

# 绪言

## 一.热学研究对象和内容

- ▲ 对象： 宏观物体（大量分子原子系统）或物体系  
—热力学系统



- 系统与外界关系  
开放、封闭、  
绝热、孤立
- 均匀性  
单相、复相
- 组成成分  
单元、多元

- ▲ 内容： 与热现象有关的性质和规律。

## 二. 热学的研究方法

### ▲ 热力学 (thermodynamics)

宏观基本实验规律  $\xrightarrow{\text{逻辑推理}}$  热现象规律

特点：普遍性、可靠性。

### ▲ 统计力学 (statistical mechanics)

对微观结构提出模型、假设  $\xrightarrow{\text{统计方法}}$  热现象规律

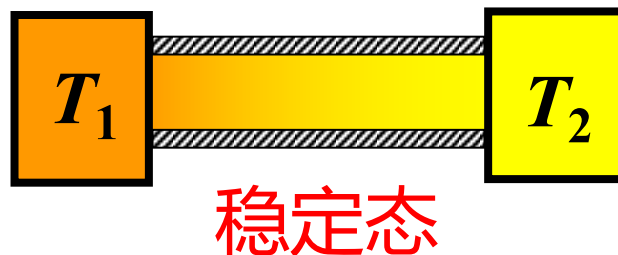
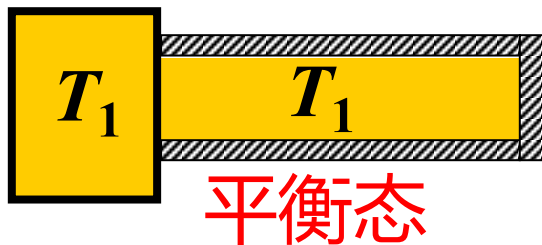
特点：可揭示本质，但受模型局限。

### 三. 几个概念

#### 1. 平衡态 (equilibrium state) :

在不受外界影响的条件下（与外界无任何形式的物质与能量交换），系统的宏观性质不随时间变化的状态（热动平衡）。

要注意区分平衡态与稳定态。



## 2.宏观量 (macroscopic quantity) :

表征系统宏观性质的物理量 (可直接测量) 。

宏观量  $\left\{ \begin{array}{l} \text{广延量(有累加性): 如 } \mathbf{M}, \mathbf{V}, \dots \\ \text{强度量(无累加性): 如 } \mathbf{p}, \mathbf{T}, \dots \end{array} \right.$

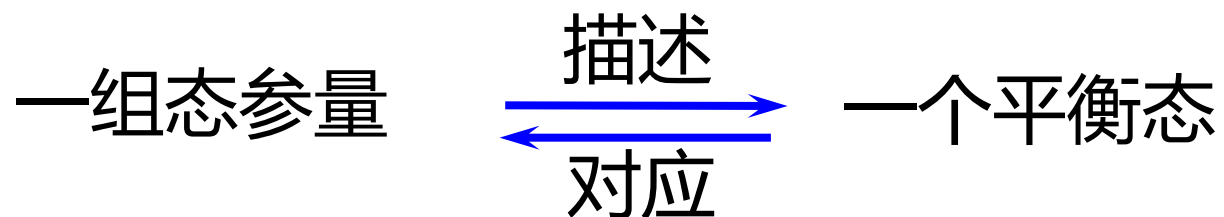
## 3.微观量 (microscopic quantity) :

描写单个微观粒子运动状态的物理量 (一般只能间接测量) 。 如分子的  $m, \vec{v}, d, \dots$

	备注	广延量	强度量	几何	力学	化学	电磁	热学
熵 $S$	$S = k \ln W$ $dS = \frac{\delta Q}{T}$	√						
温度 $T$			√					√
体积 $V$		√		√				
压强 $p$			√		√			
物质的量		√				√		
摩尔质量			√			√		
电场强度 $E$			√				√	
磁场强度 $H$			√				√	
极化强度 $P$			√				√	
磁化强度 $M$			√				√	
粒子数 $N$		√				√		
化学势 $\mu$	$\mu = \left( \frac{\partial G}{\partial N} \right)_{T, p}$		√					
内能 $U$	$dU = TdS - pdV$	√						
焓 $H$	$H = U + pV$	√						
亥姆霍兹自由能 $F$	$F = U - TS$	√						
吉布斯函数 $G$	$G = U + pV - TS$	√						
热容量 $C$	$C = \frac{\delta Q}{dT}$	√						√
体膨胀系数 $\alpha$	$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$		√		√			
相对压力系数 $\beta$	$\beta = \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_V$		√		√			
等温压缩系数 $\kappa_T$	$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$		√		√			

#### 4.物态参量（态参量）（state parameter）：

描写平衡态的宏观物理量。如：气体的  $p, V, T$



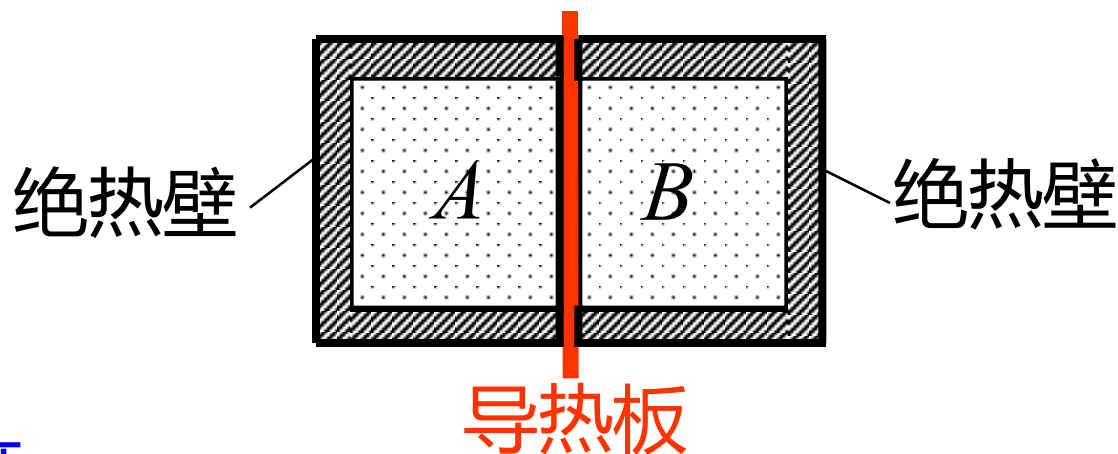
#### 5.物态方程（equation of state）：

态参量之间的函数关系： $f(p, V, T) = 0$

理想气体物态方程：
$$pV = \frac{M}{\mu} RT$$

# 第一章 温度

一. 热平衡态：两系统热接触下，相当长时间后达到的共同平衡态。



## 二. 温度

态参量  $p, V, T$  中,  $T$  是热学特有的物理量, 需要在热学中加以定义。

实验表明：若  $A$  与  $C$  热平衡， $B$  与  $C$  热平衡  
则  $A$  与  $B$  热平衡。

即：“分别与第三个系统处于同一热平衡态  
的两个系统必然也处于热平衡。”

— 热平衡定律（热力学第零定律）

定义 温度： 处于同一热平衡态下的热力学  
系统所具有的共同的宏观性质。

一切处于同一热平衡态的系统有相同的温度。

温度取决于系统内部的热运动（对质心）状态。



### 三. 温标 (temperature scales)

温标：温度的数值标度。热力学第零定律表明  
可以由已有态参量定义温度这个新态参量

$$t = t(p, V)$$

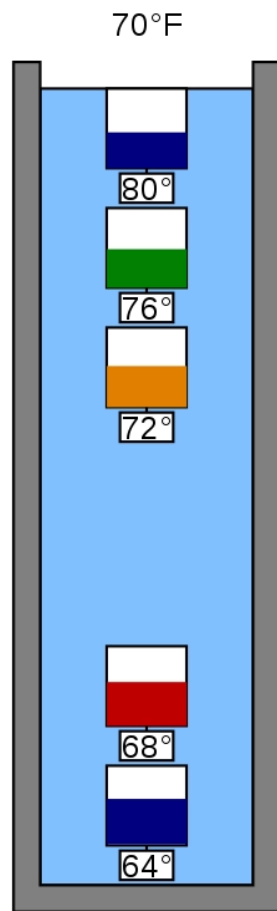
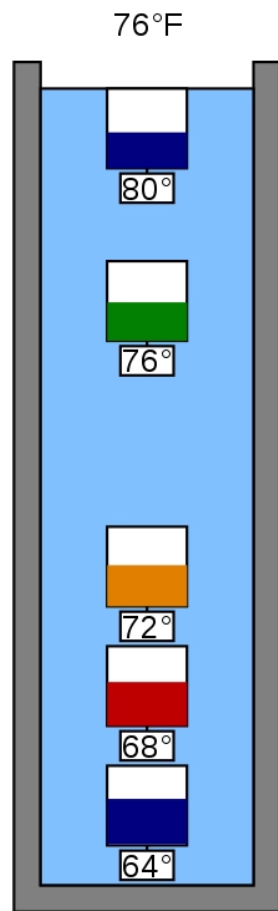
一般利用测温物质的热胀冷缩性质测量温度：

$$t_V = t(p = p_0, V), \text{ 或 } t_p = t(p, V = V_0)$$

温标的要素：测温物质，测温属性，固定标准点

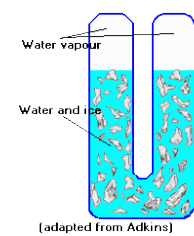
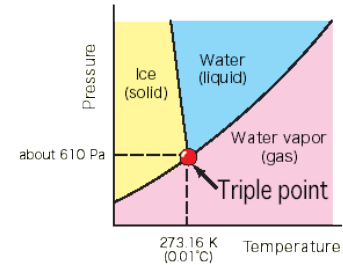


# 伽利略温度计



## ▲理想气体温标:

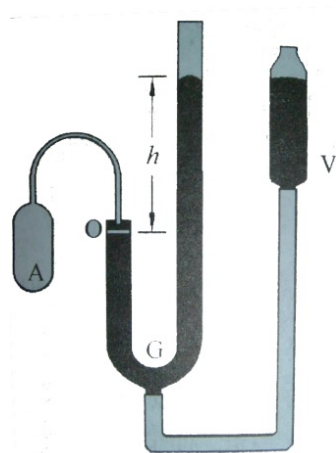
- 以气体作为测温物质
- 以水的三相点做标准
- 定压或定体



$$T(V) = 273.16\text{K} \times \lim_{p_3 \rightarrow 0} \frac{V}{V_3} \quad (p = \text{const.})$$
$$T(p) = 273.16\text{K} \times \lim_{p_3 \rightarrow 0} \frac{p}{p_3} \quad (V = \text{const.})$$

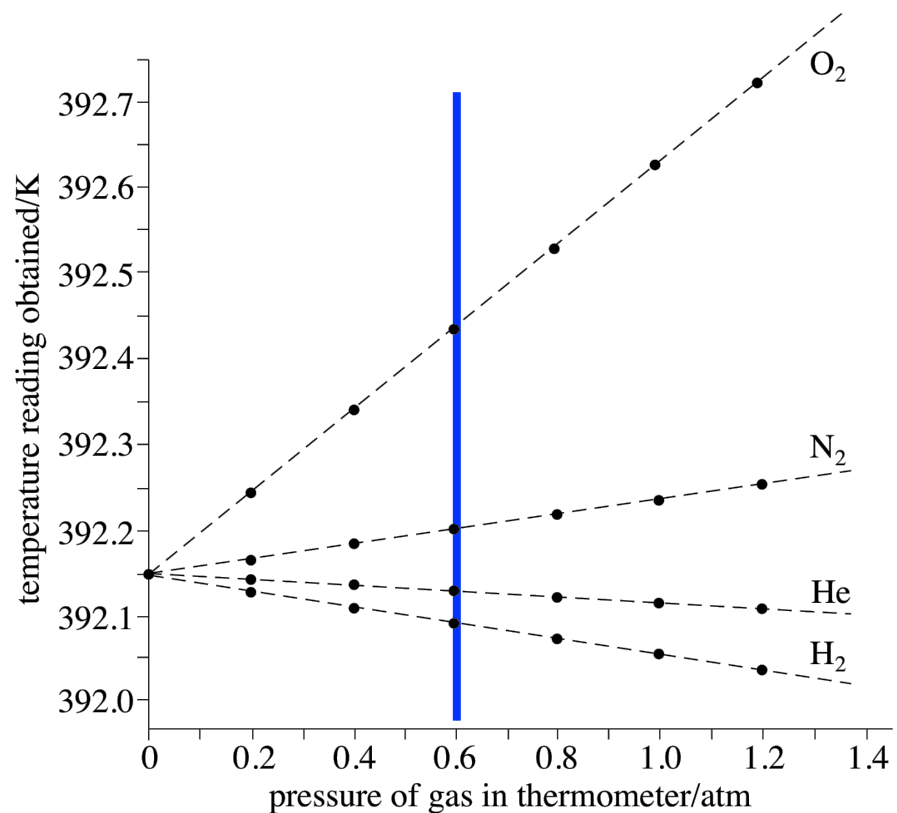
- 不同气体作为测温物质得到的温度相同吗?
- 定压或定体温标得到的温度相同吗?

# 不同气体作为测温物质得到的水汽点温度值

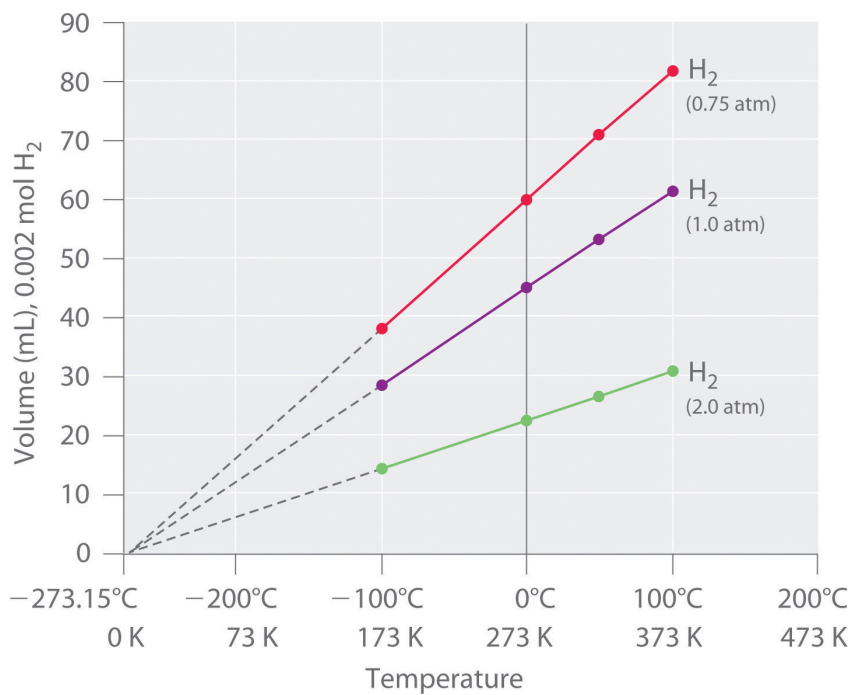


定体气体温度计示意图

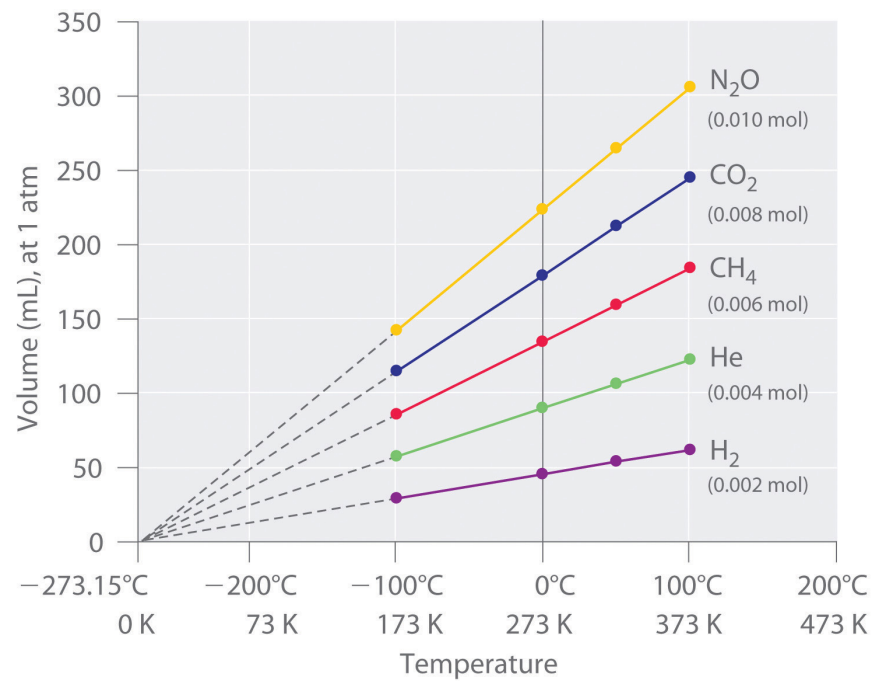
理想气体温标



在三相点时，测温泡A中的气体压强  $p_3$



(a)



(b)

▲ 热力学温标 $T$ : 不依赖测温物质及其测温属性,  
在理想气体温标有效范围内二者一致。

单位: **K (Kelvin)**, 规定:  **$T_3=273.16\text{K}$**

▲ 摄氏温标:  $t = (T - 273.15)^\circ\text{C}$   
 $t_3 = 0.01^\circ\text{C}$

▲ 华氏温标:

$$t_F = (32 + \frac{9}{5}t)^\circ\text{F} \quad \left\{ \begin{array}{l} \text{水的冰点: } 32^\circ\text{F} \\ \text{水的沸点: } 212^\circ\text{F} \end{array} \right.$$

$$t_F = 100^\circ\text{F} \rightarrow t = 37.8^\circ\text{C}$$

▲ ITS-90

## ▲ 理想气体定律:

- 玻意耳定律      等温过程  $pV = p_0V_0$  (=常数)
- 查理定律      等体过程  $p = p_0(1 + \alpha_p t)$
- 盖-吕萨克定律      等压过程  $V = V_0(1 + \alpha_V t)$

其中 $t$ 是摄氏温度,  $p_0$ 和 $V_0$ 为水冰点温度 ( $t = 0$ ) 时的压强和体积。 对于实际气体, 这些定律只是近似成立,  $\alpha_p, \alpha_V$ 与气体的种类和状态参量弱相关。

理想气体 (无限稀薄) 时:

$$\alpha_p, \alpha_V \rightarrow 1/t_0, t_0 = 273.15^\circ\text{C} \text{ (与气体种类无关)}$$

$$\begin{aligned}
 V/V_3 &= V_0/V_3(1 + \alpha_V t) \\
 &= V_0(1 + \alpha_V t)/V_0 (1 + \alpha_V t_3) \\
 &= (1 + \alpha_V t)/(1 + \alpha_V t_3) \\
 &= (1 + \frac{t}{t_0})/(1 + \frac{t_3}{t_0}) \\
 &= (t_0 + t)/(t_0 + t_3) \\
 &= T/273.16\text{K}
 \end{aligned}$$

$$\begin{aligned}
 p/p_3 &= p_0/p_3(1 + \alpha_p t) \\
 &= p_0(1 + \alpha_p t)/p_0 (1 + \alpha_p t_3) \\
 &= (1 + \alpha_p t)/(1 + \alpha_p t_3) \\
 &= (1 + \frac{t}{t_0})/(1 + \frac{t_3}{t_0}) \\
 &= (t_0 + t)/(t_0 + t_3) \\
 &= T/273.16\text{K}
 \end{aligned}$$

定压和定体温标得到的温度相同！

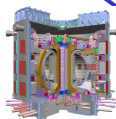


# ▲ 温度大观

**LHC**



**ITER国际热核聚变实验堆**



冶金

纵火

液氧90K

液氮77K

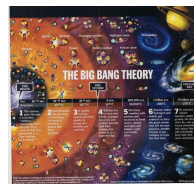
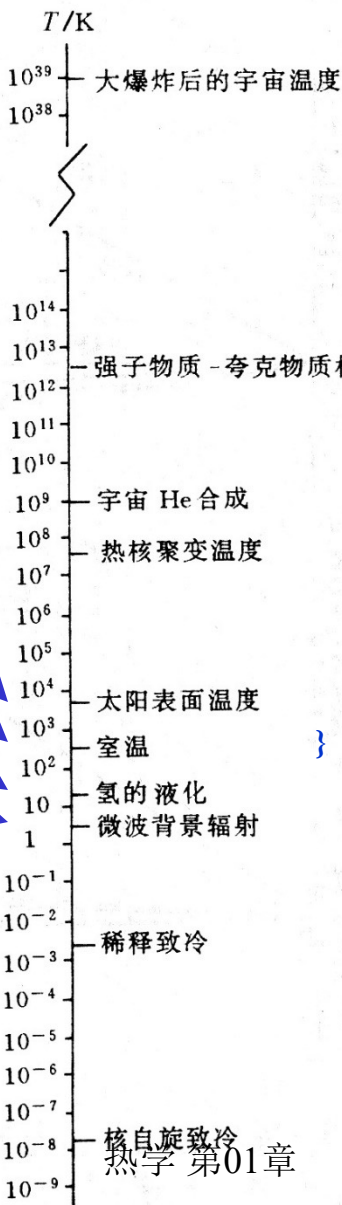
1898Dewar液氢20K

1908Onnes液氦4K

1956莱顿大学

绝热去磁1.4mK

2000Helsinki University of Technology  
2024年春季学期  
100pK



存在着 $10^9$ 种生物大分子



冰河期下降10度，  
大批物种灭绝

如果温室效应使得平均气温升高3度，海平面将上涨2-5米，迫使10亿人背井离乡

## 四. 理想气体状态方程

热力学第零定律定义了温度，同时还表明处于热平衡的系统存在一个状态方程

$$F(x_1, \dots, x_n; \theta) = 0$$

▲ 摩尔 (mole) :

从2019年5月20起, 1摩尔定义为 “精确包含  $N_A = 6.02214076 \times 10^{23}$  个原子或分子等基本单元的系统的物质的量”

## ▲ 阿伏伽德罗定律:

在相同的温度和压强下, 摩尔数相等的各种气体 (理想气体) 所占的体积相同。在  $T_0 = 273.15 \text{ K}$ ,  $p_0 = 1\text{atm}$  状态, 摩尔体积  $\omega_0 = 22.41410 \text{ L/mol}$

$$\frac{pV}{T} = \frac{p_0 V_0}{T_0} = \nu \frac{p_0 \omega_0}{T_0} = \nu R$$

$$\nu = \frac{M}{\mu} \text{ 摩尔数}$$

$$R = \frac{p_0 \omega_0}{T_0} = 8.31451 \text{ J/(mol}\cdot\text{K)}$$

▲ 理想气体的物态方程：

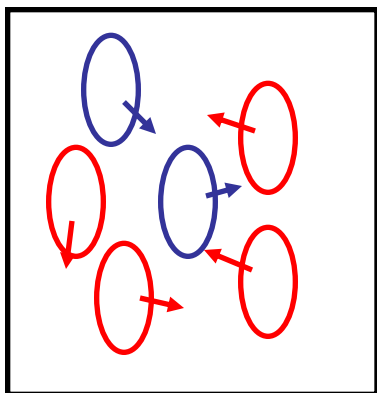
$$PV = \frac{M}{\mu} RT \longrightarrow P = \frac{1}{V} \cdot \frac{mN}{mN_A} RT$$

$$\longrightarrow \boxed{P = nkT}$$

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K}$$

— 玻尔兹曼常量 (Boltzmann Constant)

## 五. 混合理想气体物态方程:



道尔顿分压定律

$$\frac{p_1 V}{T} = \nu_1 R = \frac{m_1}{\mu_1} R = N_1 k_B$$

$$\frac{p_2 V}{T} = \nu_2 R = \frac{m_2}{\mu_2} R = N_2 k_B \quad \longrightarrow$$

$$p = p_1 + p_2$$

混合理想气体状态方程

$$\frac{pV}{T} = \nu R = \frac{m}{\mu} R = N k_B$$

$$\nu = \nu_1 + \nu_2$$

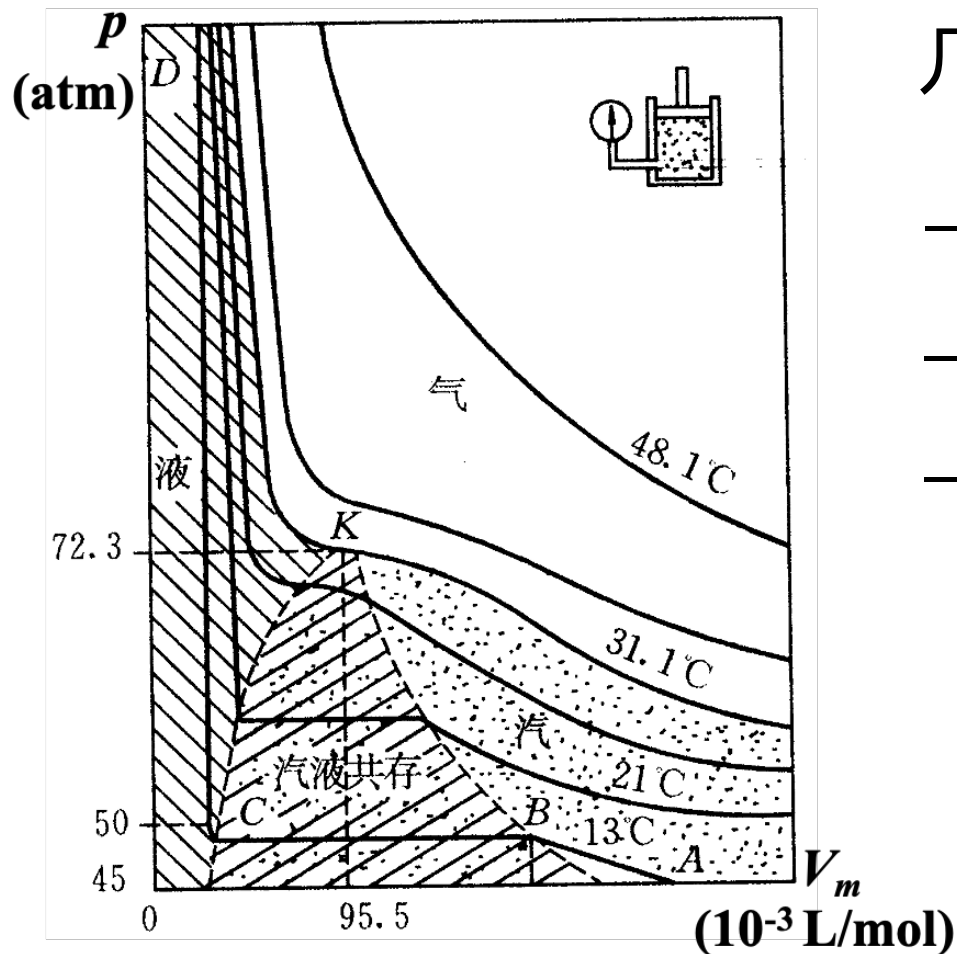
$$N = N_1 + N_2$$

$$m = m_1 + m_2$$

$$\mu = \frac{(m_1 + m_2) \mu_1 \mu_2}{m_1 \mu_2 + m_2 \mu_1}$$

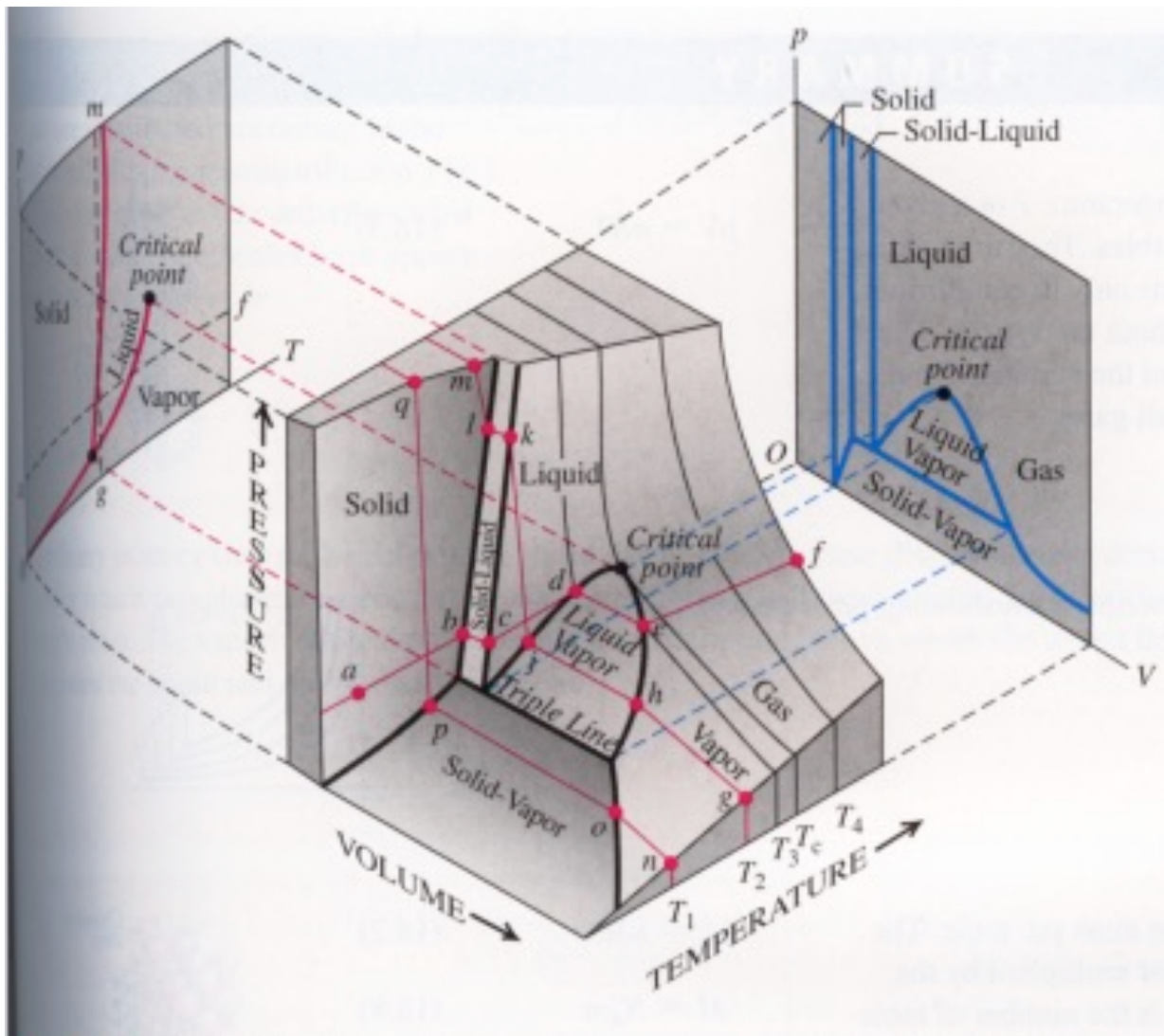
平均摩尔质量

## 六. 真实气体等温线

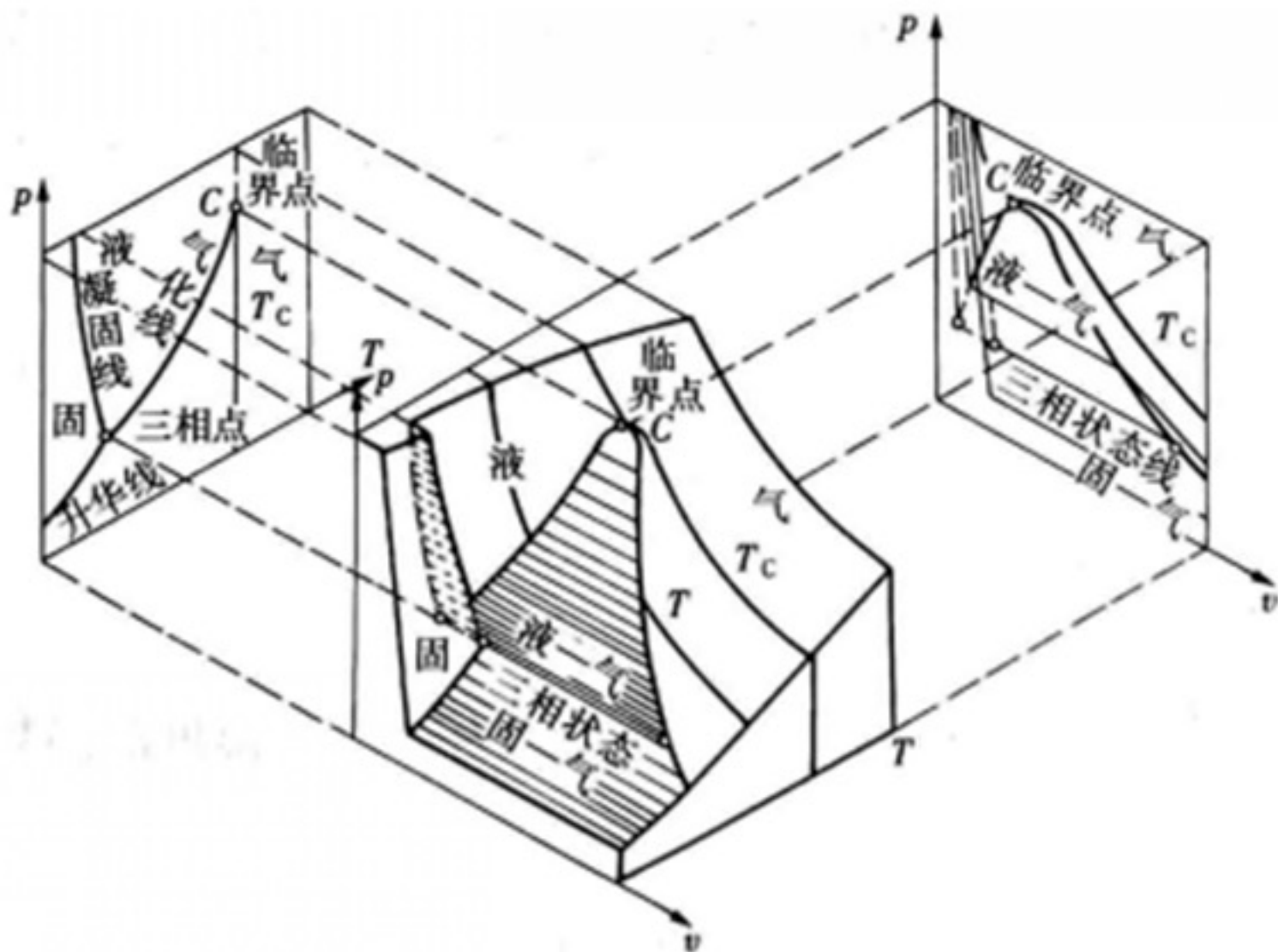


几个基本概念

- 四种状态
  - 饱和蒸汽压
  - 临界点, 临界态
- 临界等温线



**18.23** A  $pVT$ -surface for a substance that expands on melting. Projections of the boundaries on the surface on the  $pT$ - and  $pV$ -planes are also shown.








# 七. 范德瓦尔斯方程和昂尼斯方程

Kamerlingh Onnes, Heike  
born Sept. 21, 1853, Groningen, Neth. died Feb. 21, 1926, Leiden

Dutch winner of the Nobel Prize for Physics in 1913 for his work on low-temperature physics and his production of liquid helium. He discovered superconductivity, the almost total lack of electrical resistance in certain materials when cooled to a temperature near absolute zero.



From 1871 until 1873 Kamerlingh Onnes studied and worked at Heidelberg University, notably with the German physicists Robert Bunsen and Gustav Kirchhoff. Awarded a doctorate by the University of Groningen (1879), he taught at the Polytechnic School in Delft (1878-1882). From 1882 to 1923 he served as professor of experimental physics at the University of Leiden.

我很高兴把液体氦送给我最尊敬的朋友范德瓦尔斯，是他的理论一直指导了这个气体的液化

Waals, Johannes Diederik van der  
born Nov. 23, 1837, Leiden, Neth. died March 9, 1923, Amsterdam

Dutch physicist, winner of the 1902 Nobel Prize for Physics for his research on the gaseous and liquid states of matter. His work made the study of intermolecular forces possible. A self-educated man who took advantage of the opportunities offered by the University of Leiden, van der Waals first attracted notice in 1857 with his doctoral thesis, "On the Continuity of the Gaseous and Liquid States," in which he was awarded a doctorate. In pursuing his research, he knew that the ideal gas law could be derived from the kinetic theory of gases if it could be assumed that gas molecules have own volume and that there are no attractive forces between them. Taking into account that neither assumption is true, in 1873 he introduced into the law two parameters representing size and attraction and introduced a new term, known as the van der Waals equation. Since the parameters were different for each gas, he corrected his work and arrived at an equation (the law of corresponding states) that is the basis for all substances. It was this work that brought him the Nobel Prize and also led to James Clerk Maxwell and Isidor van der Waals' discovery of the critical temperature in the liquefaction of gases and liquids. Van der Waals was appointed professor of physics at the University of Amsterdam in 1877, a post he retained until 1907. The van der Waals forces, weak attractive forces between atoms or molecules, were named in his honor.



## Perfect Gas

$$pV = RT$$

分子间相互作用  
排斥与吸引

van der Waals, 1873, doctoral treatise "On the Continuity of the Liquid and Gaseous State"

## Van der Waals Gas

李椿，《热学》，P50-52

## Kamerlingh Onnes

## Onnes Equation

$$\frac{p}{k_B T} = n + B_2(T)n^2 + B_3(T)n^3 + \dots$$

$n=N/V$  数密度

位力系数

实际气体

相变

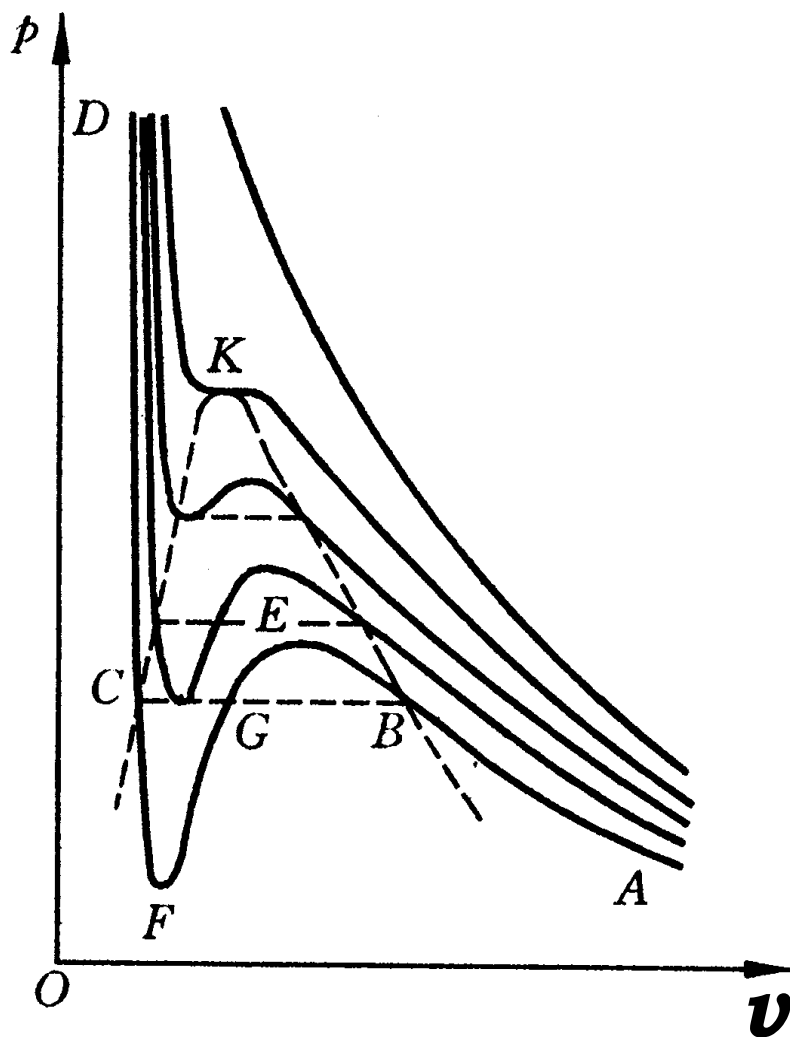
液体

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad \left(\pi + \frac{3}{\omega^2}\right)\left(\omega - \frac{1}{3}\right) = \frac{8}{3}\theta$$

$$p_c = \frac{a}{27b^2}, v_c = 3b, T_c = \frac{8a}{27Rb}$$
$$p = \pi p_c, \quad v = \omega v_c, T = \theta T_c$$

范氏对比方程

# 范氏气体等温线



$EF$  段：实际不存在

$AB$  段：汽态

$DC$  段：液态

$BE$  段：过饱和蒸汽  
(云室)

$CF$  段：过热液体  
(气泡室)

$BC$  段：饱和蒸汽与液体  
的共存态

不稳定态

## 八. 物态方程举例

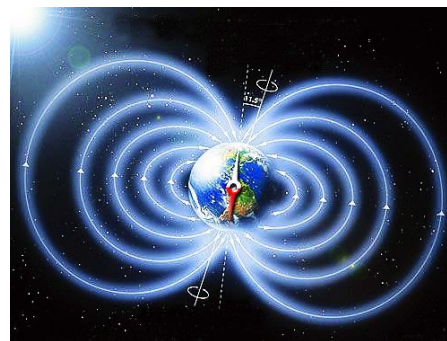
$$F(T, L) = C(T)(L - L_0)$$

胡克定律  
金属丝

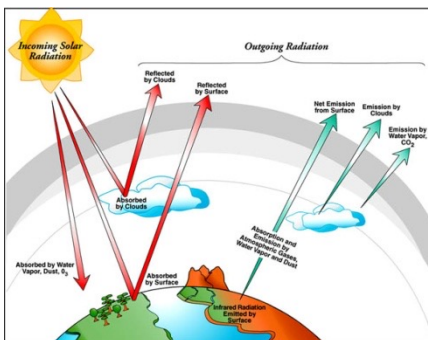


$$M = CH / T$$

居里定律  
磁介质



热辐射



$$p = \frac{a}{3} T^4$$



电介质

$$P = (a + b/T)E$$

## 九. 一般物体的状态方程

响应函数 (可以由实验测定)

$$\alpha = \lim_{\Delta T \rightarrow 0} \frac{1}{V} \left( \frac{\Delta V}{\Delta T} \right)_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad \text{膨胀系数}$$

$$\beta = \lim_{\Delta T \rightarrow 0} \frac{1}{p} \left( \frac{\Delta p}{\Delta T} \right)_V = \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_V \quad \text{压强系数}$$

$$\alpha = \kappa \beta p$$

$$\kappa = \lim_{\Delta p \rightarrow 0} -\frac{1}{V} \left( \frac{\Delta V}{\Delta p} \right)_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad \text{压缩系数}$$

气体

$$\begin{aligned}\alpha &\sim 10^{-3} \text{K}^{-1} \\ \beta &\sim 10^{-3} \text{K}^{-1} \\ \kappa &\sim 10^0 \text{atm}^{-1}\end{aligned}$$

液体

$$\begin{aligned}\alpha &\sim 10^{-4} \text{K}^{-1} \\ \beta &\sim 10^{1-2} \text{K}^{-1} \\ \kappa &\sim 10^{-6} \text{atm}^{-1}\end{aligned}$$

固体

$$\begin{aligned}\alpha &\sim 10^{-3} \text{K}^{-1} \\ \beta &\sim 10^3 \text{K}^{-1} \\ \kappa &\sim 10^{-7} \text{atm}^{-1}\end{aligned}$$

【例】由响应函数得到物态方程

设物态方程的函数形式为  $V = V(T, p)$

$$\begin{aligned}\frac{dV}{V} &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p dT + \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T dp \\ &= \alpha dT - \kappa dp\end{aligned}$$

$$\ln \frac{V}{V_0} = \int_{(T_0, p_0)}^{(T, p)} \alpha dT - \kappa dp$$

对于固体,  $(V - V_0)/V \ll 1$ ; 如果  $\alpha, \kappa$  为常数

$$V = V_0 [1 + \alpha(T - T_0) - \kappa(p - p_0)]$$