第二章

均匀物质的热力学性质

热力学基本方程

Marxwell关系式

特性函数

热辐射的热力学理论

热力学基本方程

$$dU = TdS - pdV$$

$$H = U + pV \longrightarrow dH = TdS + Vdp$$

$$F = U - TS \longrightarrow dF = -SdT - pdV$$

$$G = U - TS + pV \longrightarrow dG = -SdT + Vdp$$

利用热力学基本方程和恰当微分的条件，可以得到Maxwell方程组

Marxwell方程组

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

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

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

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

力学变量 $\longleftrightarrow$ 热学变量

不独立！

Jacobi行列式及其性质

$$\int f(x,y)dxdy = \int \left|J\right| f(u,v)dudv$$

$$J = \frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \left(\dfrac{\partial u}{\partial x}\right)_y & \left(\dfrac{\partial u}{\partial y}\right)_x \\ \left(\dfrac{\partial v}{\partial x}\right)_y & \left(\dfrac{\partial v}{\partial y}\right)_x \end{vmatrix}$$

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} \qquad \left(\frac{\partial u}{\partial x}\right)_y = \frac{\partial(u,y)}{\partial(x,y)} \qquad \frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(t,s)}\frac{\partial(t,s)}{\partial(x,y)}$$

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{1}{\dfrac{\partial(x,y)}{\partial(u,v)}} \qquad \frac{d}{dt}\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(\frac{du}{dt},v)}{\partial(x,y)} + \frac{\partial(u,\frac{dv}{dt})}{\partial(x,y)}$$

热力学函数的确定

重点：利用Marxwell关系，在热力学意义下，可以把求一切热力学量的问题归结为状态方程和某一压强下的定压热容量或某一体积下的定容热容量

熵方程

$$
\begin{aligned}
TdS &= C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \\
&= C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP
\end{aligned}
$$

内能方程

$$
dU = C_V dT + T\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV
$$

焓方程

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

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

C_P和C_P的关系

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

利用

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T} > 0$$

这个结果在物理上是显然的。因为在等压过程中，体系吸收的热量除了用以增加体系的内能外，还有一部分要用来对外做功。

但在等容过程中，体系对外做功为零，吸收的热量全部用以增加体系的内能。因此，要增加同样的温度，等压过程要比等容过程吸收更多的热量。

如果已知某一压强下的定压热容量 $C_p^0(p_0)$

$$dH = TdS + Vdp = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left[\frac{\partial\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]}{\partial T}\right]_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

$$\boxed{C_p = C_p^0 - \int_{p_0}^{p} T\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp}$$

如果已知某一体积下的定容热容量 $C_V^0(V_0)$

$$dU = TdS - pdV = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]dV$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]}{\partial T}\right]_V = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

$$\boxed{C_V = C_V^0 + \int_{V_0}^{V} T\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV}$$

例题1：实验发现，一气体的压强p与体积V的乘积以及内能U都只是温度的函数，即

$$PV = f(T)$$

$$U = U(T)$$

试根据热力学理论，讨论该气体的物态方程可能的具体形式。

例题2：证明

$$\frac{\partial(T,S)}{\partial(x,y)}=\frac{\partial(p,V)}{\partial(x,y)}$$

其中，x, y 是任意的独立变量，并由此导出四个Maxwell关系式 。

例题3：证明绝热膨胀系数 $\alpha_s = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_s$

等压膨胀系数 $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

等容压力系数 $\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v$

等温压缩系数 $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

绝热压力系数 $\beta_s = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_s$

绝热压缩系数 $\kappa_s = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s$

满足关系式：

$$\frac{\alpha}{\alpha_s} = 1-\gamma; \frac{\beta}{\beta_s} = 1-\frac{1}{\gamma}; \frac{\kappa}{\kappa_s} = \gamma$$

其中，$\gamma = C_p / C_V$

II. 特性函数和马休定理

问题：一切热力学量，包括和状态方程，需要通过什么量才能全部求出？

马休定理：在适当选择独立变量后，只要一个热力学函数就可以把均匀系在热平衡状态下的热力学性质完全决定。

这个热力学函数就叫特性函数

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

$$H = H(S, P)$$

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

$$G = G(T, P)$$

以$F = F(T,V)$为例

$$dF = -SdT - PdV \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

$$H = U + PV = F - T\left(\frac{\partial F}{\partial T}\right)_V - V\left(\frac{\partial F}{\partial V}\right)_T$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V}\frac{1}{\left(\frac{\partial^2 F}{\partial V^2}\right)_T}$$

$$\alpha = -\frac{\left(\frac{\partial^2 F}{\partial T \partial V}\right)}{V\left(\frac{\partial^2 F}{\partial V^2}\right)_T} \quad C_P = C_V + T\frac{\left(\frac{\partial^2 F}{\partial T \partial V}\right)^2}{V\left(\frac{\partial^2 F}{\partial V^2}\right)_T}$$

如果已知某一压强P_0下的C_P^0，则

$$dH = TdS + VdP = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

利用恰当微分条件

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left[\frac{\partial V - \left(\frac{\partial V}{\partial T}\right)_P}{\partial T}\right]_P = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

在固定T下

$$C_P = C_P^0 - T\int_{P_0}^{P}\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP$$

对热均匀的热力学体系，在热力学意义下，求一切热力学量的问题，最后可归结为把这些热力学量表示为状态方程和某一压强下的定压热容量或某一体积下的定容热容量。

一切热力学问题，可通过热力学函数及其微商运算，归结为状态方程 C_P^0 or C_V^0

例题1：设某种气体的状态方程为

$$\left(p+\frac{a}{T^n V^2}\right)(V-b)=NRT$$

式中a,b,n为常数，N为气体的摩尔数。证明该气体的自由能为

$$F(T,V)=-NRT\ln(V-b)-\frac{a}{T^2V}-T\int\frac{dT}{T^2}\int c_v^0 dT-TS_0+U_0$$

式中，c_v^0 为c_v在 $V\to\infty$时的极限值，并由此导出U,S,H和G的表达式。

习 题

证明下列热力学函数的微商关系式

$$(1)\quad \left(\frac{\partial U}{\partial p}\right)_V = -T\left(\frac{\partial V}{\partial T}\right)_S$$

$$(2)\quad \left(\frac{\partial U}{\partial V}\right)_p = T\left(\frac{\partial p}{\partial T}\right)_S - p$$

$$(3)\quad \left(\frac{\partial T}{\partial V}\right)_U = p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial p}{\partial U}\right)_V$$

$$(4)\quad \left(\frac{\partial T}{\partial p}\right)_H = T\left(\frac{\partial V}{\partial H}\right)_p - V\left(\frac{\partial T}{\partial H}\right)_p$$

$$(5)\quad \left(\frac{\partial T}{\partial V}\right)_H = \frac{T}{C_p} - \frac{T^2}{V}\left(\frac{\partial V}{\partial H}\right)_p$$