

第二章：均匀物质的热力学性质



[数学准备]

1、隐函数偏微分

函数 $z=z(x,y)$ 满足 $F(x,y,z)=0$

$$\left(\frac{\partial z}{\partial x}\right)_y = 1 / \left(\frac{\partial x}{\partial z}\right)_y$$

$$\left(\frac{\partial z}{\partial y}\right)_x = 1 / \left(\frac{\partial y}{\partial z}\right)_x$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1.$$



2、二元函数的全微分(式)

若: $z = z(x, y)$

则: $dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$

为函数 z 的“全微分”

则必有: $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$

即: $\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x} \right)$

也即: 偏微分运算的先后顺序可以交换!!

3、雅可比行列式

设 u, v 是独立变数 x, y 的函数 $u = u(x, y), v = v(x, y)$

雅可比定义为:

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x}.$$

性质

$$(1) \quad \left(\frac{\partial u}{\partial x} \right)_y = \frac{\partial(u, y)}{\partial(x, y)}$$

$$(2) \quad \frac{\partial(u, v)}{\partial(x, y)} = - \frac{\partial(v, u)}{\partial(x, y)}$$

$$(3) \quad \frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(x, s)} \frac{\partial(x, s)}{\partial(x, y)}$$



§ 2-1 热力学函数的全微分

主要目的:

利用数学方法  热力学函数间微分关系

已有的知识:

- 基本的热力学函数
- 内能 U 、自由能 F 、焓 H 、吉布斯(Gibbs)函数 G

$$H=U+PV, \quad F=U-TS, \quad G=H-TS$$

物态方程、内能和熵

讨论对象: 简单系统的无摩擦准静态过程,
即“可逆过程”

状态函数和自变量的选取

自变量:

$$S, p, V, T$$

状态函数:

$$U, H, F, G$$

状态函数和自变量按如下组合:

$$U = U(S, V), H = H(S, p)$$

$$F = F(T, V), G = G(T, p)$$



热力学的基本微分方程(只考虑体积变化功)

$$dU = TdS - pdV$$

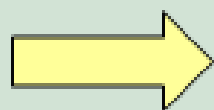
(1) 内能: $U(S, V)$, 全微分为

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

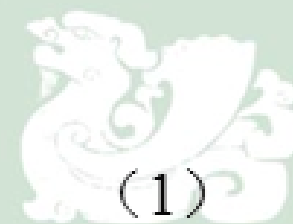
$$\left(\frac{\partial U}{\partial S} \right)_V = T, \left(\frac{\partial U}{\partial V} \right)_S = -P$$

偏导数的次序可以交换

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$



$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$$



(2) 焓的定义 $H=U+PV$

$$dU=TdS-pdV \quad \longrightarrow \quad dH=TdS+Vdp$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T, \left(\frac{\partial H}{\partial p} \right)_S = V$$

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

(2)

(3) 自由能 $F=U-TS$

$$dF = -SdT - pdV$$

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

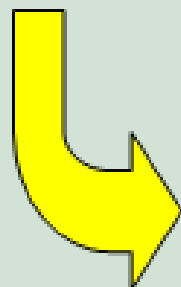
$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

(3)

(4) 吉布斯(Gibbs)函数 $G=U+pV-TS$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_P = -S$$



$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (4)$$

(1—4) 麦克斯韦 (Maxwell) 关系, or 麦氏关系

[麦克斯韦关系的总结]

1. 热力学基本方程

2. 全微分

$$dU = TdS - pdV \xrightarrow{U=U(S,V)} dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dH = TdS + Vdp \xrightarrow{H=H(S,p)} dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

$$dF = -SdT - pdV \xrightarrow{F=F(T,V)} dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$dG = -SdT + Vdp \xrightarrow{G=G(T,p)} dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

3. S, p, V, T 与 U, H, F, G 一阶偏导数的关系

$$T = \left(\frac{\partial U}{\partial S} \right)_V, \quad p = - \left(\frac{\partial U}{\partial V} \right)_S$$

$$T = \left(\frac{\partial H}{\partial S} \right)_p, \quad V = \left(\frac{\partial H}{\partial p} \right)_S$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad p = - \left(\frac{\partial F}{\partial V} \right)_T$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_p, \quad V = \left(\frac{\partial G}{\partial p} \right)_T$$



4.麦克斯韦偏微分关系

是“ S, p, V, T 一阶偏导数之间的关系”

也是“ U, H, F, G 二阶偏导数之间的关系”

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (\text{麦01}) \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (\text{麦03})$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (\text{麦02}) \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (\text{麦04})$$

同样，可从联络图中找出
全部“麦克斯韦关系”！！

