < 0$$

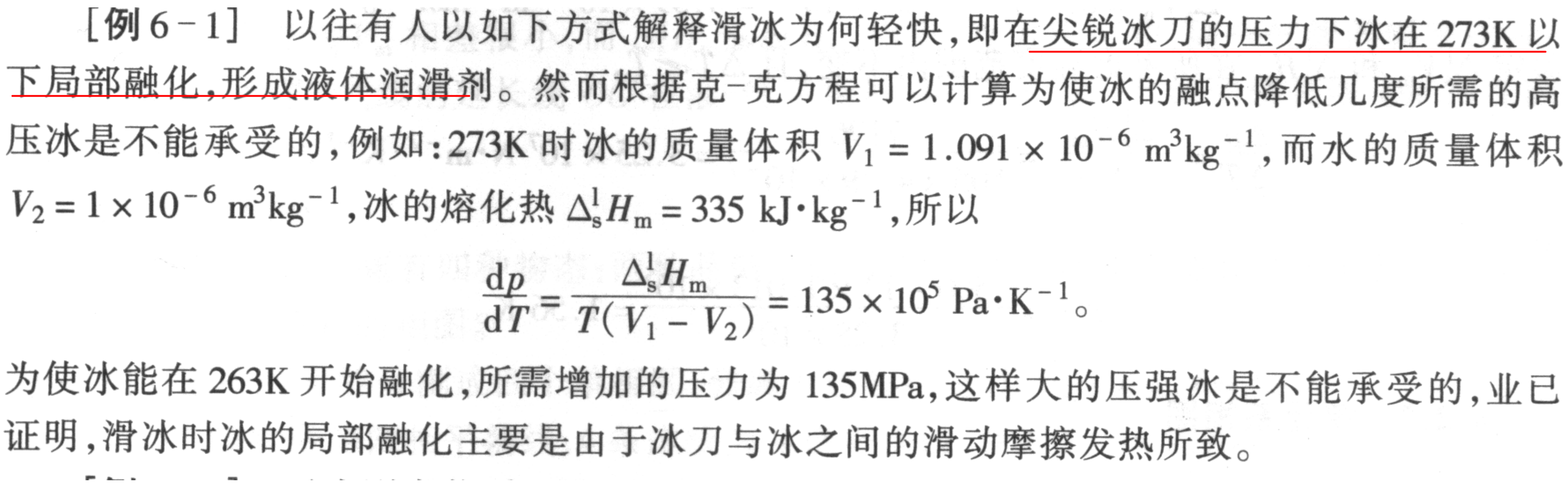
$\Delta V < 0 \quad K_f > 0$ 　ΔP与ΔT同号

$\Delta V > 0 \quad K_f < 0$ 　ΔP与ΔT异号

Water!

例子

- 滑冰为何轻快？



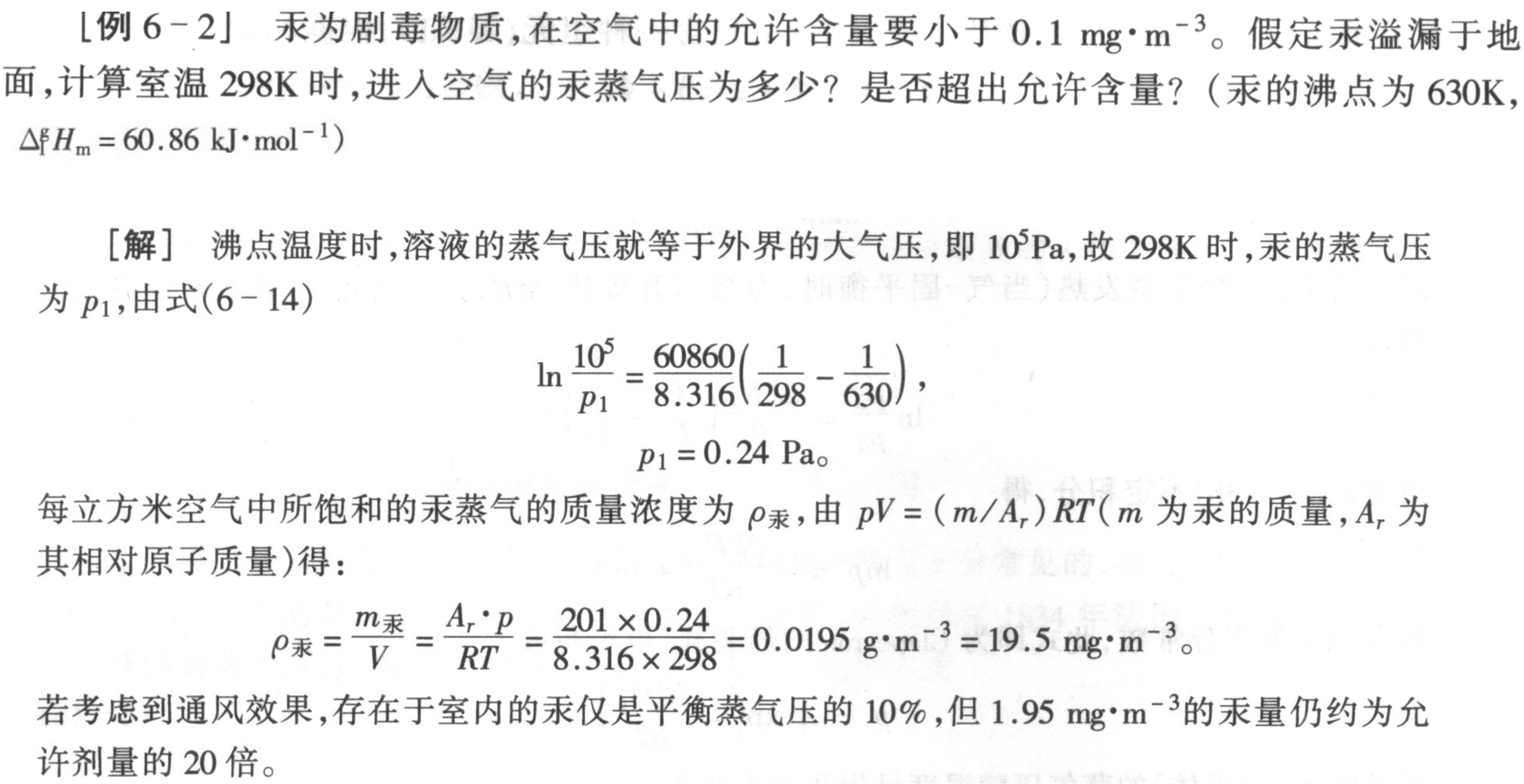
[例6－1] 以往有人以如下方式解释滑冰为何轻快，即在尖锐冰刀的压力下冰在273K以下局部融化，形成液体润滑剂。然而根据克–克方程可以计算为使冰的融点降低几度所需的高压冰是不能承受的，例如：273K时冰的质量体积 $V_1 = 1.091\times10^{-6}\ \mathrm{m^3kg^{-1}}$，而水的质量体积 $V_2 = 1\times10^{-6}\ \mathrm{m^3kg^{-1}}$，冰的熔化热 $\Delta_s^l H_m = 335\ \mathrm{kJ\cdot kg^{-1}}$，所以

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_s^l H_m}{T(V_1 - V_2)} = 135\times10^5\ \mathrm{Pa\cdot K^{-1}}。$$

为使冰能在263K开始融化，所需增加的压力为135MPa，这样大的压强冰是不能承受的，业已证明，滑冰时冰的局部融化主要是由于冰刀与冰之间的滑动摩擦发热所致。

例子

- 汞 室温时暴露在空气中的平衡含量？



［例 6－2］ 汞为剧毒物质，在空气中的允许含量要小于 0.1 $\mathrm{mg \cdot m^{-3}}$。假定汞溢漏于地面，计算室温 298K 时，进入空气的汞蒸气压为多少？是否超出允许含量？（汞的沸点为 630K，$\Delta_l^g H_m = 60.86\ \mathrm{kJ \cdot mol^{-1}}$）

［解］ 沸点温度时，溶液的蒸气压就等于外界的大气压，即 10^5Pa，故 298K 时，汞的蒸气压为 p_1，由式(6－14)

$$\ln\frac{10^5}{p_1} = \frac{60860}{8.316}\left(\frac{1}{298} - \frac{1}{630}\right),$$

$$p_1 = 0.24\ \mathrm{Pa}。$$

每立方米空气中所饱和的汞蒸气的质量浓度为 $\rho_{汞}$，由 $pV = (m/A_r)RT$（m 为汞的质量，A_r 为其相对原子质量）得：

$$\rho_{汞} = \frac{m_{汞}}{V} = \frac{A_r \cdot p}{RT} = \frac{201 \times 0.24}{8.316 \times 298} = 0.0195\ \mathrm{g \cdot m^{-3}} = 19.5\ \mathrm{mg \cdot m^{-3}}。$$

若考虑到通风效果，存在于室内的汞仅是平衡蒸气压的 10%，但 1.95 $\mathrm{mg \cdot m^{-3}}$的汞量仍约为允许剂量的 20 倍。

8.6 One-component System / H_2O

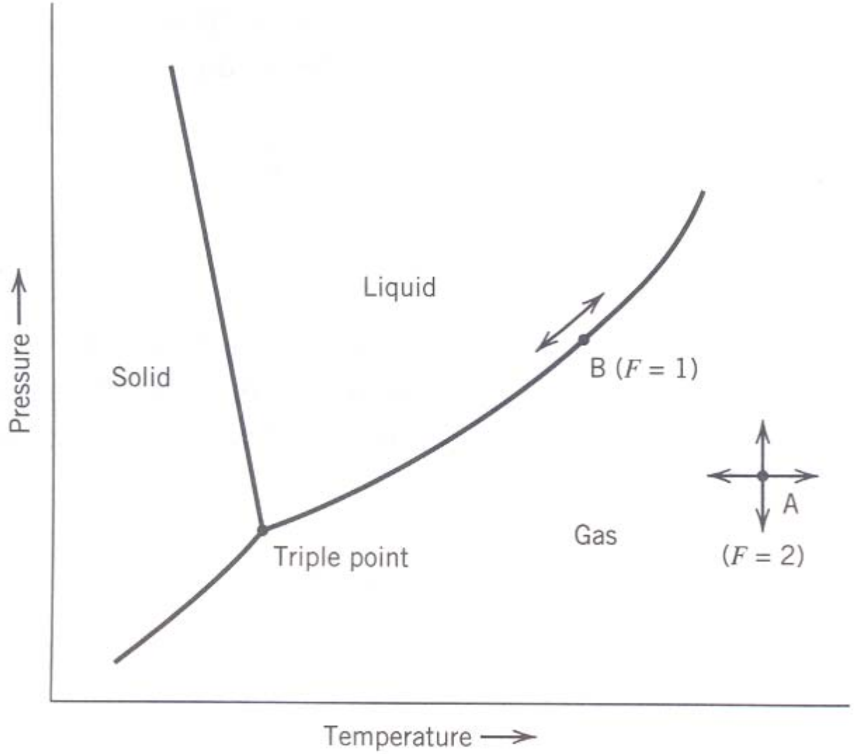


Figure 8.1 Phase diagram for water (one component). In the phase diagram for water, the solid–liquid equilibrium line slopes up and to the left from the triple point because the volume change upon solidification is positive. In most materials, the volume change upon solidification is negative, and the solid–liquid equilibrium line slopes up and to the right.

线

区域

点

三相点

两相共存点的终点

8.6 One-component System / S

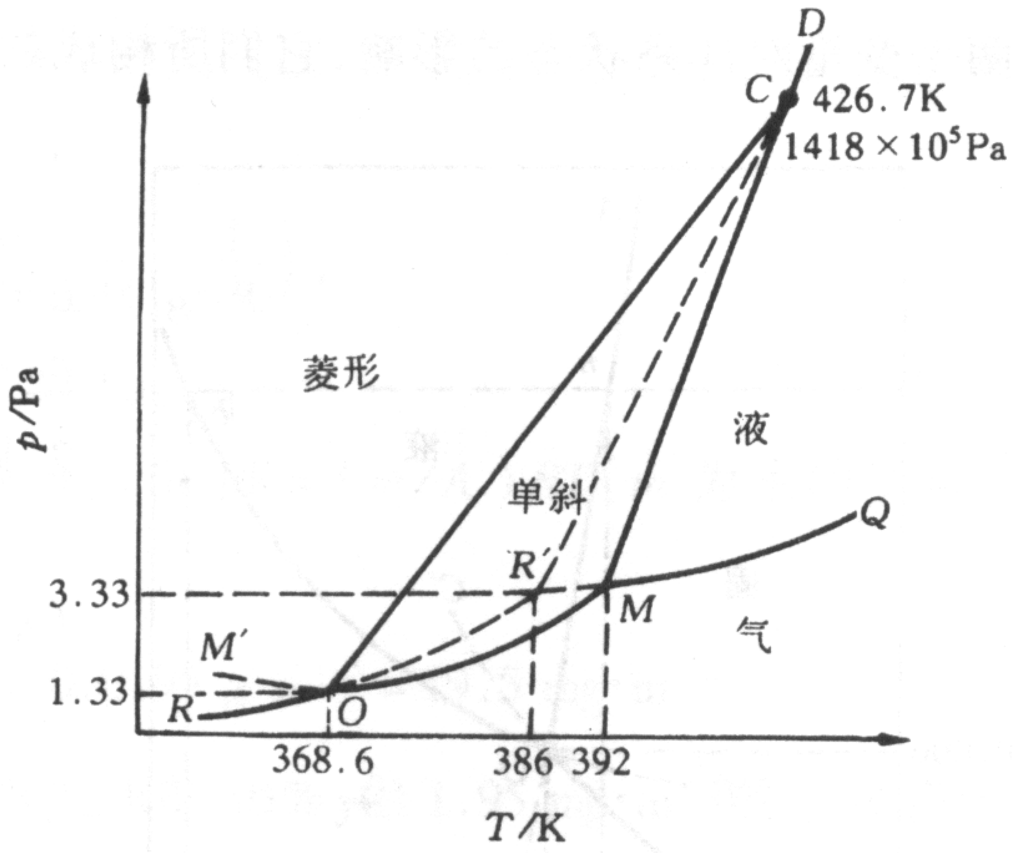


图 6-4　硫系相图

线

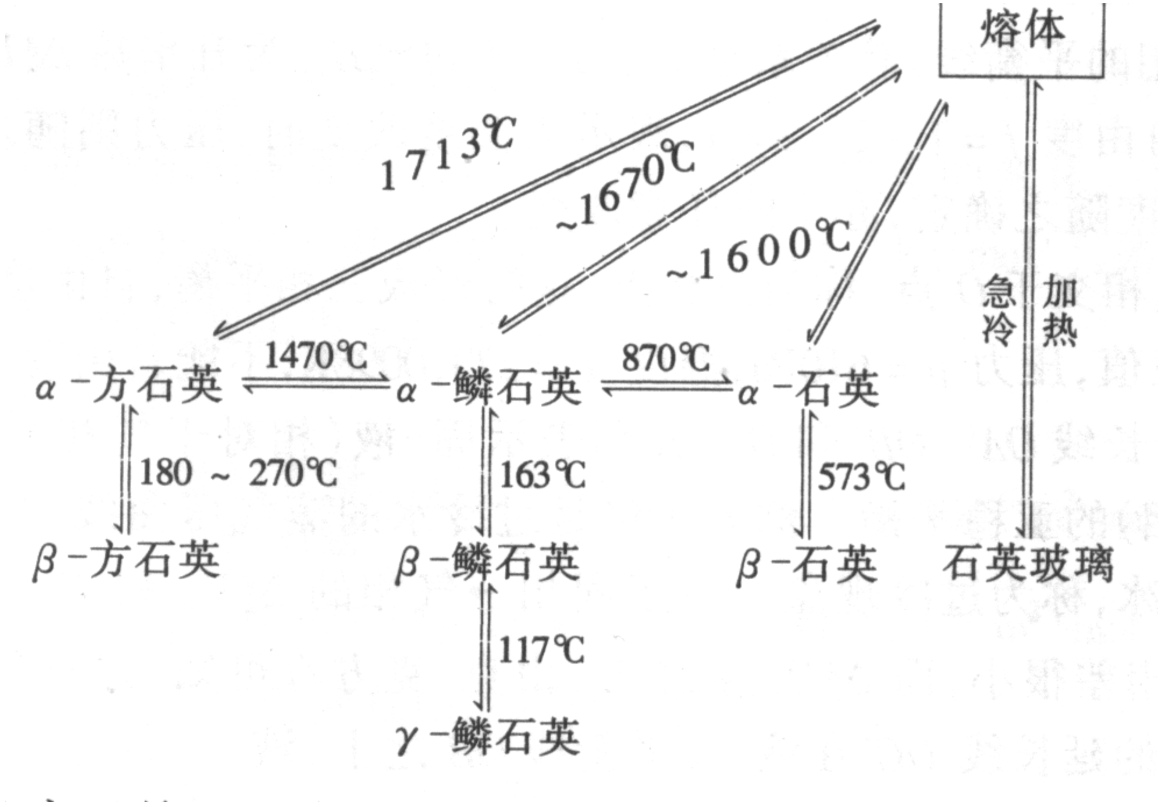
区域

点

三相点

两相共存点的终点b

8.6 One-component System / SiO_2



8.6 One-component System / SiO_2

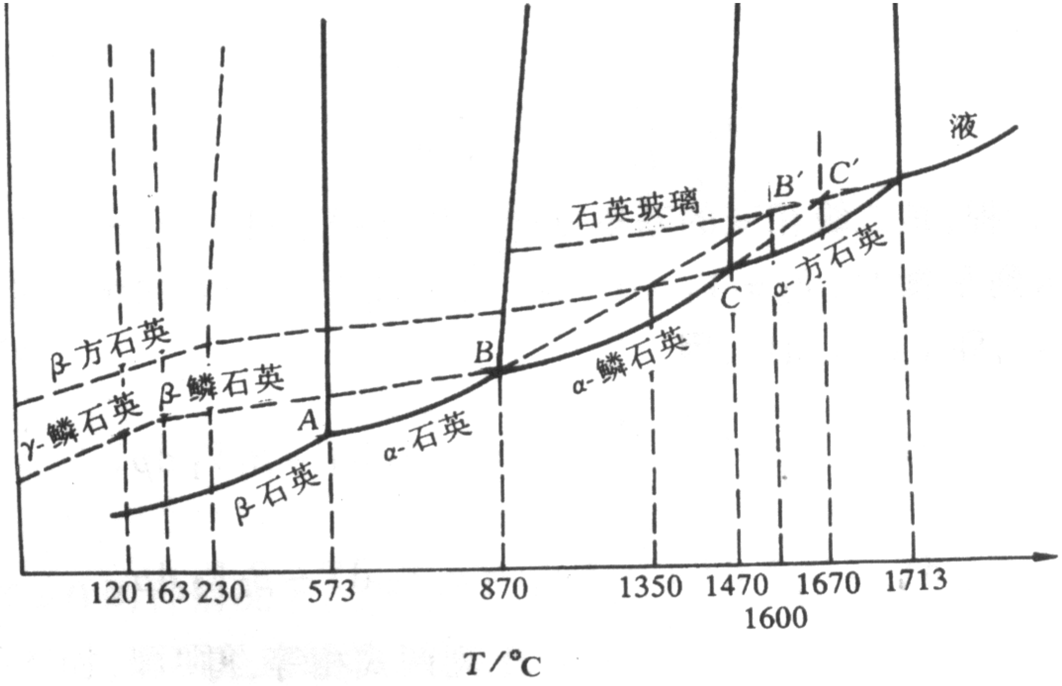


图 6-5 SiO_2 系相图

线

区域

点

三相点

两相共存点的终点

Review of Today

- Phase rule
- One-component systems

吉布斯相律

- 吉布斯相律是处于热力学平衡状态的系统中自由度与组元和相数之间关系的规律。
- 基本概念包括相、组元和自由度等。
  - 相为系统中性质与成分均匀的一部分；相平衡指的是在多相体系中所有相的强度性质均相等，体系的性质不会自发地随时间变化的状态即相平衡状态；
  - 组元为决定各平衡相的成分，而且是可以独立变化的组分（元素或化合物）；
  - 自由度是可以在一定范围内任意改变而不引起任何相的产生与消失的最大变量数。

$$\boxed{F = C - P + 2}$$

局限性

- 但相律只是对可能存在的平衡状态的一个定性描述。它可以给出一个相图中可能有些什么点、线和区，却不能给出这些点、线和区的具体位置。

单组分系统

- 相律分析

$$F = C - P + 2$$

$$\boxed{C = 1}$$

$$P \geq 1; F \geq 0$$

$$\boxed{\begin{array}{l} P = 1, F = 2 \\ P = 2, F = 1 \\ P = 3, F = 0 \end{array}}$$

- 物态转变方程式

$$\frac{dP}{dT} = \frac{\Delta_\alpha^\beta \underline{H}}{T \Delta_\alpha^\beta \underline{V}}$$

$$\boxed{P = A\exp\left(-\frac{\Delta_\alpha^\beta \underline{\underline{H}}}{RT}\right)}$$

$$\boxed{\Delta P = \frac{\Delta_\alpha^\beta \underline{\underline{H}}}{\Delta_\alpha^\beta \underline{V}} \frac{\Delta T}{T_1} = K \cdot \Delta T}$$

Homework

- Exercises in Chap 6

  P 205, 8.1