第二章

均匀物质的热力学性质

§2.1 内能、焓、自由能和吉布斯函数的全微分

主要目的：

利用数学方法 ⟶ 热力学函数间的微分关系

一、数学定义

函数 $f(x, y)$ 的全微分

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

自变量 $\Longleftrightarrow$ 状态参量(***p*, *S*, *V*, *T***)

函数 $\Longleftrightarrow$ 热力学函数（态函数）(***U*, *H*, *F*, *G***)

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

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

热力学的基本微分方程 $dU = TdS - pdV$

二、热力学量表示为偏导数

1、函数关系： $U = U(S,V)$

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

热力学基本方程 $dU = TdS - pdV$

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

2、函数关系：

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

全微分：
$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

根据焓的定义 $H = U + pV$

全微分：
$$dH = dU + pdV + Vdp$$
$$= TdS - pdV + pdV + Vdp \quad = TdS + Vdp$$

对比得：
$$T = \left(\frac{\partial H}{\partial S}\right)_p \qquad V = \left(\frac{\partial H}{\partial p}\right)_S$$

3、函数关系：

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

全微分： $$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

根据自由能的定义 $$F = U - TS$$

全微分： $$dF = dU - TdS - SdT$$

$$= TdS - pdV - TdS - SdT \quad = -SdT - pdV$$

对比得： $$-S = \left(\frac{\partial F}{\partial T}\right)_V \qquad -p = \left(\frac{\partial F}{\partial V}\right)_T$$

4、函数关系：

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

全微分：$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

根据吉布斯函数的定义 $$G = U - TS + pV$$

全微分：
$$\begin{aligned} dG &= dU - TdS - SdT + pdV + Vdp \\ &= TdS - pdV - TdS - SdT + pdV + Vdp \\ &= -SdT + Vdp \end{aligned}$$

对比得：$$-S = \left(\frac{\partial G}{\partial T}\right)_p \qquad V = \left(\frac{\partial G}{\partial p}\right)_T$$

三、麦氏关系

求偏导数的次序可以交换 $\dfrac{\partial^2 f}{\partial x \partial y}=\dfrac{\partial^2 f}{\partial y \partial x}$

在函数关系 $U=U(S,V)$ 中得到：

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

$$\Rightarrow \quad \left(\frac{\partial}{\partial V}T\right)_S=\frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial S}\right)_V\right]_S=\frac{\partial^2 U}{\partial V \partial S}$$

$$\left(\frac{\partial}{\partial S}(-p)\right)_V=\frac{\partial}{\partial S}\left[\left(\frac{\partial U}{\partial V}\right)_S\right]_V=\frac{\partial^2 U}{\partial S \partial V}$$

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

在函数关系 $H = H(S, p)$ 中得到：

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

$$\Rightarrow \left(\frac{\partial}{\partial p}T\right)_S = \frac{\partial}{\partial p}\left[\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \frac{\partial^2 H}{\partial p \partial S}$$

$$\left(\frac{\partial}{\partial S}V\right)_p = \frac{\partial}{\partial S}\left[\left(\frac{\partial H}{\partial p}\right)_S\right]_p = \frac{\partial^2 H}{\partial S \partial p}$$

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

在函数关系 $F=F(T,V)$ 中得到：

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

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

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

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

在函数关系 $G=G(T,p)$ 中得到：

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

$$\Rightarrow \quad \left(\frac{\partial}{\partial p}(-S)\right)_T=\frac{\partial}{\partial p}\left[\left(\frac{\partial G}{\partial T}\right)_p\right]_T=\frac{\partial^2 G}{\partial p\partial T}$$

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

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

热力学微分关系

热力学函数	热力学基本方程	热力学偏导数	麦克斯韦关系
U	$dU = TdS - pdV$	$T = \left(\frac{\partial U}{\partial S}\right)_V$ $p = -\left(\frac{\partial U}{\partial V}\right)_S$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H = U + pV$	$dH = TdS + Vdp$	$T = \left(\frac{\partial H}{\partial S}\right)_p$ $V = \left(\frac{\partial H}{\partial p}\right)_S$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$F = U - TS$	$dF = -SdT - pdV$	$S = -\left(\frac{\partial F}{\partial T}\right)_V$ $p = -\left(\frac{\partial F}{\partial V}\right)_T$	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
$G = H - TS$	$dG = -SdT + Vdp$	$S = -\left(\frac{\partial G}{\partial T}\right)_p$ $V = \left(\frac{\partial G}{\partial p}\right)_T$	$-\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T$

说明：

1、表中这套热力学关系是从热力学基本方程 $dU = TdS - pdV$ 导出的，从变量变换的角度看，只可能导出其它三个基本方程。

2、利用表中关系，加上 C_p 、C_V 和附录一中的几个偏微分学公式，就可以研究均匀闭系的各种热力学性质。

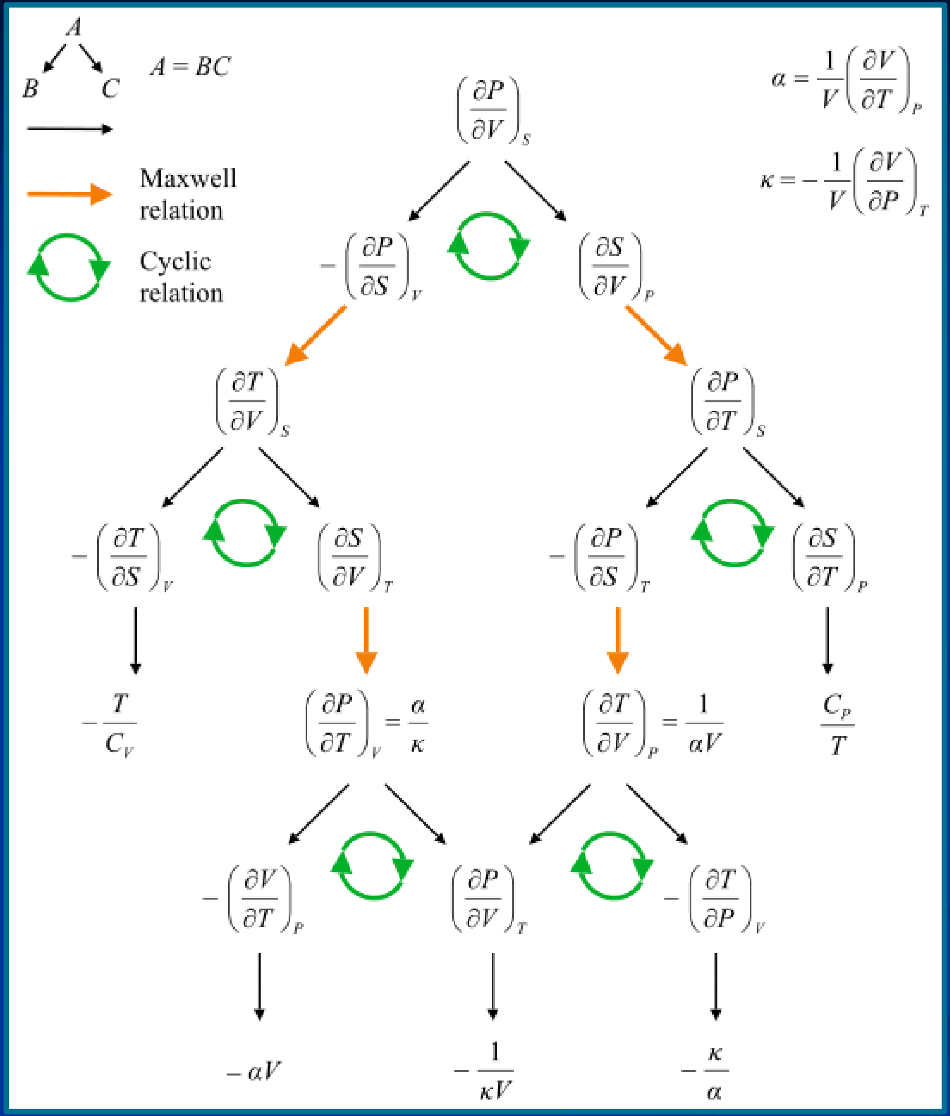
3 、表中关系是解决热力学问题的基础，应熟记它们。

简单记忆麦克斯韦关系的一种方法，如下：

$$\begin{array}{l} T \longrightarrow V \\ \\ p \longrightarrow S \end{array} \quad \Longrightarrow \quad -\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial S}\right)_V \qquad -\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T$$

$$\begin{array}{cc} T & V \\ \downarrow & \downarrow \\ p & S \end{array} \quad \Longrightarrow \quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

麦氏关系



https://en.wikipedia.org/wiki/Maxwell_relations

§ 2.2 麦氏关系的简单应用

上节导出了麦氏关系：

$$(1)\quad \left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V \qquad (2)\quad \left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_p$$

$$dU=TdS-pdV \qquad dH=TdS+Vdp$$

$$(3)\quad \left(\frac{\partial p}{\partial T}\right)_V=\left(\frac{\partial S}{\partial V}\right)_T \qquad (4)\quad \left(\frac{\partial V}{\partial T}\right)_p=-\left(\frac{\partial S}{\partial p}\right)_T$$

$$dF=-SdT-pdV \qquad dG=-SdT+Vdp$$

麦氏关系给出了热力学量的偏导数之间的关系。利用麦氏关系，可以把一些不能直接从实验测量的物理量以物态方程（或体胀系数和等温压缩系数）和热容量等可以直接从实验测量的物理量表达出来表示出来。

一、 选**T**、**V**为状态参量，熵为：$S = S(T, V)$

内能为： $U = U(S, V) = U(S(T, V), V) = U(T, V)$

全微分：$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

$$= T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]dV$$

利用麦氏关系：

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

可得：

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

对比得：

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

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

公式 $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ 的意义：

对于理想气体： $pV_m = RT$

$$\longrightarrow \left(\frac{\partial U_m}{\partial V_m}\right)_T = T\frac{R}{V_m} - p = \frac{TR - pV_m}{V_m} = 0$$

对于理想气体，内能只是温度的函数。

焦耳定律

对于范式气体：$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

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

$$\longrightarrow\quad\left(\frac{\partial U_m}{\partial V_m}\right)_T=\frac{RT}{V_m-b}-p=\frac{a}{V_m^2}$$

温度不变时，范氏气体的内能随体积的变化率。与体积有关。

二、选T、p为状态参量，熵为： $S = S(T, p)$

焓为：$H = H(S, p) = H(S(T, p), p) = H(T, p)$

全微分： $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$ $dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$

热力学基本方程： $dH = TdS + Vdp$

$$dH = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp$$

利用麦氏关系：

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

对比得： $C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

三、选 p、V为状态参量，熵为：$S=S(p,V)$

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

$$dS=\left(\frac{\partial S}{\partial p}\right)_V dp+\left(\frac{\partial S}{\partial V}\right)_p dV \qquad dU=\left(\frac{\partial U}{\partial p}\right)_V dp+\left(\frac{\partial U}{\partial V}\right)_p dV$$

$$dU=TdS-pdV=T\left[\left(\frac{\partial S}{\partial p}\right)_V dp+\left(\frac{\partial S}{\partial V}\right)_p dV\right]-pdV$$

$$=T\left(\frac{\partial S}{\partial p}\right)_V dp+\left[T\left(\frac{\partial S}{\partial V}\right)_p-p\right]dV$$

利用麦氏关系：$\left(\frac{\partial p}{\partial T}\right)_V=\left(\frac{\partial S}{\partial V}\right)_T \quad \left(\frac{\partial V}{\partial T}\right)_p=-\left(\frac{\partial S}{\partial p}\right)_T$

$$dU=-T\left(\frac{\partial V}{\partial T}\right)_S dp+\left[T\left(\frac{\partial p}{\partial T}\right)_S-p\right]dV$$

对比得：$\left(\frac{\partial U}{\partial p}\right)_V=-T\left(\frac{\partial V}{\partial T}\right)_S \quad \left(\frac{\partial U}{\partial V}\right)_p=T\left(\frac{\partial p}{\partial T}\right)_S-p$

四、计算任意简单系统的定压热容量与定容热容量之差

由 $C_p - C_V = T\left(\frac{\partial S}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_V$

$$f(x,z) = f(x, y(x,z))$$

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$S(T,p) = S(T, V(T,p))$$

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

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

对于理想气体

$$= nR$$

利用麦氏关系：$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

对于任意简单系统

$$= TpV \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right) = TpV\beta\alpha = \frac{VT\alpha^2}{\kappa_T}$$

$$\alpha = \kappa_T \beta p$$

固体与液体的 C_V 很难测量，通过 C_p 计算之。

附　　雅可比行列式

x, y 是状态参量，u 和 v 是热力学函数：

$$u(x,y), \qquad v(x,y).$$

雅可比行列式定义

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

性质：

1) $$\left(\frac{\partial u}{\partial x}\right)_y = \frac{\partial(u,y)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\cdot 1 - \frac{\partial u}{\partial y}\cdot 0$$

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

3) $$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(x,s)}\frac{\partial(x,s)}{\partial(x,y)} \qquad \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial s} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial s} \end{vmatrix}\begin{vmatrix} \frac{\partial x}{\partial x} & \frac{\partial x}{\partial y} \\ \frac{\partial s}{\partial x} & \frac{\partial s}{\partial y} \end{vmatrix} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial s}\frac{\partial s}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial s}\frac{\partial s}{\partial y} \end{vmatrix} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

4) $$\frac{\partial(u,v)}{\partial(x,y)} = 1\Big/\frac{\partial(x,y)}{\partial(u,v)}$$

例1、求证绝热压缩系数与等温压缩系数之比等于定容热容量与定压热容量之比。

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S, \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

证明：

$$\frac{\kappa_S}{\kappa_T} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\frac{\partial(V,S)}{\partial(p,S)}}{\frac{\partial(V,T)}{\partial(p,T)}} = \frac{\frac{\partial(V,S)}{\partial(V,T)}}{\frac{\partial(p,S)}{\partial(p,T)}}$$

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

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T\left(\frac{\partial S}{\partial T}\right)_V}{T\left(\frac{\partial S}{\partial T}\right)_p} = \frac{C_V}{C_p}$$

例2、求证

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

证明：

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\frac{\partial(S,p)}{\partial(T,p)}$$

利用麦氏关系：$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

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

例3、考虑一理想气体，其熵为

$$S = \frac{n}{2}\left\{\sigma + 5R\ln\frac{U}{n} + 2R\ln\frac{V}{n}\right\}$$

其中，***n***为摩尔数，***R***为气体常数，***U***为能量，***V***为体积，***σ***为常数，求出定压和定容热容量。

解：

$$dU = TdS - pdV$$

温度***T***为

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} = \frac{5}{2}nR\frac{1}{U}$$

$$U = \frac{5}{2}nRT \qquad C_V = \frac{5}{2}nR$$

$$C_p = C_V + nR = \frac{7}{2}nR$$