

# 第3章 流体的热力学性质

## 本章内容

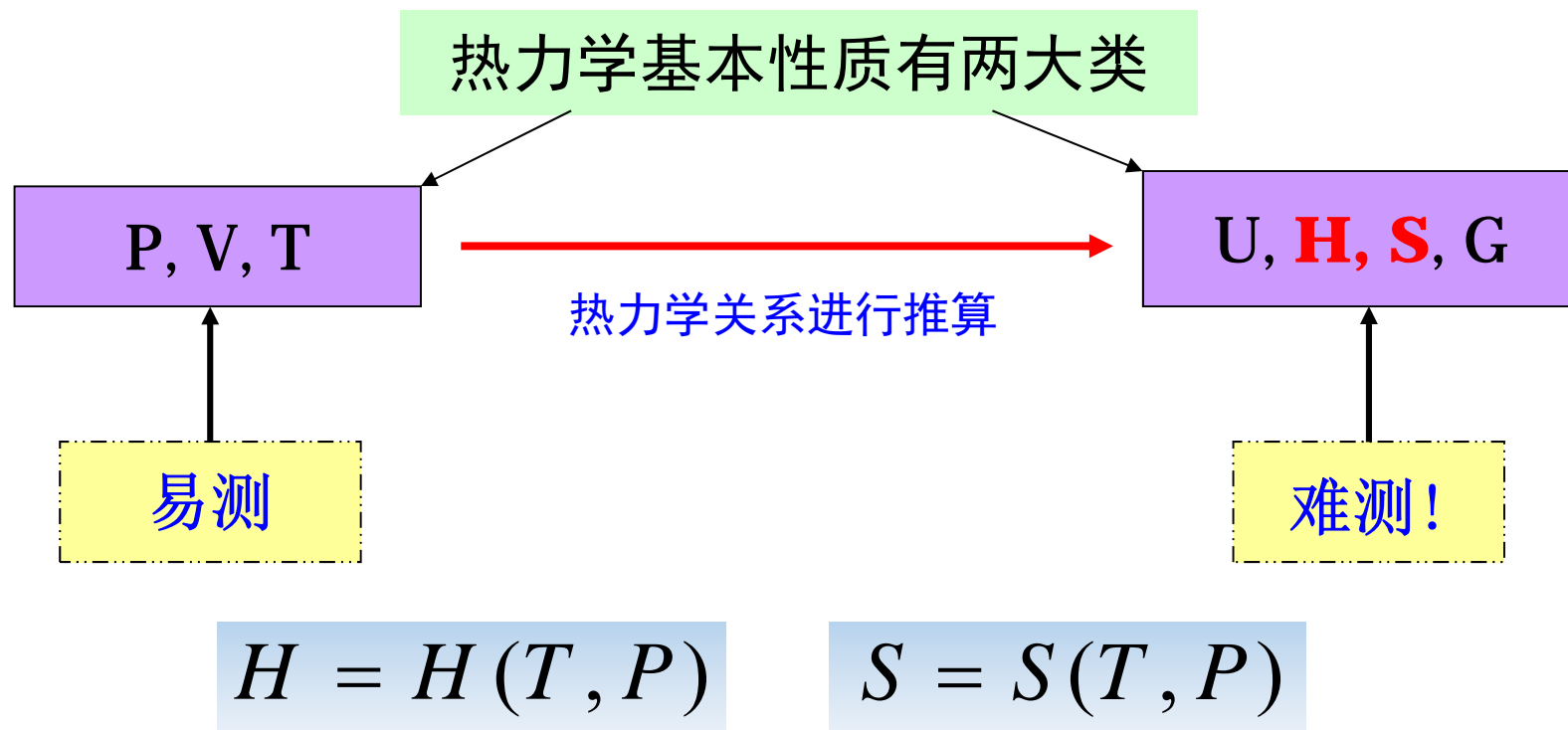
- 3.1 流体的热力学关系
- 3.2 焓变和熵变的计算
- 3.3 两相系统的热力学性质
- 3.4 常用的热力学图表

## The 1<sup>st</sup> Law:

$$\frac{dE}{dt} = \sum_i m_i \left( H_{m,i} + gz_i + \frac{1}{2} u_i^2 \right) + \sum_i \frac{dQ_i}{dt} + \sum_i \frac{dW_{si}}{dt}$$

## The 2<sup>nd</sup> Law:

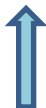
$$\Delta S_{iso} = \Delta S_{sys} + \Delta S_{sur} \geq 0$$



## 3.1 流体的热力学关系

闭口系热力学第一定律

$$dU = TdS - pdV$$



$$H \equiv U + pV$$

$$A \equiv U - TS$$

$$G \equiv H - TS$$

热力学基本关系式

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

状态参数的微分特征

设  $z = z(x, y)$

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

充要条件:

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

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

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

$$dU = TdS - pdV$$

类似地,

$$dH = TdS + Vdp$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

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

$$\begin{aligned} \left( \frac{\partial U}{\partial S} \right)_V &= T \\ \left( \frac{\partial U}{\partial V} \right)_S &= -p \end{aligned}$$

$$\begin{aligned} \left( \frac{\partial U}{\partial S} \right)_V &= \left( \frac{\partial H}{\partial S} \right)_p = T \\ \left( \frac{\partial U}{\partial V} \right)_T &= \left( \frac{\partial A}{\partial V} \right)_T = -p \\ \left( \frac{\partial H}{\partial p} \right)_S &= \left( \frac{\partial G}{\partial p} \right)_T = V \\ \left( \frac{\partial A}{\partial T} \right)_V &= \left( \frac{\partial G}{\partial T} \right)_p = -S \end{aligned}$$

系数关系式

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



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



$$\left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y$$

### Maxwell关系式

$$dU = TdS - pdV$$



$$dH = TdS + Vdp$$



$$dA = -pdV - SdT$$



$$dG = Vdp - SdT$$



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

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

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

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

## 总结

函数	独立变数	微分式	Maxwell 关系式	系数关系式
$\Delta U = Q - W$	$U = f(S, V)$	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$\left(\frac{\partial U}{\partial V}\right)_S = -P, \left(\frac{\partial U}{\partial S}\right)_V = T$
$H = U + PV$	$H = f(S, P)$	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$\left(\frac{\partial H}{\partial P}\right)_S = V, \left(\frac{\partial H}{\partial S}\right)_P = T$
$A = U - TS$	$A = f(V, T)$	$dA = -PdV - SdT$	$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$	$\left(\frac{\partial A}{\partial T}\right)_V = -S, \left(\frac{\partial A}{\partial V}\right)_T = -P$
$G = H - TS$	$G = f(P, T)$	$dG = VdP - SdT$	$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$	$\left(\frac{\partial G}{\partial T}\right)_P = -S, \left(\frac{\partial G}{\partial P}\right)_T = V$

## 其他有用的定义式

定压比热容

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

定容比热容

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

## 3.2 焓变和熵变的计算

焓变的计算

$$H = H(T, P)$$

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

$$\left( \frac{\partial H}{\partial T} \right)_P = C_P$$

$$dH = TdS + VdP$$



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

The Maxwell Eqn

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

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



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

## 3.2 焓变和熵变的计算

熵变的计算

$$S = S(T, P)$$

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

$$dH = TdS + VdP$$



$$\left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

$$\left( \frac{\partial H}{\partial T} \right)_P = C_P$$

$$\left( \frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}$$

The Maxwell Eqn

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



$$dS = \frac{C_P}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$



理想气体的焓变和熵变的计算

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

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

For ideal gas:  $V = \frac{RT}{P}$

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

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

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P = 0$$

$$dH = C_p dT$$

$$dS = \frac{C_p}{T} dT - \frac{R}{P} dP$$

理想气体的焓变和熵变的计算(续)

$$dH = C_P dT$$

$$dS = \frac{C_P}{T} dT - \frac{R}{P} dP$$

从标准状态0到温度T,压力P积分得,

$$H^{id} = H_0^{id} + \int_{T_0}^T C_P^{id} dT$$

$$S^{id} = S_0^{id} + \int_{T_0}^T C_P^{id} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

为了方便改写成,

$$H^{id} = H_0^{id} + C_{pmH}^{id} (T - T_0) \quad S^{id} = S_0^{id} + C_{pmS}^{id} \ln(T/T_0) - R \ln(p/p_0)$$

其中,

$$C_{pmH}^{id} = \frac{\int_{T_0}^T C_P^{id} dT}{T - T_0}$$

$$C_{pmS}^{id} = \frac{\int_{T_0}^T C_P^{id} \frac{dT}{T}}{\ln \frac{T}{T_0}}$$

$C_p^{id}$  只是温度的函数,

$$C_p^{id} = a + bT + cT^{-2} \quad \text{or} \quad C_p^{id}/R = A + BT + CT^2 + DT^{-2}$$

从温度 $T_1$ 到温度 $T_2$ 积分得,

$$C_{pmH}^{id}/R = A + BT_{am} + (C/3)(4T_{am}^2 - T_1T_2) + D/(T_1T_2)$$

$$C_{pmS}^{id}/R @ A + BT_{lm} + T_{am}T_{lm} + C + D/(T_1T_2),$$

$$T_{am} @ \frac{T_1 + T_2}{2}$$

$$T_{lm} = \frac{T_2 - T_1}{\ln(T_2/T_1)}$$

**Ex3.1 计算氯气从 $T_1=500\text{K}$ ,  $P_1=1.013 \times 10^7\text{Pa}$ 到 $T_2=300\text{K}$ ,  $P_2=1.013 \times 10^5\text{Pa}$ 过程中的焓变和熵变。**

$$H^{id} = H_0^{id} + \int_{T_0}^T C_P^{id} dT$$

$$S^{id} = S_0^{id} + \int_{T_0}^T C_P^{id} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

氯气的理想气体热容表达式为

$$C_{pg}^{ig} = R(3.056 + 5.3708 \times 10^{-3} T - 0.8098 \times 10^{-5} T^2 + 0.5693 \times 10^{-8} T^3 - 0.15256 \times 10^{-11} T^4)$$

$$\begin{aligned} \Delta H^{ig} &= \int_{T_1}^{T_2} C_{pg}^{ig} dT \\ &= 8.314 \times \int_{300}^{500} (3.056 + 5.3708 \times 10^{-3} T - 0.8098 \times 10^{-5} T^2 + 0.5693 \times 10^{-8} T^3 - 0.15256 \times 10^{-11} T^4) dT \\ &= \left\{ 8.314 \times \left[ 3.056 \times (T_2 - T_1) + \frac{5.3708 \times 10^{-3}}{2} \times (T_2^2 - T_1^2) - \frac{0.8098 \times 10^{-5}}{3} (T_2^3 - T_1^3) + \right. \right. \\ &\quad \left. \left. \frac{0.5693 \times 10^{-8}}{4} (T_2^4 - T_1^4) - \frac{0.15256 \times 10^{-11}}{5} (T_2^5 - T_1^5) \right] \right\} \\ &= 7025.0 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned}
\Delta S^{\text{ig}} &= \Delta S_T^{\text{ig}} + \Delta S_p^{\text{ig}} = R \ln \frac{p_1}{p_2} + \int_{300}^{500} \frac{C_{p,g}^{\text{ig}}}{T} dT \\
&= 8.314 \ln \frac{0.1013}{10.13} + 8.314 \\
&\quad \times \int_{255.15}^{366.15} (3.056 + 5.3708 \times 10^{-3} T - 0.8098 \times 10^{-5} T^2 + 0.5693 \times 10^{-8} T^3 - 0.15256 \times 10^{-11} T^4) \frac{dT}{T} \\
&= 8.314 \ln \frac{0.1013}{10.13} + 8.314 \times \\
&\quad \left[ 3.056 \times \ln \frac{500}{300} + 5.3708 \times 10^{-3} \times (T_2 - T_1) - \frac{0.8098}{2} \times 10^{-5} \times (T_2^2 - T_1^2) + \right. \\
&\quad \left. \frac{0.5693}{3} \times 10^{-8} \times (T_2^3 - T_1^3) - \frac{0.15256}{4} \times 10^{-11} \times (T_2^4 - T_1^4) \right] \\
&= (-38.287 + 17.897) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -20.391 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
\end{aligned}$$

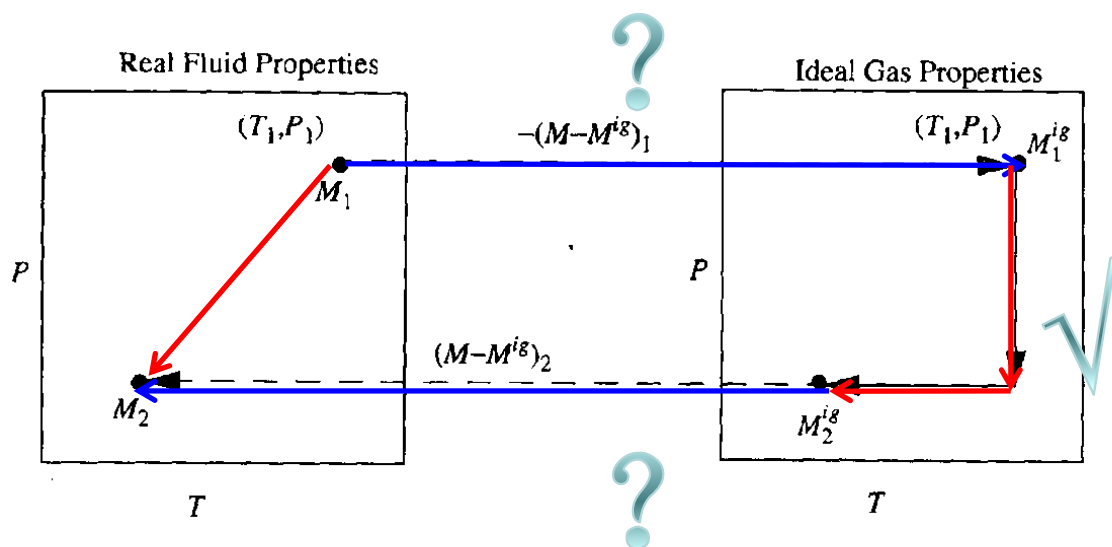
## 剩余性质的引入

### 真实气体的焓变和熵变的计算

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

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

真实气体的定压比热容不容易获得，因此要绕开真实气体的定压比热容。



- 过程1：实际流体  $(T_1, P_1) \Rightarrow$  与该实际流体有相同分子式的假想理想气体  $(T_1, P_1)$ ；(相同  $\{T, P\}$ )
- 过程2：假想理想气体  $(T_1, P_1) \Rightarrow (T_2, P_2)$
- 过程3：假想理想气体  $(T_2, P_2) \Rightarrow$  实际流体  $(T_2, P_2)$  (相同  $\{T, P\}$ )

点函数在两状态间的数值变化与路径无关

## 剩余性质

## Residual Properties

定义

$$M^R = M - M^{id}$$

M代表摩尔热力学性质

在等温条件下对P微分得,

$$\left(\frac{\partial M^R}{\partial P}\right)_T = \left(\frac{\partial M}{\partial P}\right)_T - \left(\frac{\partial M^{id}}{\partial P}\right)_T \implies d(M^R) = \left[ \left(\frac{\partial M}{\partial P}\right)_T - \left(\frac{\partial M^{id}}{\partial P}\right)_T \right] dP$$

从P→0到P进行积分,

$$M^R = (M^R)_0 + \int_{P \rightarrow 0}^P \left[ \left(\frac{\partial M}{\partial P}\right)_T - \left(\frac{\partial M^{id}}{\partial P}\right)_T \right] dP$$

当P→0时, 对于H和S来说,  $(M^R)_0 = 0$

$$M^R = \int_{P \rightarrow 0}^P \left[ \left(\frac{\partial M}{\partial P}\right)_T - \left(\frac{\partial M^{id}}{\partial P}\right)_T \right] dP$$

$$M^R = \int_{P \rightarrow 0}^P \left[ \left( \frac{\partial M}{\partial P} \right)_T - \left( \frac{\partial M^{id}}{\partial P} \right)_T \right] dP$$

当M=H时,

$$\because \left( \frac{\partial H^{id}}{\partial P} \right)_T = 0, \left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$

$$H^R = \int_0^P \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

当M=S时,

$$\text{又} \because \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P, \left( \frac{\partial V^{id}}{\partial T} \right)_P = \frac{R}{P}$$

$$S^R = \int_0^P \left[ \frac{R}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

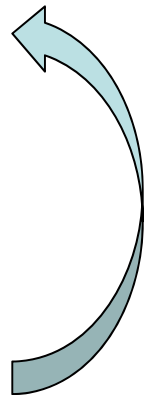
对于实际气体满足,

$$V = \frac{ZRT}{P}$$

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{ZR}{P} + \frac{RT}{P} \left( \frac{\partial Z}{\partial T} \right)_P$$

$$\frac{H^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

$$\frac{S^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dp}{P} - \int_0^P (Z - 1) \frac{dP}{P}$$



## 剩余焓和剩余熵的计算方法

$$\begin{aligned}\frac{H_m^R}{RT} &= \int_0^P \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP \\ &= -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}\end{aligned}$$

$$\begin{aligned}\frac{S_m^R}{R} &= \int_0^P \left[ \frac{R}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dP \\ &= -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dp}{P} - \int_0^P (Z - 1) \frac{dP}{P}\end{aligned}$$

状态方程法

维里方程

立方型状态方程

普遍化方法

普遍化维里系数法

普遍化压缩因子法



## 剩余焓和剩余熵的计算方法-二阶维里方程

$$Z = \frac{PV}{RT} = 1 + B'P = 1 + \frac{BP}{RT}$$

$$V = \frac{RT}{P} + B$$

在等压条件下对T求导得,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

$$V - T\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{P} + B - T\left(\frac{R}{P} + \frac{dB}{dT}\right) = B - T\frac{dB}{dT}$$

$$H^R = \int_0^P \left[ V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

$$H^R = \int_0^P \left[ V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP = \int_0^P \left[ B - T\frac{dB}{dT} \right] dP = \left[ B - T\frac{dB}{dT} \right] P$$

$$S^R = \int_0^P \left[ \frac{R}{P} - \left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

$$s^R(T, P) = -P \frac{dB}{dT}$$

## 剩余焓和剩余熵的计算方法-RK方程

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \quad b = \frac{0.08664RT_c}{P_c}$$

$$H^R = \int_0^P \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$$

RK方程  $p=f(T,V)$

$$H^R = PV - RT + \int_\infty^V \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \quad (T \text{一定}) \quad \Leftrightarrow \quad \left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{v-b} + \frac{0.5a}{T^{1.5}v(v+b)}$$

$$\frac{H^R}{RT} = Z - 1 - \frac{1.5a}{bRT^{1.5}} \ln \left( 1 + \frac{b}{V} \right)$$

类似的有,

$$\frac{S^R}{R} = \ln \frac{P(V-b)}{RT} - \frac{a}{2bRT^{1.5}} \ln \left( 1 + \frac{b}{V} \right)$$

SRK方程

$$\frac{H^R}{RT} = Z - 1 - \frac{1}{bRT} \left[ a - T \left( \frac{da}{dT} \right) \right] \ln \left( 1 + \frac{b}{V} \right)$$

$$\frac{S^R}{R} = \ln \frac{P(V-b)}{RT} + \frac{1}{bR} \left( \frac{da}{dT} \right) \ln \left( 1 + \frac{b}{V} \right)$$

PR方程

$$\frac{H^R}{RT} = Z - 1 - \frac{1}{2\sqrt{2}bRT} \left[ a - T \left( \frac{da}{dT} \right) \right] \ln \frac{V + (\sqrt{2}+1)b}{V - (\sqrt{2}-1)b}$$

$$\frac{S^R}{R} = \ln \frac{P(V-b)}{RT} - \frac{1}{2\sqrt{2}bRT^{1.5}} \left( \frac{da}{dT} \right) \ln \frac{V + (\sqrt{2}+1)b}{V - (\sqrt{2}-1)b}$$

### 剩余焓和剩余熵的计算方法-RK方程(续)

$$\frac{H^R}{RT} = Z - 1 - \frac{1.5a}{bRT^{1.5}} \ln \left( 1 + \frac{b}{V} \right)$$

$$\frac{S^R}{R} = \ln \frac{P(V-b)}{RT} - \frac{a}{2bRT^{1.5}} \ln \left( 1 + \frac{b}{V} \right)$$

$$\text{设 } h = \frac{b}{V_m} = \frac{Bp}{Z} \quad \frac{A}{B} = \frac{a}{bRT^{1.5}}$$

$$\text{故有 } \frac{H_m - H_m^{id}}{RT} = \frac{H_m^R}{RT} = Z - 1 - \frac{3}{2} \frac{A}{B} \ln(1+h) \quad \text{等温条件下}$$

同理可得：

$$\frac{S_m - S_m^{ig}}{R} = \frac{S_m^R}{R} = \ln [Z(1-h)] - \frac{1}{2} \frac{A}{B} \ln(1+h)$$

**Ex 3.2.** 利用RK方程计算125℃, 10MPa下丙烯的剩余焓H<sup>R</sup>.

解: 查得丙烯的临界值,

$$T_c = 365.6K, p_c = 4.665MPa$$

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} = \frac{0.42748(8.314)^2(365.6)^{2.5}}{4.665 \times 10^6}$$

$$= 16.19 Pa \cdot m^6 \cdot K^{0.5} / mol^2$$

$$b = \frac{0.08664RT_c}{P_c} = \frac{0.08664(8.314)(365.6)}{4.665 \times 10^6} = 5.644 \times 10^{-5} m^3 / mol$$

将以上参数代入RK方程, 并求解 $V_m$ :

$$10 \times 10^6 = \frac{(8.314)(398.15)}{V_m - 5.644 \times 10^{-5}} - \frac{1.619 \times 10^7}{(398.15)^{0.5} V_m (V_m + 5.644 \times 10^{-5})}$$
$$V_m = 1.422 \times 10^{-4} m^3 / mol$$

求算  $h$  和  $A/B$  :

$$h = \frac{b}{V_m} = \frac{BP}{Z} = \frac{5.644 \times 10^{-5}}{1.422 \times 10^{-4}} = 0.4004$$

$$\frac{A}{B} = \frac{a}{bRT^{1.5}} = \frac{16.19}{5.644 \times 10^{-5} \times 8.314 \times (398.15)^{1.5}} = 4.331$$

$$\text{故有: } Z = \frac{1}{1-h} - \frac{A}{B} \left( \frac{h}{1+h} \right) = 0.4295$$

$$\frac{H_m - H_m^{id}}{RT} = \frac{H_m^R}{RT} = Z - 1 - \frac{3}{2} \frac{A}{B} \ln(1+h) = -2.758$$

$$H_m^R = (-2.758) \times 8.314 \times 398.15 = -9130.73 \text{ J/mol}$$

$$S_m^R = ? \quad \frac{S_m - S_m^{ig}}{R} = \frac{S_m^R}{R} = \ln [Z(1-h)] - \frac{1}{2} \frac{A}{B} \ln(1+h)$$

## 剩余焓和剩余熵的计算方法-普遍化压缩因子法

$$\frac{H_m^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

$$\frac{S_m^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P}$$

$$P = P_c P_r, T = T_c T_r, dP = P_c dP_r, dT = T_c dT_r$$

$$\frac{H_m^R}{RT_c} = -T_r^2 \int_0^{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{S_m^R}{R} = -T_r \int_0^{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z - 1) \frac{dP_r}{P_r}$$

$$Z = Z^0 + \omega Z^1$$

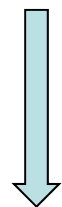
$$\left( \frac{\partial Z}{\partial T_r} \right)_{P_r} = \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} + \omega \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r}$$

$$\frac{H_m^R}{RT_c} = -T_r^2 \int_0^{P_r} \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \omega T_r^2 \int_0^{P_r} \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{S_m^R}{R} = - \int_0^{P_r} \left[ T_r \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} + Z^0 - 1 \right] \frac{dP_r}{P_r} - \omega \int_0^{P_r} \left[ T_r \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r} + Z^1 \right] \frac{dP_r}{P_r}$$

## 剩余焓和剩余熵的计算方法-普遍化压缩因子法

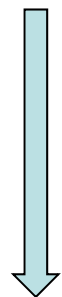
$$\frac{H_m^R}{RT_c} = -T_r^2 \int_0^{P_r} \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \omega T_r^2 \int_0^{P_r} \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$



$$\frac{(H_m^R)^0}{RT_c} = -T_r^2 \int_0^{P_r} \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}; \quad \frac{(H_m^R)^1}{RT_c} = -T_r^2 \int_0^{P_r} \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}$$

$$\frac{S_m^R}{R} = - \int_0^{P_r} \left[ T_r \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} + Z^0 - 1 \right] \frac{dP_r}{P_r} - \omega \int_0^{P_r} \left[ T_r \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r} + Z^1 \right] \frac{dP_r}{P_r}$$



$$\frac{(S_m^R)^0}{R} = - \int_0^{P_r} \left[ T_r \left( \frac{\partial Z^0}{\partial T_r} \right)_{P_r} + Z^0 - 1 \right] \frac{dP_r}{P_r}; \quad \frac{(S_m^R)^1}{R} = - \int_0^{P_r} \left[ T_r \left( \frac{\partial Z^1}{\partial T_r} \right)_{P_r} + Z^1 \right] \frac{dP_r}{P_r}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}$$

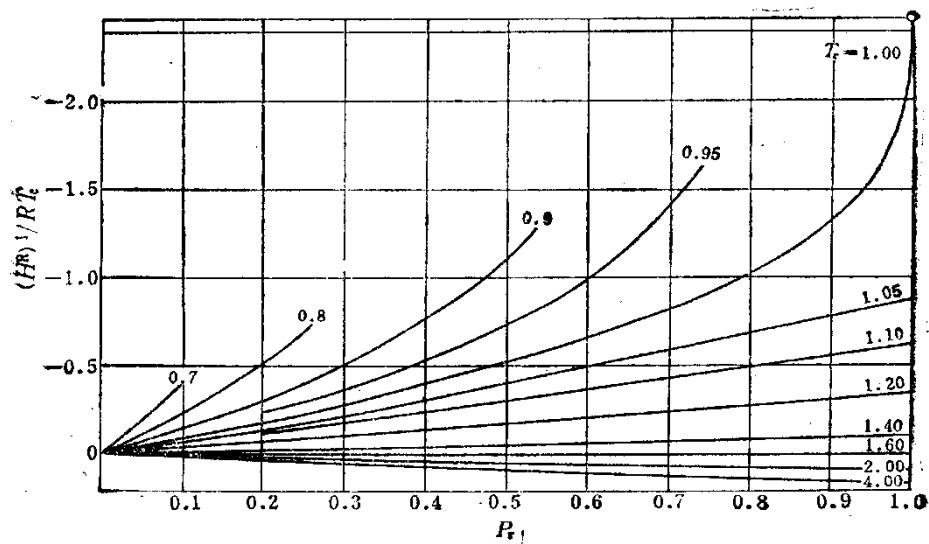
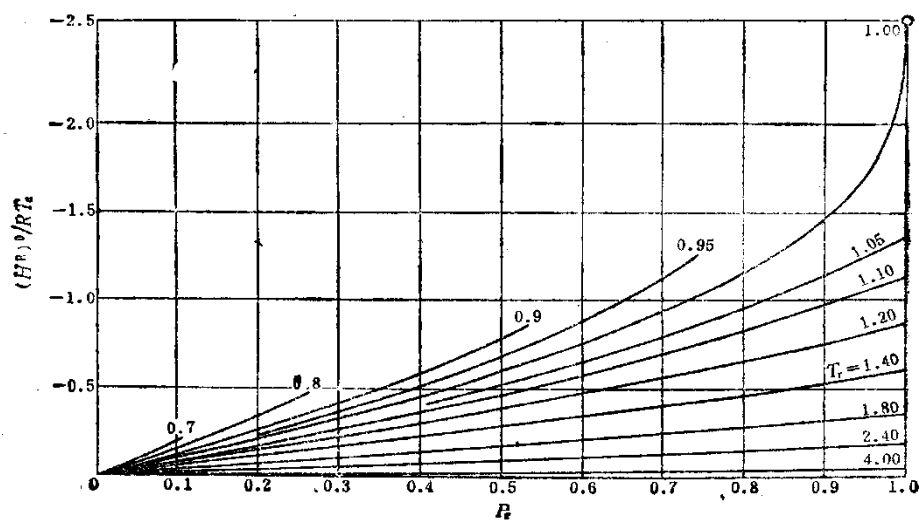
## 剩余焓和剩余熵的计算方法-普遍化压缩因子法

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}$$

在不同的对比温度 $T_r$ 和对比压力 $P_r$ 下，由普遍化关联图查询每一项，

$$\frac{(H^R)^0}{RT_c}, \frac{(H^R)^1}{RT_c}, \frac{(S^R)^0}{R}, \frac{(S^R)^1}{R}$$





## 剩余焓和剩余熵的计算方法-普遍化维里系数法

$$Z = 1 + \frac{BP}{RT} = 1 + \left( \frac{BP_c}{RT_c} \right) \left( \frac{P_r}{T_r} \right) + \frac{BP_c}{RT_c} = B^0 + \omega B^1$$

$$Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r} \Rightarrow \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} = P_r \left( \frac{dB^0 / dT_r}{T_r} - \frac{B^0}{T_r^2} \right) + \omega P_r \left( \frac{dB^1 / dT_r}{T_r} - \frac{B^1}{T_r^2} \right)$$

$$\frac{H_m^R}{RT_c} = -T_r^2 \int_0^{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{S_m^R}{R} = -T_r \int_0^{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z - 1) \frac{dP_r}{P_r}$$

$$\frac{H_m^R}{RT_c} = P_r \left[ B^0 - T_r \frac{dB^0}{dT_r} + \omega \left( B^1 - T_r \frac{dB^1}{dT_r} \right) \right]$$

$$\frac{S_m^R}{R} = -P_r \left( \frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right)$$

其中,

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$

## 实际气体熵变和焓变的计算

对于某系统从状态1变化到状态2：

$$H_2 = H_0^{id} + \int_{T_0}^{T_2} C_p^{id} dT + H_2^R \quad H_1 = H_0^{id} + \int_{T_0}^{T_1} C_p^{id} dT + H_1^R$$

实际路径:  $1 \rightarrow 2$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_p^{id} dT + H_2^R - H_1^R$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p^{id}}{T} dT - nR \ln \frac{p_2}{p_1} + S_2^R - S_1^R$$

假想路径:

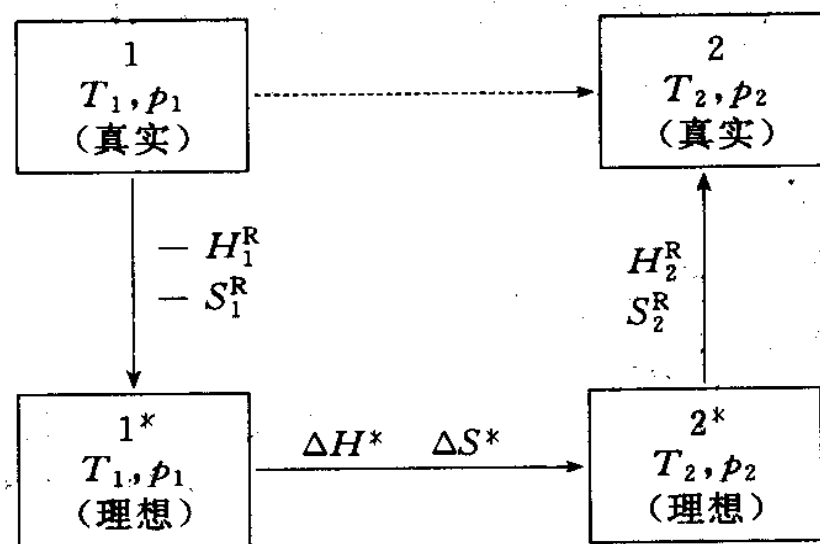
$$1 \rightarrow 1^{id} \quad H_1^{id} - H_1 = -H_1^R$$

$$S_1^{id} - S_1 = -S_1^R$$

$$1^{id} \rightarrow 2^{id} \quad \Delta H^{id} \quad \Delta S^{id}$$

$$2^{id} \rightarrow 2 \quad H_2 - H_2^{id} = H_2^R$$

$$S_2 - S_2^{id} = S_2^R$$



- 例**3.3** 丁烯, 200°C, 7MPa,  $V_m=?$   $H_m=?$   $S_m=?$

解: 从附录中查得热力学参数,

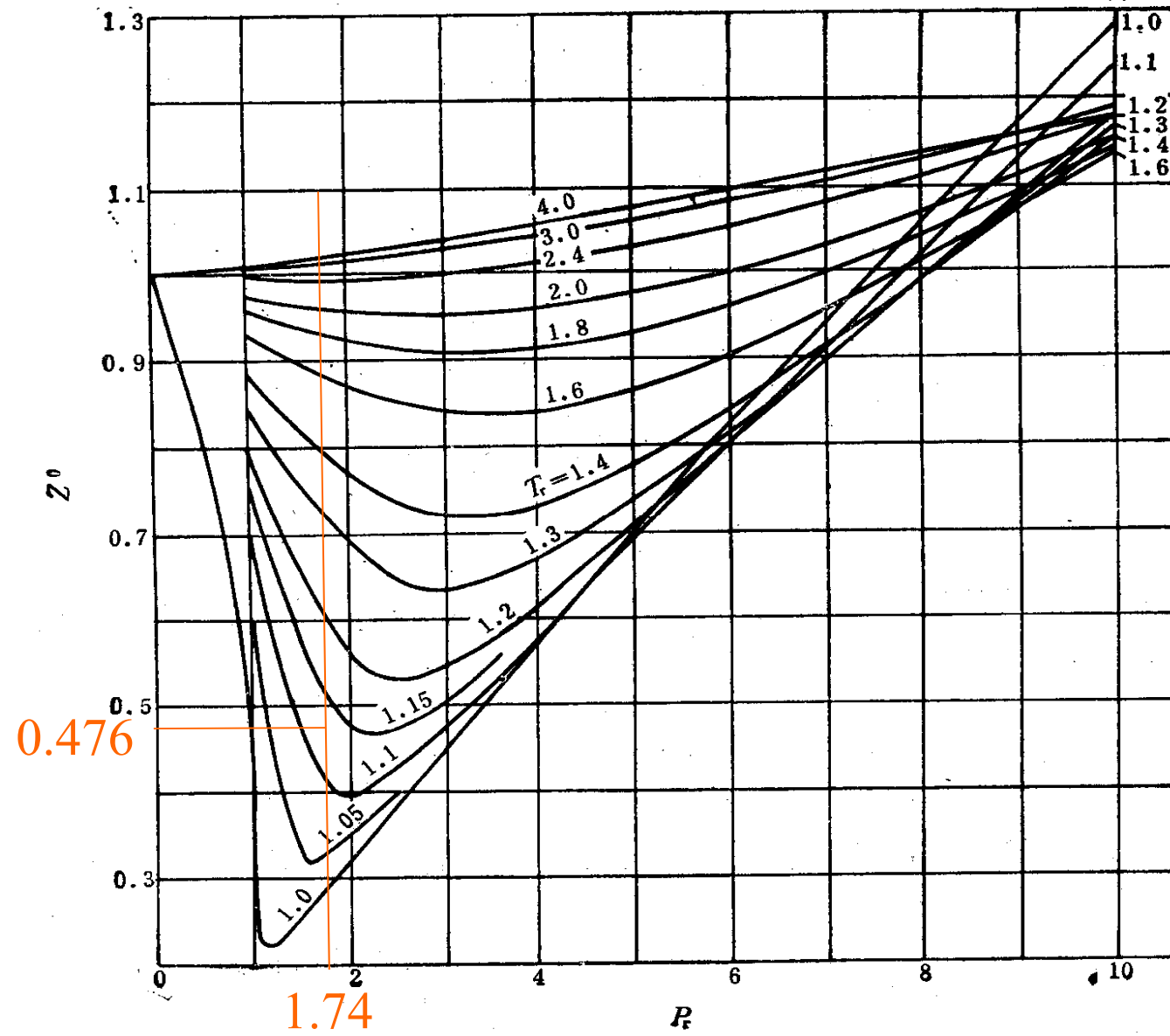
$$T_c = 419.6\text{K}, p_c = 4.02\text{MPa}, \omega = 0.187, T_b = 267\text{K}$$

$$C_{p,m}^{id} / R = 1.967 + 31.630 \times 10^{-3} T - 9.837 \times 10^{-6} T^2 (T : K)$$

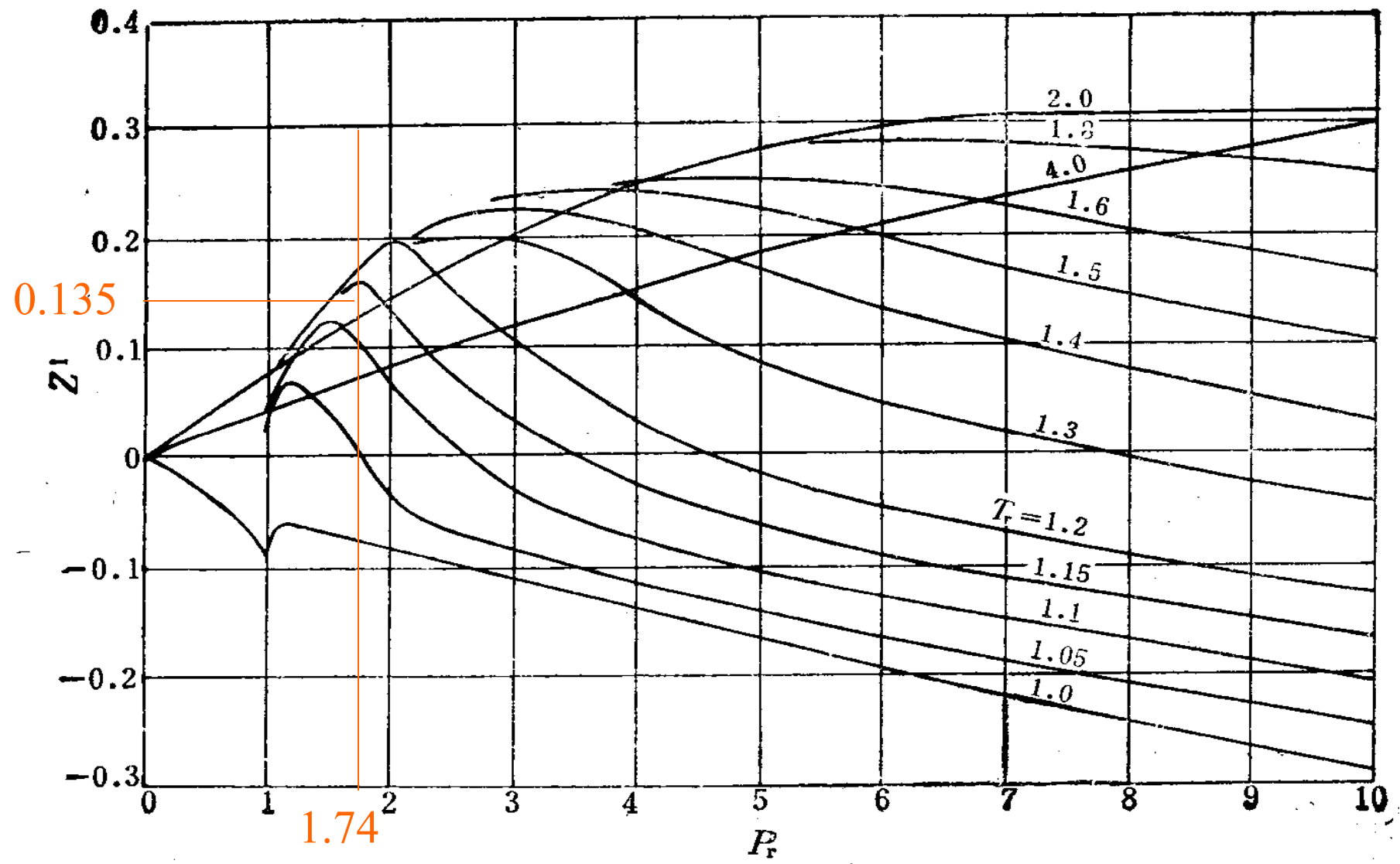
参考态: 饱和液体, 273.15 K,  $H_0 = 0$ ,  $S_0 = 0$     液体 or 气体 ?

$$T_r = \frac{200 + 273.15}{419.6} = 1.13 \qquad p_r = \frac{7}{4.02} = 1.74$$

查找  $Z^0$  和  $Z^1$



p18



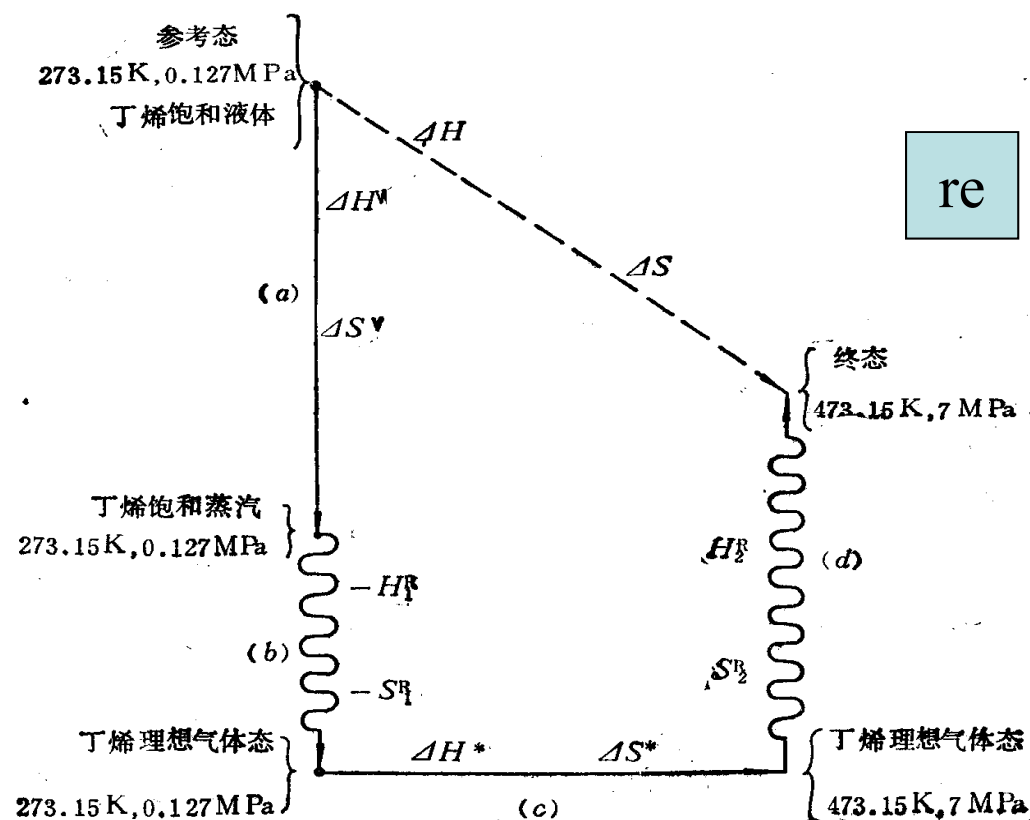
$$Z^0 = 0.476, Z^1 = 0.135$$

$$Z = Z^0 + \omega Z^1 = 0.476 + 0.187 \times 0.135 = 0.501$$

$$V_m = \frac{ZRT}{P} = \frac{0.501 \times 8.314 \times 10^3 \times 473.15}{7 \times 10^6} = 0.2815 \text{ m}^3 \cdot \text{kmol}^{-1}$$

H 和 S:

- (a) 在  $T_1, P_1$  下蒸发
- (b) 在  $T_1, P_1$  下转变为理想气体
- (c) 理想气体从  $T_1, P_1$  变为  $T_2, P_2$
- (d) 在  $T_2, P_2$  下转变为实际气体



(a)

0°C时的蒸汽压力：

$$\ln P^s = A - \frac{B}{T} = 7.8312 - \frac{2702.2}{273.15} = -2.0615$$

根据沸点和临界点获得A和B值：

$$\ln 0.10133 = A - \frac{B}{267} \quad \ln 4.02 = A - \frac{B}{419.6} \quad \begin{matrix} A = 7.8312 \\ B = 2702.2 \end{matrix}$$

$$P^s \Big|_{T=273.15} = 0.1272 \text{ MPa} \quad \text{即：} P_1 = 0.1272 \text{ MPa}$$

沸腾时的蒸发潜热可采用Riedel方程计算：

$$\frac{\Delta H_b^v}{T_b R} = \frac{1.092(\ln P_c + 1.2896)}{0.930 - T_{rb}} = \frac{1.092(\ln 4.02 + 1.2896)}{0.930 - 0.636} = 9.958$$

$$\Delta H_b^v = 9.958 \times 8.314 \times 267 = 22105 \text{ J.mol}^{-1}$$

在其他温度下的蒸发潜热可采用Watson方程计算：

$$\frac{\Delta H_2}{\Delta H_1} = \left( \frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \quad \frac{\Delta H^v}{\Delta H_b^v} = \left( \frac{1 - 0.651}{1 - 0.636} \right)^{0.38}$$

在其他温度下的蒸发潜热可采用**Watson**方程计算:

$$\frac{\Delta H_2}{\Delta H_1} = \left( \frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \quad \frac{\Delta H^v}{\Delta H_b^v} = \left( \frac{1 - 0.651}{1 - 0.636} \right)^{0.38}$$

$$\Delta H_m^v = 21753 \text{ J/mol}$$

$$\Delta S_m^v = \Delta H_m^v / T = 21753 / 273.15 = 79.64 \text{ J / (mol} \cdot \text{K)}$$

(b) 在 $T_1, P_1$ 下变换为理想气体

$$T_r = 273.15 / 419.6 = 0.651, P_r = 0.1272 / 4.02 = 0.0316$$

采用普遍化维里关系式:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$

$$B^0 = -0.756 \quad \frac{dB^0}{dT_r} = 2.06 \quad B^1 = -0.904 \quad \frac{dB^1}{dT_r} = 6.73$$





$$B^0 = -0.756 \quad \frac{dB^0}{dT_r} = 2.06$$

$$B^1 = -0.904 \quad \frac{dB^1}{dT_r} = 6.73$$

$$P_r = 0.0316$$

$$\frac{H_m^R}{RT_c} = P_r \left[ B^0 - T_r \frac{dB^0}{dT_r} + \omega \left( B^1 - T_r \frac{dB^1}{dT_r} \right) \right]$$

$$\begin{aligned} \frac{H_{1m}^R}{RT_c} &= 0.0316 [(-0.756 - 0.651 \times 2.06) + 0.187(-0.904 - 0.651 \times 6.73)] \\ &= -0.0978 \end{aligned}$$

$$\frac{S_m^R}{R} = -P_r \left( \frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right)$$

$$\frac{S_{1m}^R}{R} = -0.0317(2.06 + 0.187 \times 6.73) = -0.105$$

$$H_{1m}^R = (-0.0978) \times 8.314 \times 419.6 = -341 \text{ J} \cdot \text{mol}^{-1}$$

$$S_{1m}^R = -0.105 \times 8.314 = -0.87 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

(c) 理想气体从 $T_1, p_1$ 变化到 $T_2, p_2$

$$\Delta H_m^{id} = \int_{T_1}^{T_2} C_{pm}^{id} dT = 20546 \text{ J/mol}$$

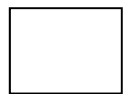
$$\Delta S_m^{id} = \int_{T_1}^{T_2} \frac{C_{pm}^{id}}{T} dT - R \ln \frac{p_2}{p_1} = 55.47 - 33.31 = 22.16 \text{ J/(mol} \cdot \text{K)}$$

(d) 在 $T_2, p_2$ 下变换为实际气体:

$$T_r = 1.13, P_r = 1.74$$



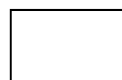
$$(H_2^R)^0 / RT_c = -2.34$$



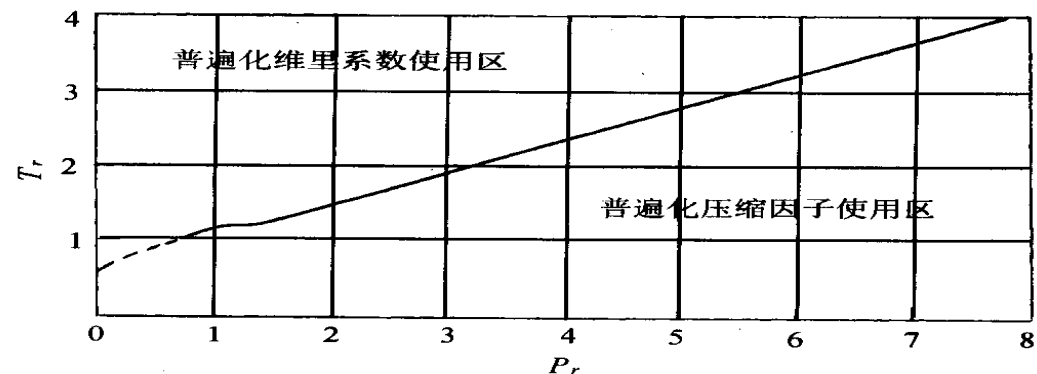
$$(H_2^R)^1 / RT_c = -0.62$$



$$(S_2^R)^0 / R = -1.63$$



$$(S_2^R)^1 / R = -0.56$$



$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} = -2.34 + 0.187 \times (-0.62) = -2.46$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} = -1.63 + 0.187 \times (-0.56) = -1.73$$

$$H_{2m}^R = (-2.46) \times 8.314 \times 419.6 = -8582 J \cdot mol^{-1}$$

$$S_{2m}^R = (-1.73) \times 8.314 = -14.38 J \cdot mol^{-1} \cdot K^{-1}$$

将上述4个过程的 H 和 S 加和：

$$H_m = \Delta H_m = 21753 + 341 + 20564 - 8582 = 34076 J \cdot mol^{-1}$$

$$S_m = \Delta S_m = 79.14 + 0.87 + 22.16 - 14.38 = 88.29 J \cdot mol^{-1} \cdot K^{-1}$$

# Home Work

3.5, 3.7, 3.8

### 3.3 两相系统的热力学性质

$$H_m = (1-x)H_m^l + xH_m^v$$

$$S_m = (1-x)S_m^l + xS_m^v$$

其中， $x$ 为干度，等于两相混合物中气体的质量分数。

## 3.4 常用的热力学图表

### 温度-比熵图 T-s图

饱和液体: A-C

饱和蒸汽: C-B

液态区域:  $f=2$

气态区域:  $f=2$

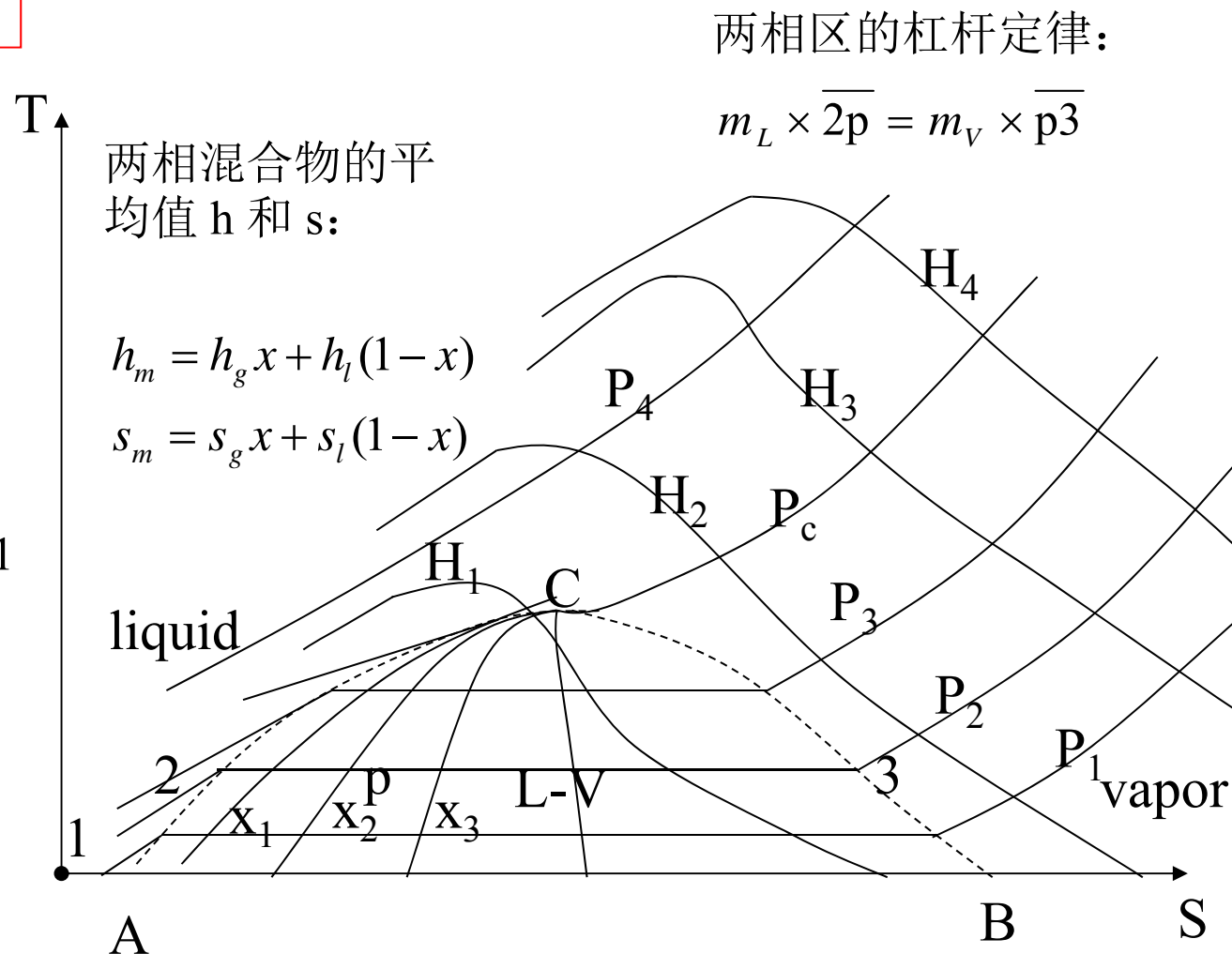
临界点: C  $f=0$

在线A-C 和 C-B上:  $f=1$

在两相区中:

$$T\Delta S = r \quad p \uparrow, r \downarrow$$

$$r_c = \lim_{T \rightarrow T_c} = T_c \times 0 = 0$$

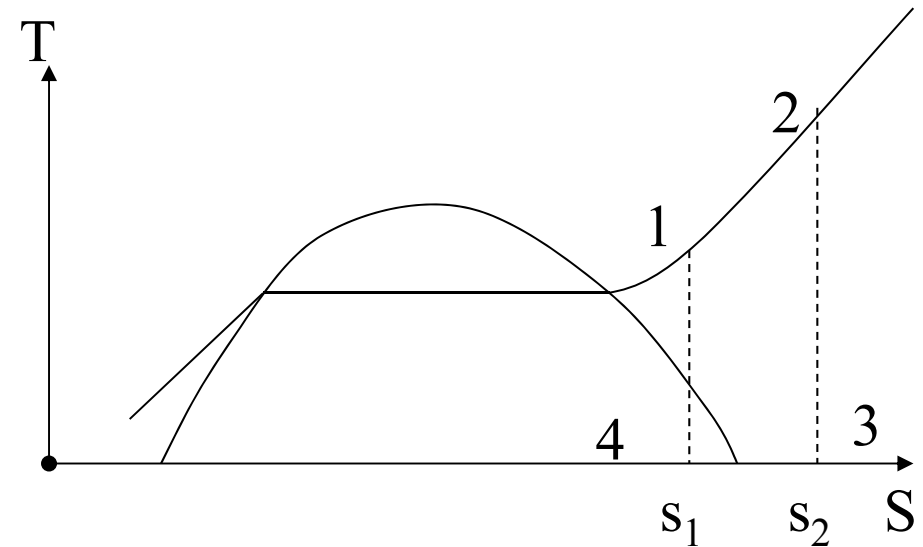


a. 等压变温过程 1→2

$$W_s = 0, Q = \Delta H$$

$$dH = TdS + VdP \Big|_{p=\text{const}} = TdS$$

$$Q = \Delta H = \int_{s_1}^{s_2} TdS \quad \text{The area 12341}$$



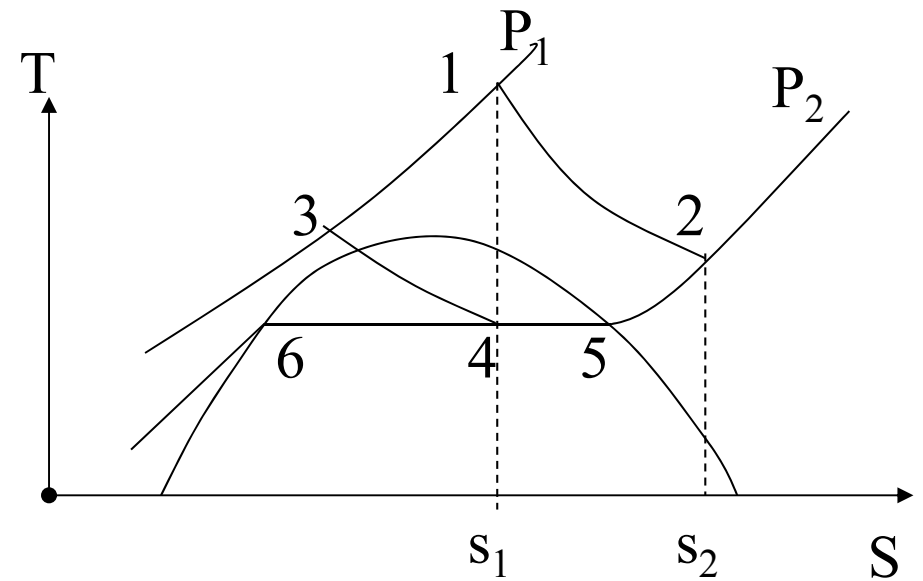
b. 节流过程 1→2

$$\Delta S_{sur} = 0$$

$$\Delta S_{sys} = S_2 - S_1$$

如果节流后进入两相区 3→4, 可采用杠杆定律进行组分的计算

$$\text{饱和液体量} \times \overline{64} = \text{饱和蒸汽量} \times \overline{45}$$



### c. 等熵膨胀过程

$$Q = 0, W_{s(R)} = \Delta H = H_2 - H_1$$

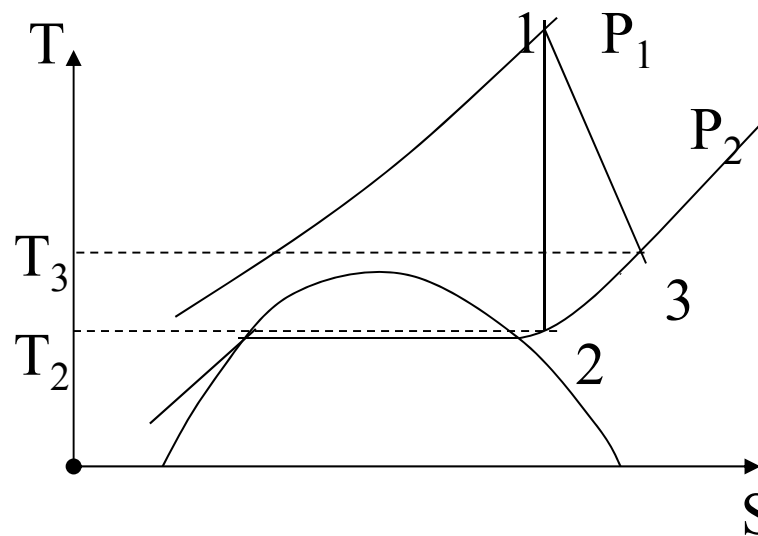
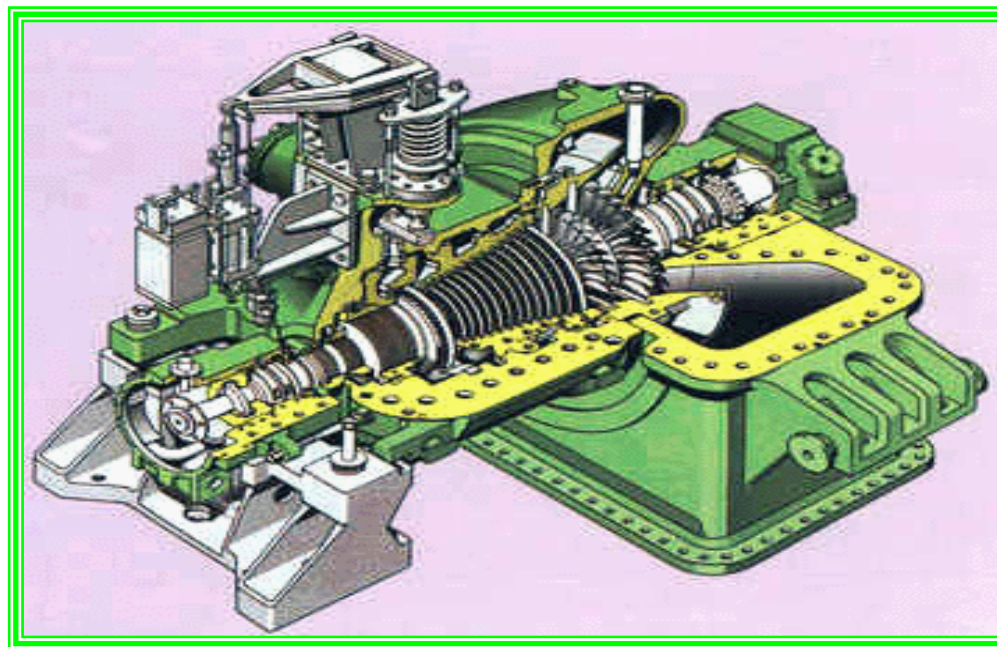
若为不可逆过程  $1 \rightarrow 3$ :

$$W_s = \Delta H = H_3 - H_1$$

等熵过程的效率:

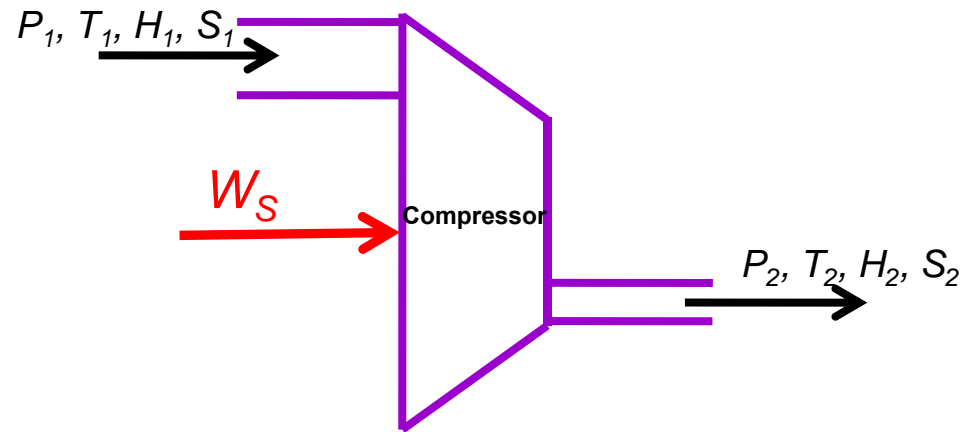
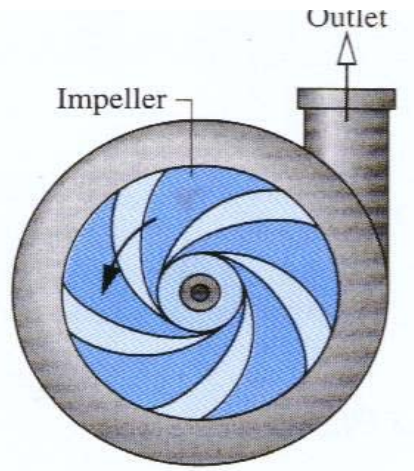
$$\eta_s = \frac{W_s}{W_{s(R)}} = \frac{H_3 - H_1}{H_2 - H_1}$$

$$W_s = \eta_s W_{s(R)}$$



re





#### d. 等熵压缩

$$Q = 0, W_{s(R)} = \Delta H = H_2 - H_1$$

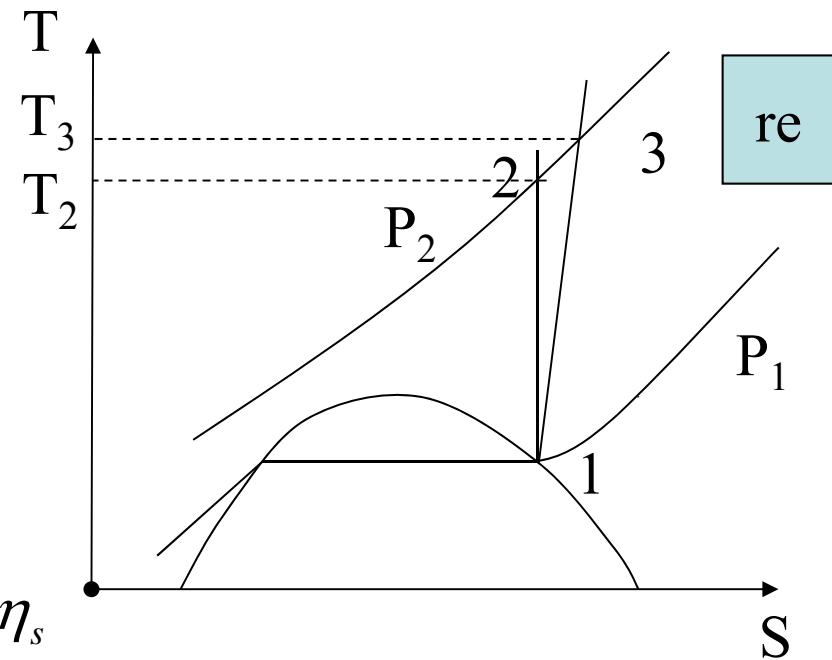
若为不可逆过程  $1 \rightarrow 3$ :

$$W_s = \Delta H = H_3 - H_1$$

等熵过程的效率:

$$\eta_s = \frac{W_{s(R)}}{W_s} = \frac{H_2 - H_1}{H_3 - H_1}$$

$$W_s = W_{s(R)} / \eta_s$$



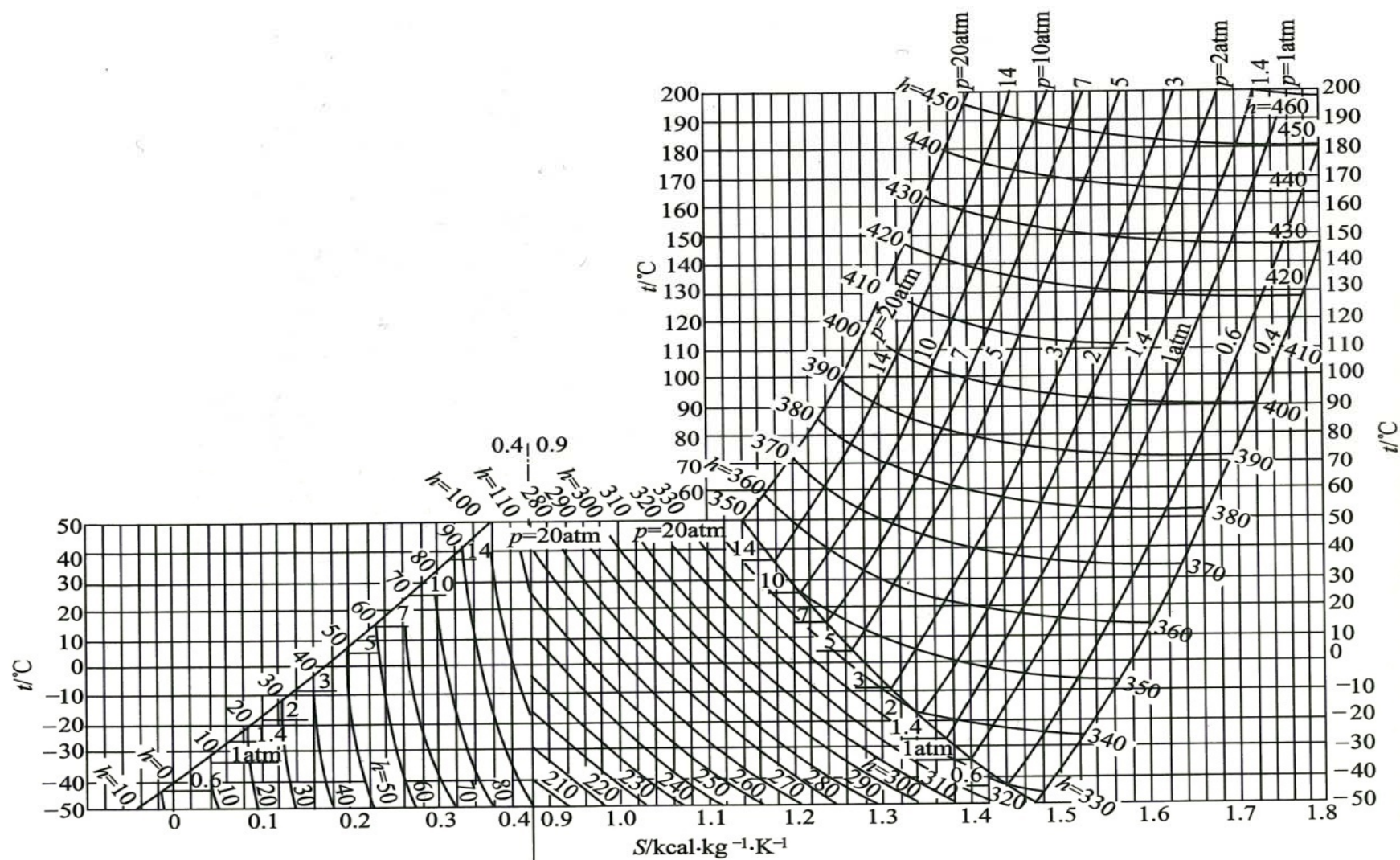


图 5-6(b) 氨的  $T$ - $S$  图 (可供查用)

例.  $\text{NH}_3$ , 从  $-8^\circ\text{C}$ ,  $0.304\text{MPa}$  绝热压缩到  $1.419\text{MPa}$ .  $\eta_s=0.8$ .  
 $W_{s(R)}=?$ ,  $W_s=?$   $\Delta S_g=?$

解: a. 对于可逆压缩过程

由 T-S 图可知,

$H_1=1443.5\text{kJ/kg}$ ,  $S_1=S_2=5.5438\text{ kJ}/(\text{kg}\cdot\text{K})$ ,  $H_2=1665.2\text{kJ/kg}$ ,  
因此有,  $W_{s(R)}=H_2-H_1=1665.2-1443.5=221.7\text{ kJ/kg}$

b. 对于不可逆压缩过程,  $\eta_s=0.8$

$$W_s = W_{s(R)} / \eta_s = 221.7 / 0.8 = 277.1\text{ kJ} / \text{kg}$$

$$\Delta H = H_2' - H_1 = W_s$$

$$H_2' = W_s + H_1 = 277.1 + 1443.5 = 1720.6\text{ kJ} / \text{kg}$$

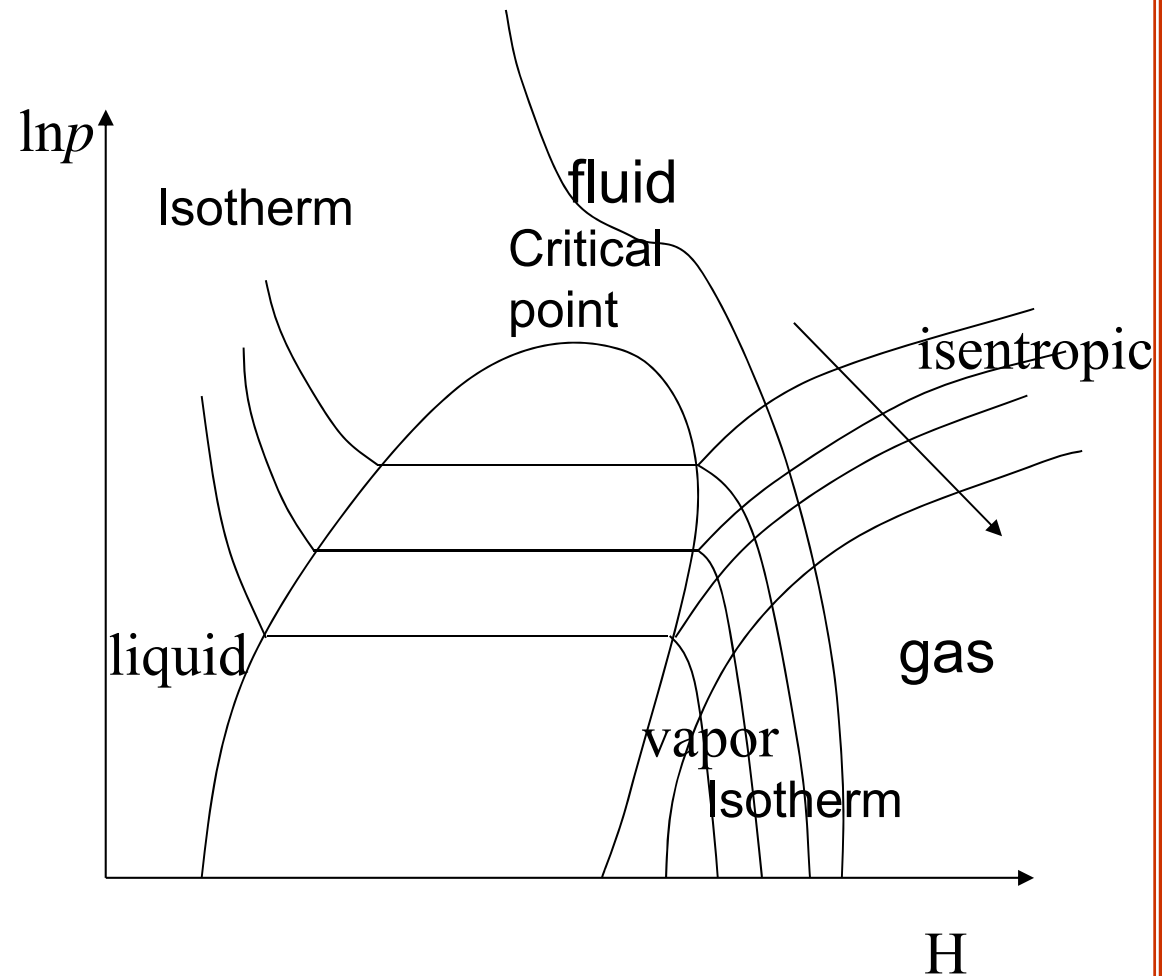
由 T-S 图可知,  $S_2'=5.6484\text{ kJ}/(\text{kg}\cdot\text{K})$

$$\Delta S_g = S_2' - S_1 = 5.6484 - 5.5438 = 0.1046\text{ kJ} / \text{kg}$$

## 压力-比焓图 p-H图

### p-H graph 压焓图

- ✓ 方便制冷过程的优化及其能量衡算;
- ✓ 两相区中水平线的长度表示汽化潜热的大小, 即: 线段越短, 汽化潜热越小;
- ✓ 液体的等温线很陡;
- ✓ 当压力很低时, 蒸汽的等温线也很陡。





氨(NH<sub>3</sub>)的  
压 焓 图

