前节内容回顾

❖ 1 封闭系统的热力学第一定律

$$\Delta U = Q + W$$

❖ 2 热力学基本关系式及微分关系

$$dU = TdS - pdV \qquad dA = -SdT - pdV$$

$$dH = TdS + Vdp \qquad dG = -SdT + Vdp$$

$$\boxed{dZ = Mdx + Ndy \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

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

3 偏离函数

- 偏离函数是研究态相对于同温度的理想气体参考态的热力学函数的差值。

$$\boxed{M - M_0^{ig} = M(T,p) - M^{ig}(T,p_0)}$$

参考态是理想气体，与研究态同温度同组成，压力可相同也可以不同

应用：

$$
\begin{aligned}
& M(T_2,p_2)-M(T_1,p_1) \\
& =\left[M(T_2,p_2)-M^{ig}(T_2,p_0)\right] \\
& -\left[M(T_1,p_1)-M^{ig}(T_1,p_0)\right] \\
& +\left[M^{ig}(T_2,p_0)-M^{ig}(T_1,p_0)\right]
\end{aligned}
$$

要求状态1和2具有相同的组成，并取相同组成的参考态

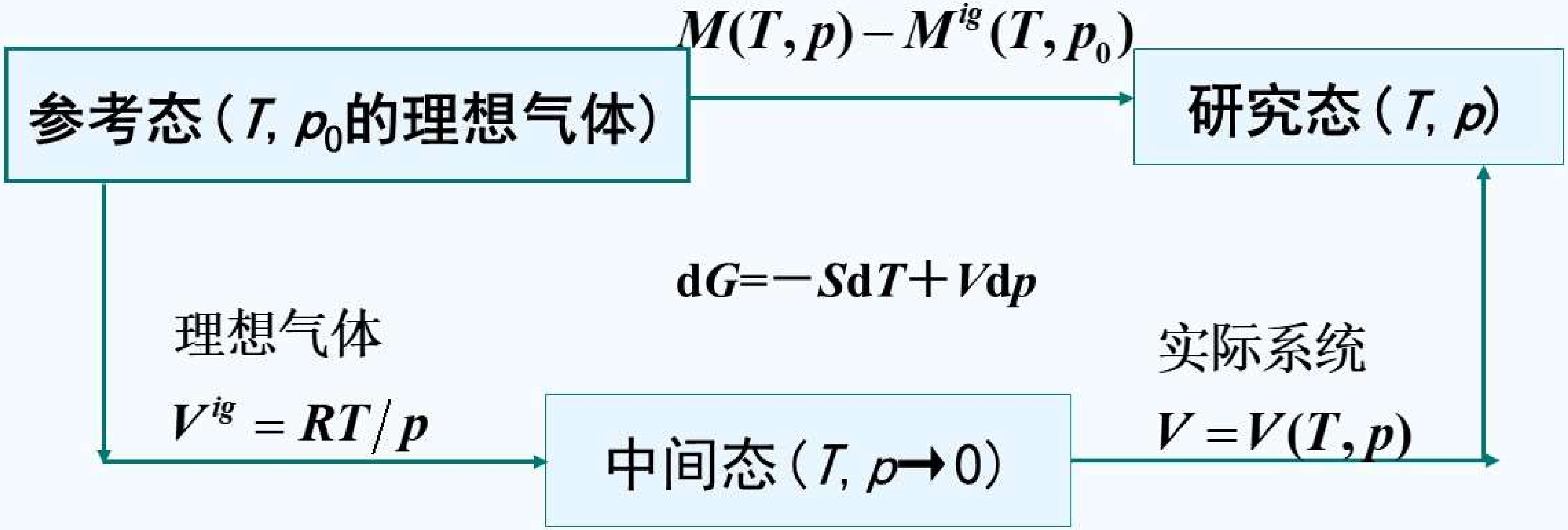
❖ §3-5 T，p为独立变量的偏离函数

❖ 在由状态方程模型推导偏

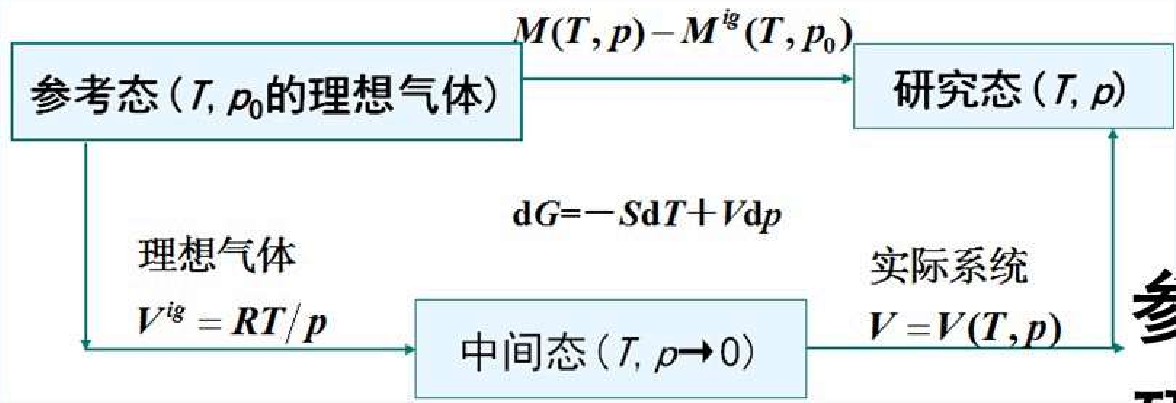
对于$V=V$（T，p）形式的状

列的变化途径进行推导较为

$$dU = TdS - pdV$$
$$dH = TdS + Vdp$$
$$dA = -SdT - pdV$$
$$dG = -SdT + Vdp$$



- 1 偏离吉氏函数
- 已知$dG=-SdT+Vdp$, 等温时,$[dG=Vdp]_T$



参考态→中间态→研究态积分上式

$$\int_{G^{ig}(T,p_0)}^{G(T,p)} dG=\int_{p_0}^{0} V^{ig}dp+\int_{0}^{p} Vdp$$

$$=\left[\int_{p_0}^{0} V^{ig}dp+\int_{0}^{p} V^{ig}dp\right]+\left[\int_{0}^{p} Vdp-\int_{0}^{p} V^{ig}dp\right]$$

$$= \int_{p_0}^{p} V^{ig} dp + \int_{0}^{p} \left(V - V^{ig} \right) dp$$

$$= \int_{p_0}^{p} \frac{RT}{p} dp + \int_{0}^{p} \left(V - \frac{RT}{p} \right) dp$$

$$= RT \ln \frac{p}{p_0} + \int_{0}^{p} \left(V - \frac{RT}{p} \right) dp$$

$V = V(T, p)$ 代入状态方程的具体形式积分计算

❖ 由此得偏离吉氏函数

$$G(T,p)-G^{ig}(T,p_0)=RT\ln\frac{p}{p_0}+\int_0^p\left(V-\frac{RT}{p}\right)dp$$

（3-37）

标准化处理后得

$$\frac{G-G_0^{ig}}{RT}-\ln\frac{p}{p_0}=\frac{1}{RT}\int_0^p\left(V-\frac{RT}{p}\right)dp$$

2 偏离熵

由Maxwell关系式 $S=-\left(\frac{\partial G}{\partial T}\right)_p$ 得

$$S-S_0^{ig}=-\left[\frac{\partial(G-G_0^{ig})}{\partial T}\right]_p=-\left\{\frac{\partial\left[RT\ln\frac{p}{p_0}+\int_0^p\left(V-\frac{RT}{p}\right)dp\right]}{\partial T}\right\}_p$$

$$=-R\ln\frac{p}{p_0}+\int_0^p\left[\frac{R}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

- 标准化处理后得：

$$\frac{S-S_0^{ig}}{R}+\ln\frac{p}{p_0}=\frac{1}{R}\int_0^p\left[\frac{R}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp \qquad (3\text{-}39)$$

- 3 其它偏离函数
- 由热力学基本关系式，经过数学推导可得其它偏离函数

1）偏离焓

$$H = G + TS$$

$$H - H^{ig} = \left(G - G^{ig}\right) + T\left(S - S^{ig}\right)$$

$$= \left[\cancel{RT\ln\frac{p}{p_0}} + \int_0^p \left(V - \frac{RT}{p}\right)dp\right] + T\left\{\cancel{-R\ln\frac{p}{p_0}} + \int_0^p \left[\frac{R}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right]dp\right\}$$

$$= \int_0^p \left[V \cancel{-\frac{RT}{p}} \cancel{+\frac{RT}{p}} - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

$$\Rightarrow \frac{H - H^{ig}}{RT} = \frac{1}{RT}\int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

2）偏离热力学能

$$U = H - pV$$

$$U - U^{ig} = \left(H - H^{ig}\right) - p\left(V - V^{ig}\right)$$

$$= \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp - pV + pV^{ig}$$

$$= \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp - ZRT + RT$$

$$\Rightarrow \frac{U - U^{ig}}{RT} = 1 - Z + \frac{1}{RT}\int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

3）偏离亥氏函数

$$A = U - TS$$

$$\frac{A - A_0^{ig}}{RT} - \ln\frac{p}{p_0} = 1 - Z + \frac{1}{RT}\int_0^p \left[V - \left(\frac{RT}{p}\right)\right]dp$$

4）偏离等压热容

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

$$\frac{C_P-C_p^{ig}}{R}=-\frac{T}{R}\int_0^p\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp$$

以T、p为独立变量时，适合于以V为显函数的状态方程$V=V(T,p)$来推导偏离函数

- 例 P40 3-2

偏离焓3-43 $$\frac{H-H^{ig}}{RT}=\frac{1}{RT}\int_0^p\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

$$p(V-b)=RT+\frac{ap^2}{T}\Rightarrow V=\frac{RT}{p}+\frac{ap}{T}+b$$

$$V=\frac{RT}{p}+\frac{ap}{T}+b$$

$$\left(\frac{\partial V}{\partial T}\right)_p=\frac{R}{p}-\frac{ap}{T^2}$$

$$=\frac{1}{RT}\int_0^p\left[\left(\frac{RT}{p}+\frac{ap}{T}+b\right)-T\left(\frac{R}{p}-\frac{ap}{T^2}\right)\right]dp$$

$$=\frac{1}{RT}\int_0^p\left[\frac{2ap}{T}+b\right]dp$$

$$=\frac{1}{RT}\left(\frac{ap^2}{T}+bp\right)\Bigg|_0^p=\frac{1}{RT}\left(\frac{ap^2}{T}+bp\right)$$

偏离熵3-39

$$V=\frac{RT}{p}+\frac{ap}{T}+b$$

$$\left(\frac{\partial V}{\partial T}\right)_p=\frac{R}{p}-\frac{ap}{T^2}$$

$$\frac{S-S_0^{ig}}{R}+\ln\frac{p}{p_0}=\frac{1}{R}\int_0^p\left[\frac{R}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

$$=\frac{1}{R}\int_0^p\left[\frac{R}{p}-\left(\frac{R}{p}-\frac{ap}{T^2}\right)\right]dp$$

$$=\frac{1}{R}\int_0^p\frac{ap}{T^2}dp=\frac{ap^2}{2RT^2}$$

偏离摩尔定压热容3-46

$$V=\frac{RT}{p}+\frac{ap}{T}+b$$

$$\left(\frac{\partial V}{\partial T}\right)_p=\frac{R}{p}-\frac{ap}{T^2}$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_p=\frac{2ap}{T^3}$$

$$\frac{C_P-C_p^{ig}}{R}=-\frac{T}{R}\int_0^p\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp$$

$$=-\frac{T}{R}\int_0^p\frac{2ap}{T^3}dp$$

$$=-\frac{1}{R}\int_0^p\frac{2ap}{T^2}dp=-\frac{ap^2}{RT^2}$$

$$\Rightarrow C_P=C_p^{ig}-\frac{ap^2}{T^2}=c+\frac{d}{T}-\frac{ap^2}{T^2}$$

$$H-H^{ig}=\frac{ap^2}{T}+bp \qquad \int_{T_1}^{T_2} C_p^{ig}\,\mathrm{d}T=\int_{T_1}^{T_2}\left(c+\frac{d}{T}\right)\mathrm{d}T$$

- 计算状态1→2的焓变

$$H(T_2,p_2)-H(T_1,p_1)=\left[H(T_2,p_2)-H^{ig}(T_2)\right]$$

$$-\left[H(T_1,p_1)-H^{ig}(T_1)\right]+\left[H^{ig}(T_2)-H^{ig}(T_1)\right]$$

$$=\left(\frac{ap_2^2}{T_2}+bp_2\right)-\left(\frac{ap_1^2}{T_1}+bp_1\right)+\int_{T_1}^{T_2}\left(c+\frac{d}{T}\right)\mathrm{d}T$$

$$= a\left(\frac{p_2^2}{T_2} - \frac{p_1^2}{T_1}\right) + b\left(p_2 - p_1\right) + c\left(T_2 - T_1\right) + d\ln\left(\frac{T_2}{T_1}\right)$$

- 假设：a=2000MPa^{-1}·K$^{0.5}$·cm^3·mol^{-1}, b=4cm^3·mol^{-1}, c=9MPa·K^{-1}·cm^3·mol^{-1}, d=0.2MPa·cm^3·mol^{-1}, p_1=0.5MPa, T_1=298K, p_2=2MPa, T_2=373K, 状态1→2的焓变值=?

$$\Delta H = a\left(\frac{p_2^2}{T_2} - \frac{p_1^2}{T_1}\right) + b\left(p_2 - p_1\right) + c\left(T_2 - T_1\right) + d\ln\left(\frac{T_2}{T_1}\right)$$

- 同理 $S(T_2,p_2)-S(T_1,p_1)=\left[S(T_2,p_2)-S^{ig}(T_2,p_2)\right]$

$$-\left[S(T_1,p_1)-S^{ig}(T_1,p_1)\right]+\left[S^{ig}(T_2,p_2)-S^{ig}(T_1,p_1)\right]$$

$$S-S^{ig}=\frac{ap^2}{2T^2}$$

$$\int_{T_1}^{T_2}\left(\frac{C_p^{ig}}{T}\right)\mathrm{d}T-R\ln\frac{p_2}{p_1}$$

$$=\frac{ap_2^2}{2T_2^2}-\frac{ap_1^2}{2T_1^2}+\int_{T_1}^{T_2}\left(\frac{c+\frac{d}{T}}{T}\right)\mathrm{d}T-R\ln\frac{p_2}{p_1}$$

$$=\frac{a}{2}\left(\frac{p_2^2}{T_2^2}-\frac{p_1^2}{T_1^2}\right)+c\ln\left(\frac{T_2}{T_1}\right)-d\left(\frac{1}{T_2}-\frac{1}{T_1}\right)-R\ln\frac{p_2}{p_1}$$

- § 3-6 *T*，*V*为独立变量的偏离函数
- 工程上用得更多地*p-V-T*关系是以*p*为显函数的$p=p$（*T*，*V*）形式的状态方程，这时，以T，V为独立变量使用起来更方便。
- 推导的变化途径如图

$$M(T,V)-M^{ig}(T,V^0)$$

参考态(T, V^0的理想气体) → 研究态(T,V)

$$dA=-SdT-pdV$$

理想气体

$$p^{ig}=RT/V$$

中间态($T,V\to\infty$)

实际系统

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

$$dU=TdS-pdV$$

$$dH=TdS+Vdp$$

$$dA=-SdT-pdV$$

$$dG=-SdT+Vdp$$

1 偏离亥氏函数

- 由基本关系式$dA=-SdT-pdV$，可得等温条件下$[dA=-pdV]_T$
- 按照所设计的变化途径积分得，

$$A(T,V)-A^{ig}(T,V_0)=\int_{V_0}^{\infty}-p^{ig}dV+\int_{\infty}^{V}-pdV$$

$$=-\int_{V_0}^{\infty}\frac{RT}{V}dV-\int_{\infty}^{V}pdV$$

$$=\left[-\int_{V_0}^{\infty}\frac{RT}{V}dV-\int_{\infty}^{V}\frac{RT}{V}dV\right]-\left[\int_{\infty}^{V}pdV-\int_{\infty}^{V}\frac{RT}{V}dV\right]$$

$$=-\left[\int_{V_0}^{V}\frac{RT}{V}dV\right]-\left[\int_{\infty}^{V}\left(p-\frac{RT}{V}\right)dV\right]$$

$$=-RT\ln\frac{V}{V_0}+\left[\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV\right]$$

$p=p(T,V)$ 代入状态方程的具体形式积分计算

❖ 即偏离亥氏函数为

$$A-A_0^{ig}=-RT\ln\frac{V}{V_0}+\left[\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV\right]$$

由于 $$\frac{V}{V_0}=\frac{ZRT/p}{RT/p_0}=Z\left(\frac{p_0}{p}\right)$$

所以又有

$$A-A_0^{ig}=-RT\ln Z+RT\ln\frac{p}{p_0}+\left[\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV\right]$$

- 标准化处理后得

$$\frac{A-A_0^{ig}}{RT}-\ln\frac{p}{p_0}=-\ln Z+\frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV \quad (3\text{-}51)$$

2 偏离熵

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

$$S-S_0^{ig}=-\left[\frac{\partial\left(A-A_0^{ig}\right)}{\partial T}\right]_V$$

$$=-\left\{\frac{\partial\left[-RT\ln\frac{V}{V_0}+\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV\right]}{\partial T}\right\}_V$$

$$= R\ln\frac{V}{V_0} + \int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{R}{V}\right]dV$$

$$= R\ln Z - R\ln\frac{p}{p_0} + \int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{R}{V}\right]dV$$

- 标准化处理后得

$$\frac{S - S_0^{ig}}{R} + \ln\frac{p}{p_0} = \ln Z + \frac{1}{R}\int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{R}{V}\right]dV$$

- 3 其它偏离函数
- 由定义式及热力学基本关系式，经过数学推导可得其它偏离函数
- 1）偏离热力学能
- U=A+TS

$$\frac{U-U_0^{ig}}{RT}=\frac{1}{RT}\int_{\infty}^{V}\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV$$

2）偏离焓

- H=U+pV

$$\frac{H-H_0^{ig}}{RT}=Z-1+\frac{1}{RT}\int_{\infty}^{V}\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV$$

3）偏离吉氏函数

- G=H-TS=A+ pV

$$\frac{G-G_0^{ig}}{RT}-\ln\frac{p}{p_0}=Z-1-\ln Z+\frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV$$

4）偏离等容热容

$$\frac{C_V - C_V^{ig}}{R} = \frac{T}{R}\int_{\infty}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV$$

5）偏离等压热容

$$\frac{C_p - C_p^{ig}}{R} = \frac{T}{R}\int_{\infty}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV - \frac{T}{R}\frac{\left(\partial p/\partial T\right)_V^2}{\left(\partial p/\partial V\right)_T} - 1$$

以T、V为独立变量的$C_p(T,V)$的偏离函数在工程上应用较多。

❖ 例： 气体符合van der Waals（vdW）方程，导出偏离亥氏函数、偏离焓、偏离熵、偏离等容热容

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

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

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0$$

❖ 偏离亥氏函数

$$\frac{A-A_0^{ig}}{RT}-\ln\frac{p}{p_0}=-\ln Z+\frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V}-p\right)dV$$

$$=-\ln Z+\frac{1}{RT}\int_{\infty}^{V}\left[\frac{RT}{V}-\left(\frac{RT}{V-b}-\frac{a}{V^2}\right)\right]dV$$

$$=-\ln Z+\int_{\infty}^{V}\left(\frac{1}{V}-\frac{1}{V-b}\right)dV+\frac{1}{RT}\int_{\infty}^{V}\frac{a}{V^2}dV$$

$$=-\ln Z+\ln\frac{V}{V-b}-\frac{a}{RTV}$$

偏离熵

$$\frac{S-S_0^{ig}}{R}+\ln\frac{p}{p_0}=\ln Z+\frac{1}{R}\int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V-\frac{R}{V}\right]dV$$

$$=\ln Z+\frac{1}{R}\int_{\infty}^{V}\left[\frac{R}{(V-b)}-\frac{R}{V}\right]dV$$

$$=\ln Z+\ln\frac{V-b}{V}$$

偏离焓

$$\frac{H-H_0^{ig}}{RT}=Z-1+\frac{1}{RT}\int_{\infty}^{V}\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV$$

$$=Z-1+\frac{1}{RT}\int_{\infty}^{V}\left[T\cancel{\frac{R}{V-b}}-\left(\cancel{\frac{RT}{V-b}}-\frac{a}{V^2}\right)\right]dV$$

$$=Z-1+\frac{1}{RT}\int_{\infty}^{V}\frac{a}{V^2}dV=Z-1-\frac{a}{RTV}$$

偏离等容热容

$$\frac{C_V - C_V^{ig}}{R} = \frac{T}{R}\int_{\infty}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV$$

$$= 0$$

- 常用状态方程的偏离焓、偏离熵、偏离定压热容见 P47表3-1

- 练习3.3：
- 1 某流体符合状态方程$p(V-b)=RT$，写出以T,p为独立变量的状态方程，以T,V为独立变量的状态方程。
- 2 某流体符合状态方程$p(V-b)=RT$，推导其偏离焓、偏离熵与p-V-T的关系（以T,p为独立变量；以T,V为独立变量）

以T,p为独立变量的计算为例

$$p(V-b)=RT \qquad V=\frac{RT}{p}+b$$

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

$$H-H^{ig}=\int_0^P\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dp=\int_0^P\left[\frac{RT}{p}+b-T\frac{R}{p}\right]dp=bp$$

$$S-S_0^{ig}+R\ln\frac{p}{p_0}=\int_0^P\left[\frac{R}{p}-\left(\frac{\partial V}{\partial T}\right)_p\right]dp=\int_0^P\left[\frac{R}{p}-\frac{R}{p}\right]dp=0$$

以T,V为独立变量计算为例

$$p(V-b)=RT$$

$$p=\frac{RT}{V-b}$$

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

$$\frac{H-H_0^{ig}}{RT}=Z-1+\frac{1}{RT}\int_{\infty}^{V}\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV$$

$$=Z-1+\frac{1}{RT}\int_{\infty}^{V}\left[\cancel{T\left(\frac{R}{V-b}\right)}-\cancel{p}\right]dV$$

$$=Z-1=\frac{pV}{RT}-1=\frac{b}{V-b}$$

$$\frac{S-S_0^{ig}}{R}+\ln\frac{p}{p_0}=\ln Z+\frac{1}{R}\int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V-\frac{R}{V}\right]dV$$

$$=\ln Z+\frac{1}{R}\int_{\infty}^{V}\left[\frac{R}{(V-b)}-\frac{R}{V}\right]dV$$

$$=\ln Z+\ln\frac{V-b}{V}=\ln\frac{p\cancel{V}}{RT}\cdot\frac{V-b}{\cancel{V}}=\ln 1=0$$