本章的主要任务就是将纯物质和均相定组成混合物系统的一些有用的热力学性质表达成为能够直接测定的p、V、T及C_p*（理想气体热容）的普遍化函数，再结合状态方程和C_p*模型，就可以得到从p、V、T推算其它热力学性质的具体关系式。即可以实现由一个状态方程和理想气体热容模型推算其它热力学性质。

$$dG = Vdp - SdT$$

$$dH = TdS + Vdp$$

$$dA = -pdV - SdT$$

$$dU = TdS - pdV$$

适用于只有体积功存在的均相封闭系统，另外热力性质间有如下定义式：

$$H = U + pV$$

$$A = U - TS$$

$$G = H - TS$$

对于点函数：$z = f(x, y),$有如下关系式：

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

令：$M = \left(\dfrac{\partial z}{\partial x}\right)_y$ $\qquad N = \left(\dfrac{\partial z}{\partial y}\right)_x$

则：$dz = Mdx + Ndy$

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

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

上述三式可用来判断z是否为状态函数以及求得x与y之间的数学关系。

将其应用到热力学的基本关系式中，就可得到Maxwell关系式。

热力学基本关系式   Maxwell关系式

$$dU = TdS - pdV$$

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

$$dH = TdS + Vdp$$

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

$$dA = -pdV - SdT$$

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

$$dG = Vdp - SdT$$

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

能量方程的导数式：

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

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

$$\left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T = V$$

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

上述关系式的意义在于：可用易于测得的热力学数据来计算那些难于测量的热力学数据。其它的关系式：

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

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \qquad k = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

β – 体积膨胀系数；

k – 等温压缩系数；

重要的应用在于用易于测得的热力学数据（pVT）来计算那些难于测量的热力学数据，如焓H、熵S

对于熵S，其随p,V的变化可用下式：

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

但S随T的变化如何计算？

由 $\quad dU = TdS - pdV \quad$ 当 $dV = 0$时

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

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

代入到 $\left(\dfrac{\partial U}{\partial T} \right)_V = T \left(\dfrac{\partial S}{\partial T} \right)_V$ 中得：

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V = \frac{1}{T} C_V$$

由 $\quad dH = TdS + Vdp \quad$ 当 $dp = 0$ 时

得 $\quad \left(\dfrac{\partial H}{\partial T} \right)_p = T \left(\dfrac{\partial S}{\partial T} \right)_P$

$$C_p = \left(\dfrac{\partial H}{\partial T} \right)_p$$

代 入 到 $\left(\dfrac{\partial H}{\partial T} \right)_p = T \left(\dfrac{\partial S}{\partial T} \right)_p$ 中 得 :

$$\left(\dfrac{\partial S}{\partial T} \right)_p = \dfrac{1}{T} \left(\dfrac{\partial H}{\partial T} \right)_p = \dfrac{1}{T} C_p$$

例3－1 将S表示成p、V、T、C_V的函数

解： $S = S(T,V)$

得 $dS = \left(\dfrac{\partial S}{\partial T}\right)_V dT + \left(\dfrac{\partial S}{\partial V}\right)_T dV$

因 $\left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{1}{T}C_V$ $\qquad \left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V$

故 $dS = C_V\dfrac{dT}{T} + \left(\dfrac{\partial p}{\partial T}\right)_V dV$

例3－2 将S表示成p、V、T、C_p的函数

解： $S = S(T, p)$

得 $dS = \left(\dfrac{\partial S}{\partial T} \right)_p dT + \left(\dfrac{\partial S}{\partial p} \right)_T dp$

因 $\left(\dfrac{\partial S}{\partial T} \right)_p = \dfrac{1}{T} C_p$ $\left(\dfrac{\partial S}{\partial p} \right)_T = -\left(\dfrac{\partial V}{\partial T} \right)_p$

故 $dS = C_p \dfrac{dT}{T} - \left(\dfrac{\partial V}{\partial T} \right)_p dp$

工程上主要用到$\triangle H$、$\triangle S$，需把dH、dS与p、T、V、C_P、C_V等易测的性质关联起来。

对于单相、纯（定）组分体系，自由度$F=2$，热力学函数可以表示为两个强度性质的函数，通常选T、p。应用3.1节所讲内容，可求得dH、dS与p、T、V、C_P、C_V关系式。

热容表示物系升高1K是所吸收的热量。不同过程热容值不同，若过程在恒压下进行，其热容称为定压热容C_p，若过程在恒容下进行，其热容称为定容热容C_V。

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

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

(1)理想气体定压热容 ($C_{p,g}^{ig}$)

$$C_{p,g}^{ig} = A + BT + CT^2$$

$$C_{p,g}^{ig} = A + BT + CT^2 + DT^3$$

$$C_{p,g}^{ig} = A + BT + CT^2 + DT^3 + ET^4$$

(2)真实气体定压热容（ $C_{\mathrm{p,g}}$ ）

$$C_{\mathrm{p,g}} - C_{\mathrm{p,g}}^{\mathrm{ig}} = \Delta C_p$$

$$\Delta C_p = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial H^{ig}}{\partial T} \right)_p = \frac{\partial}{\partial T}(H - H^{ig})_p$$

或用对比态法计算：

$$\Delta C_p = \Delta C_p^0 + \omega \Delta C_p^1$$

真实气体的定压热容既是温度的函数，又是压力的函数。其实验数据很少，工程上的经验关联式很少。

液体的定压热容 $C_{p,1}$ 随压力变化很小

在一定温度范围内，可用下式计算：

$$C_{p,1} = A + BT + CT^2$$

其它估算方法有基团贡献法与对比态法，

或可查有关文献手册

k的定义式为：

$$k = \frac{C_p}{C_V}$$

对气体：

$$k = \frac{C_{p,g}}{C_{V,g}} = \frac{C_{p,g}^{ig} + \Delta C_p}{C_{p,g}^{ig} + \Delta C_p - (C_{p,g} - \Delta C_{V,g})}$$

对理想气体：

$$k = \frac{C_p}{C_p - R}$$
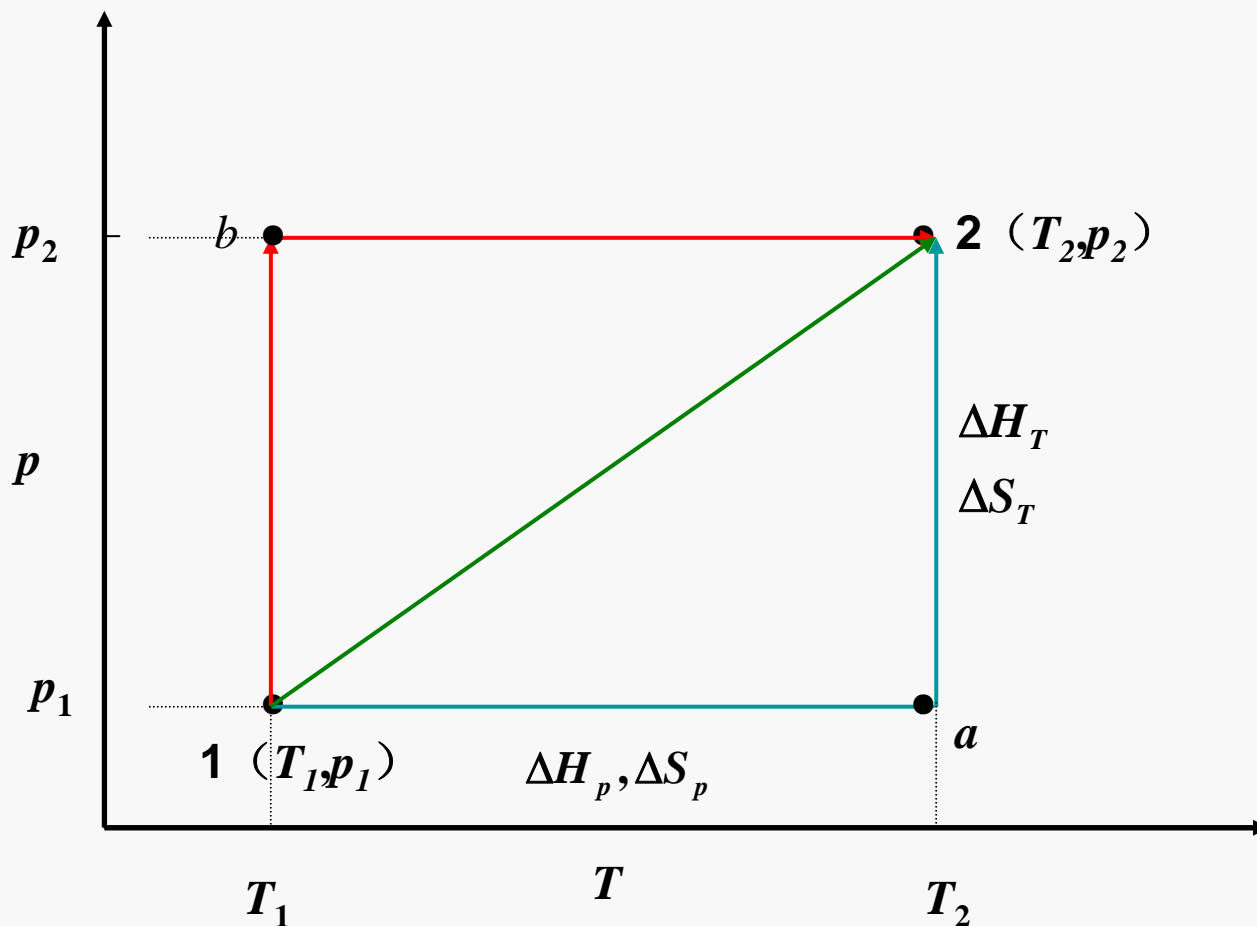
$$\Delta M = \Delta M_T + \Delta M_p$$

3.2.2.1理想气体的H随T、p的变化

$$\because C_{p,g}^{ig} = \left(\frac{\partial H^{ig}}{\partial T} \right)_p$$

$$\therefore \Delta H_p^{ig} = \int_{T_1}^{T_2} C_p^{ig} dT$$

对于理想气体：$\Delta H_T^{ig} = 0$

3.2.2.2理想气体的S随T、p的变化

$$\because \left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}C_p$$

$$\therefore \Delta S_p^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT$$

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

$$对理想气体: \left(\frac{\partial V^{ig}}{\partial T}\right)_p = \frac{R}{p} \Rightarrow \left(\frac{\partial S^{ig}}{\partial p}\right)_T = -\frac{R}{p}$$

3.2.2.2理想气体的S随T、p的变化

$$\therefore \Delta S_T^{ig} = -\int_{p_1}^{p_2} \frac{R}{p} dp = R \ln \frac{p_1}{p_2}$$

$$\therefore \Delta S^{ig} = \Delta S_p^{ig} + \Delta S_T^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} + R \ln \frac{p_1}{p_2}$$

3.2.3.1 真实气体的*H*随T、*p*的变化

$$\because H = f(T, p)$$

$$\therefore dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\because C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\therefore dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\because dH = TdS + Vdp$$

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

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

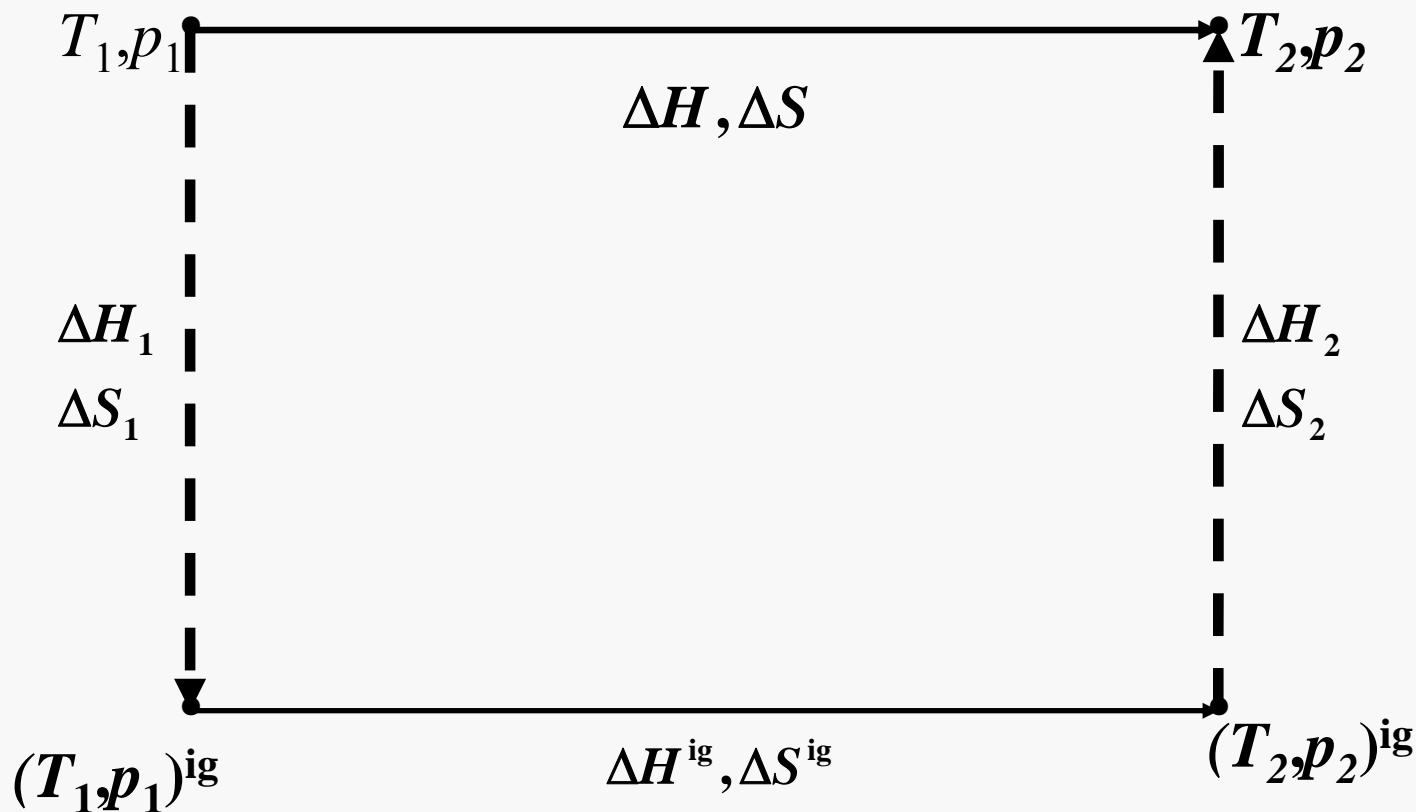$$\therefore dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]dp$$

$$\because S = f(T, p)$$

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$\because \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial H} \bullet \frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial S}{\partial H}\right)_p \left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{T}$$

$$\therefore dS = \frac{C_p}{T} dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$dS = \frac{C_p}{T}dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

将式 $\left(\dfrac{\partial S}{\partial p}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_p$ 代入得：

$$\therefore dS = \frac{C_p}{T}dT - \left(\frac{\partial V}{\partial T}\right)_p dp$$

由于高压下定压热容难于解决的问题，对于真实气体，按理想气体的计算方法进行计算行不通，为了计算在始态1与终态2之间的焓变和熵变，就必须设计另外的计算途径，如下图所示：

T_1, p_1 $\xrightarrow{\quad \Delta H, \Delta S \quad}$ T_2, p_2

ΔH_1
ΔS_1

ΔH_2
ΔS_2

$(T_1, p_1)^{\text{ig}}$ $\xrightarrow{\quad \Delta H^{\text{ig}}, \Delta S^{\text{ig}} \quad}$ $(T_2, p_2)^{\text{ig}}$

$$\Delta H = \Delta H_1 + \Delta H^{\text{ig}} + \Delta H_2$$

$$\Delta S = \Delta S_1 + \Delta S^{\text{ig}} + \Delta S_2$$

定义：所谓剩余性质，是真实状态下流体的热力学性质与在同一温度、压力下处于理想气体状态时广度热力学性质之间的差额。

$$M^{\mathrm{R}} = M(T, p) - M^{\mathrm{ig}}(T, p)$$

$$H^{\mathrm{R}} = H(T, p) - H^{\mathrm{ig}}(T, p)$$

$$S^{\mathrm{R}} = S(T, p) - S^{\mathrm{ig}}(T, p)$$

$$V^{\mathrm{R}} = V(T, p) - V^{\mathrm{ig}}(T, p)$$

由剩余性质定义，真实气体的热力学性质：

$$M = M^{ig} + M^R$$

对于焓和熵

$$H = H^{ig} + H^R$$

$$S = S^{ig} + S^R$$

对于理想气体：

$$dH^{ig} = C_P^{ig} dT \qquad dS^{ig} = \frac{C_P^{ig}}{T} dT - \frac{R}{P} dP$$

将T_0和p_0下的理想气体作为参比态，参比态的焓值和熵值分别用H_0^{ig}和S_0^{ig}表示。对上两式由T_0和p_0开始积分到T和p。

$$H^{ig} = H_0^{ig} + \int_{T_0}^{T} C_p^{ig} dT$$

$$S^{ig} = S_0^{ig} + \int_{T_0}^{T} \frac{C_p^{ig}}{T} dT - R \ln \frac{p}{p_0}$$

$$H = H^{ig} + H^R = H_0^{ig} + \int_{T_0}^{T} C_p^{ig} dT + H^R$$

$$S = S^{ig} + S^R = S_0^{ig} + \int_{T_0}^{T} \frac{C_p^{ig}}{T} dT - R \ln \frac{p}{p_0} + S^R$$

$$M^R = M - M^*$$

在等温的条件下将上式对 p 微分

$$\left(\frac{\partial M^R}{\partial p}\right)_T = \left(\frac{\partial M}{\partial p}\right)_T - \left(\frac{\partial M^{ig}}{\partial p}\right)_T$$

$$dM^R = \left[\left(\frac{\partial M}{\partial P}\right)_T - \left(\frac{\partial M^{ig}}{\partial P}\right)_T\right]dP \qquad (\text{等温})$$

$$M^R = \left(M^R\right)_0 + \int_{P_0}^{P}\left[\left(\frac{\partial M}{\partial P}\right)_T - \left(\frac{\partial M^{ig}}{\partial P}\right)_T\right]dP \qquad (\text{等温})$$

当 $P_0 \to 0$ 时，$\qquad \left(H^R\right)_0 = 0, \qquad \left(S^R\right)_0 = 0$

注意：此时 $\left(V^R\right)_0 \neq 0$，但并不影响焓熵。

$$H^R = \left(H^R\right)_0 + \int_{p_0}^{p} \left[\left(\frac{\partial H}{\partial p}\right)_T - \left(\frac{\partial H^{ig}}{\partial p}\right)_T\right] dp \qquad \left(\text{等温}\right)$$

$$\because \left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\frac{\partial H^{ig}}{\partial p}\right)_T = 0$$

$$\therefore H^R = \int_{p_0}^{p} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

$$S^R = \left(S^R\right)_0 + \int_{p_0}^{p} \left[\left(\frac{\partial S}{\partial p}\right)_T - \left(\frac{\partial S^{ig}}{\partial p}\right)_T\right] dp \qquad \left(等温\right)$$

$$\because \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\frac{\partial S^{ig}}{\partial p}\right)_T = -\frac{R}{p}$$

$$\therefore S^R = \int_{p_0}^{p} \left[\frac{R}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right]_T dp$$

$a.$维里方程: $Z = \dfrac{pV}{RT} = 1 + \dfrac{Bp}{RT}$

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

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

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

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

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

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

$$S^R = \int_0^P \left[\frac{R}{P} - \frac{R}{P} - \frac{dB}{dT}\right] dP = -\frac{dB}{dT}P$$

*b.*立方型状态方程

首先得解决$\left(\dfrac{\partial V}{\partial T}\right)_p$ 的计算

$\because \left(\dfrac{\partial p}{\partial T}\right)_V \left(\dfrac{\partial T}{\partial V}\right)_p \left(\dfrac{\partial V}{\partial p}\right)_T = -1$

$\therefore \left(\dfrac{\partial V}{\partial T}\right)_p = -\left(\dfrac{\partial p}{\partial T}\right)_V \left(\dfrac{\partial V}{\partial p}\right)_T$

*b.*立方型状态方程

$$\therefore \left[\left(\frac{\partial V}{\partial T} \right)_P \right]_T dp = - \left[\left(\frac{\partial p}{\partial T} \right)_V dV \right]_T$$

又 $\because Vdp = d(pV) - pdV$

将上二式代入到 $H^R = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$

得 $H^R = \int_0^p Vdp - \int_0^p T \left(\frac{\partial V}{\partial T} \right)_p dp$

*b.*立方型状态方程

$$\therefore H^R = \int_{(pV)_{p=0}}^{pV} d(pV) - \int_{V\to\infty}^{V} pdV + \int_{V\to\infty}^{V} T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$\therefore H^R = pV - RT + \int_{V\to\infty}^{V} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p \right] dV$$

$$S^R = \int_{p_0}^{p} \left[\frac{R}{p} - \left(\frac{\partial V}{\partial T}\right)_p \right]_T dp = \int_{0}^{P} \frac{R}{P} dP + \int_{V\to\infty}^{V} \left(\frac{\partial p}{\partial T}\right)_V dV$$

R-K方程：

$$H^R = pV - RT - \frac{3a}{2T^{0.5}b}\ln\left(1 + \frac{b}{V}\right)$$

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

S-R-K方程：

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

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

例 用RK方程计算633K，9.678×10^6Pa下水的H^R和S^R

$T_c=647.1K$, $p_c=220.5×10^5Pa$

解：

$$a = 0.42748 \frac{R^2 T_C^{2.5}}{p_C}$$

$$= 0.42748 × \frac{8.314^2 × 647.1^{2.5}}{220.5 × 10^5}$$

$$= 14.274 \, Pa · m^6 · K^{0.5} · mol^{-2}$$

$$b = 0.08664 \frac{R T_C}{p_C} = 0.08664 × \frac{8.314 × 647.1}{220.5 × 10^5}$$

$$= 2.114 × 10^{-5} m^3 / mol$$

$$A = \frac{ap}{R^2 T^{2.5}} = \frac{14.274 \times 9.678 \times 10^6}{8.314^2 \times 633^{2.5}} = 0.1982$$

$$B = \frac{bp}{RT} = \frac{2.114 \times 10^{-5} \times 9.678 \times 10^6}{8.314 \times 633} = 0.03888$$

$$Z = \frac{1}{1-h} - \frac{A}{B}\left(\frac{h}{1+h}\right) \qquad h = \frac{b}{V} = \frac{B}{Z}$$

$$Z^0 = 1 \quad h = 0.0388 \Rightarrow Z^1 = 0.8496 \quad h = 0.04576$$

$$\Rightarrow Z^2 = 0.8248 \quad h = 0.04713$$

$$\Rightarrow Z^3 = 0.8199 \quad h = 0.04741$$

$$\Rightarrow Z^4 = 0.8189 \quad h = 0.04747$$

$$\Rightarrow Z^5 = 0.8187 \quad h = 0.04748$$

$$V = \frac{ZRT}{p} = 0.8187 \times \frac{8.314 \times 633}{9.678 \times 10^6} = 4.4518 \times 10^{-4} m^3 / mol$$

$$H^R = pV - RT - \frac{3a}{2T^{0.5}b} \ln(1 + \frac{b}{V})$$

$$= 9.678 \times 10^6 \times 4.4518 \times 10^{-4}$$

$$-8.314 \times 633 - \frac{3 \times 14.274}{2 \times 633^{0.5} \times 2.114 \times 10^{-5}} \times \ln(1 + \frac{2.114 \times 10^{-5}}{4.4518 \times 10^{-4}})$$

$$= -2821.9 J / mol$$

同理：$S^R = R \ln(V - b) - R \ln \frac{RT}{p} - \frac{a}{2T^{1.5}b} \ln \left(1 + \frac{b}{V}\right)$

$$S^R = -2.069 J / mol \cdot K$$

$$\because H^R = p\left[B - T\frac{dB}{dT}\right]_T \qquad S^R = -p\frac{dB}{dT}$$

$$\therefore \frac{H^R}{RT} = \frac{p}{R}\left[\frac{B}{T} - \frac{dB}{dT}\right]_T \qquad \frac{S^R}{R} = -\frac{p}{R} \times \frac{dB}{dT}$$

$$\text{又} \because B = \frac{RT_C}{p_C}\left[B^0 + \omega B^1\right]$$

$$\therefore \frac{dB}{dT} = \frac{RT_C}{p_C}\left[\frac{dB^0}{dT} + \omega\frac{dB^1}{dT}\right]$$

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

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

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$

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

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

欲使这两个式子普遍化，应把它们与Z关联

$$\frac{H^R}{RT} = -T \int_0^p \left(\frac{\partial Z}{\partial T} \right)_p \frac{dp}{p}$$

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

$$p = p_c p_r \qquad\qquad dp = p_c dp_r$$

$$T = T_c T_r \qquad\qquad dT = T_c dT_r$$

将上述关系代入前二式得：

$$\frac{H^R}{RT_C} = -T_r^2 \int_0^{p_r} \left(\frac{\partial Z}{\partial T_r}\right)_{p_r} \frac{dp_r}{p_r}$$

$$\frac{S^R}{R} = -T_r \int_0^{p_r} \left(\frac{\partial Z}{\partial T_r}\right)_{p_r} \frac{dp_r}{p_r} - \int_0^{p_r} (Z-1) \frac{dp_r}{p_r}$$

$$\therefore H^R = f(T_r, p_r, \omega)$$

$$S^R = f(T_r, p_r, \omega)$$

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

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

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{p_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{p_r} \frac{dp_r}{p_r} - \omega T_r^2 \int_0^{p_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{p_r} \frac{dp_r}{p_r}$$

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

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

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

$$\left\{ \begin{array}{cc} \dfrac{(H^R)^0}{RT_C} & \dfrac{(H^R)^1}{RT_C} \\ \dfrac{(S^R)^0}{R} & \dfrac{(S^R)^1}{R} \end{array} \right\} = f(T_r, p_r) \xrightarrow{\text{查图}} \left\{ \begin{array}{c} H^R \\ S^R \end{array} \right\}$$
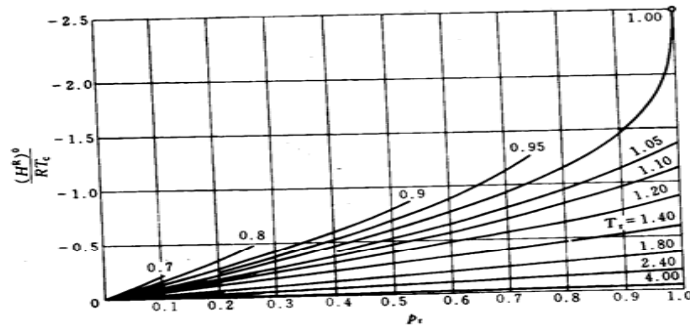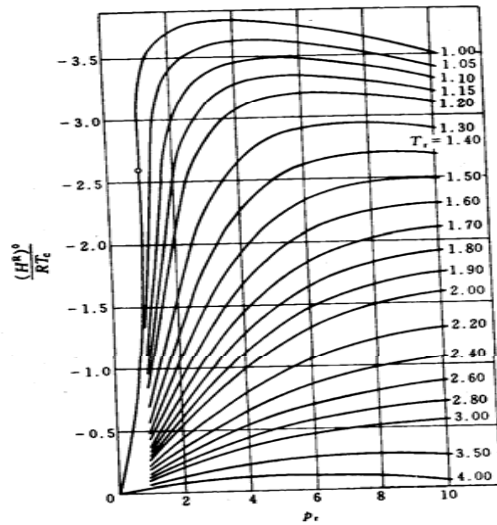
图 3-2 $(H^R)^0/RT_c$ 的普遍化关联 $(p_r < 1)$

图 3-4 $(H^R)^1/RT_c$ 的普遍化关联 $(p_r < 1)$
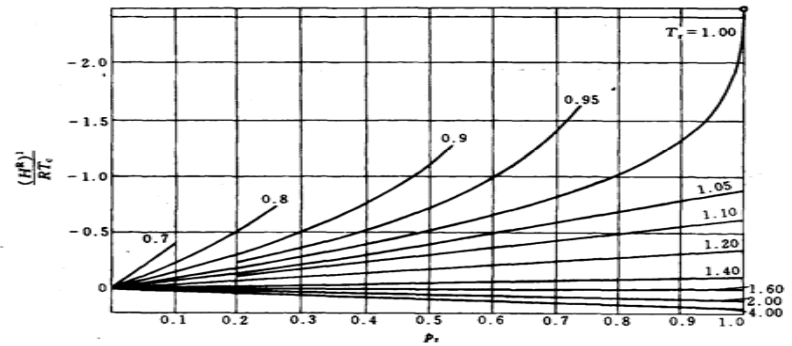
图 3-3 $(H^R)^0/RT_c$ 的普遍化关联 $(p_r > 1)$
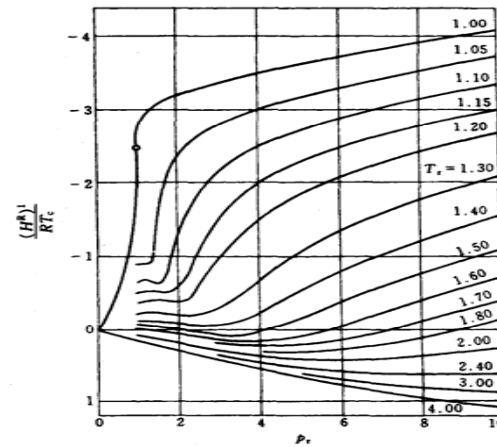
图 3-5 $(H^R)^1/RT_c$ 的普遍化关联 $(p_r > 1)$
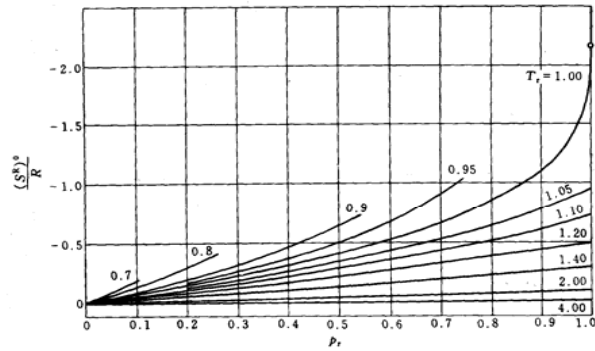
图 3-6　$(S^R)^0/R$ 的普遍化关联（$p_r < 1$）
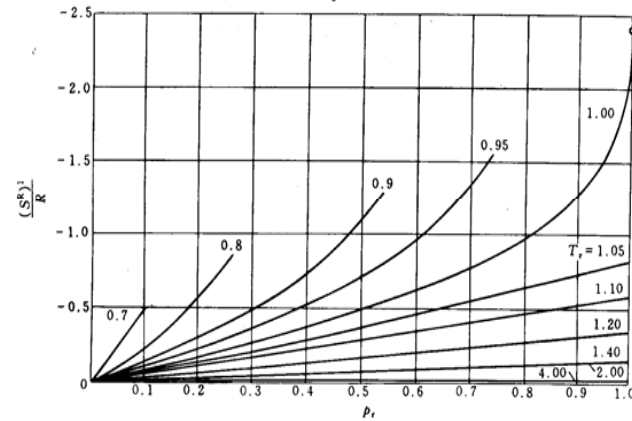
图 3-8　$(S^R)^1/R$ 的普遍化关联（$p_r < 1$）
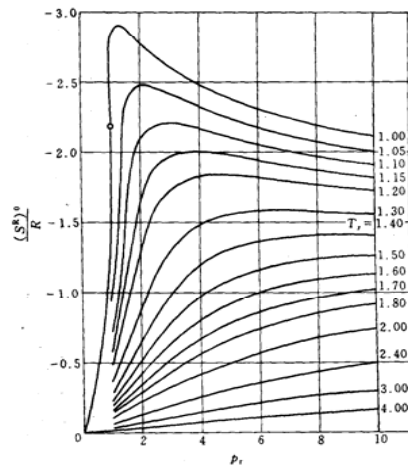
图 3-7　$(S^R)^0/R$ 的普遍化关联（$p_r > 1$）
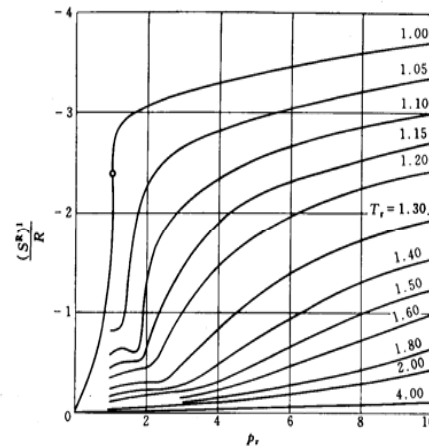
图 3-9　$(S^R)^1/R$ 的普遍化关联（$p_r > 1$）

例 3 － 5 试 用 普 遍 化 法 计 算 丙 烷 气 体 在 378K、0.507MPa下的剩余焓和剩余熵。

已知：T_C＝369.8K，p_C=4.248MPa，w=0.152

解：

$$T_r = \frac{378}{369.8} = 1.022 \qquad P_r = \frac{0.507}{4.248} = 0.1194$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.32456 \qquad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} = 0.6379$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.017977 \qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} = 0.64475$$

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

$$= 0.119 \left[\frac{-0.325}{1.022} - 0.638 + 0.152 \times \left(\frac{-0.018}{1.022} - 0.645 \right) \right]$$

$$= -0.126$$

$$H^R = -0.126 \times 8.314 \times 378 = -396 J/mol$$

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

$$= -0.119 \times (0.638 + 0.152 \times 0.645) = -0.088$$

$$S^R = -0.088 \times 8.314 = -0.732 J/(mol \cdot K)$$

饱和液体的摩尔焓、摩尔熵与相同温度和压力下的饱和蒸气的摩尔焓、摩尔熵相差很大，它们之间的差值分别被称为此T、p下该物质的蒸发焓、蒸发熵，即：

$$\Delta_v H = H^v - H^l$$

$$\Delta_v S = S^v - S^l$$

对于纯物质的摩尔吉布斯自由能G在发生相变的过程中保持不变，即

$$G^v = G^l \qquad \text{在一定的温度和压力下}$$

当两相系统发生变化是，为了维持两相平衡，两相吉布斯自由能的变化相等，即：

$$dG^v = dG^l$$

$$dG^v = V^v dp^s - S^v dT$$

$$dG^l = V^l dp^s - S^l dT$$

$$V^v dp^s - S^v dT = V^l dp^s - S^l dT$$

$$\frac{dp^s}{dT} = \frac{S^v - S^l}{V^v - V^l} = \frac{\Delta_v S}{\Delta_v V}$$

$$\because \Delta_v H = T \Delta_v S \qquad \therefore \frac{dp^s}{dT} = \frac{\Delta_v H}{T \Delta_v V}$$

$$Clapeyron方程: \frac{dp^s}{dT} = \frac{\Delta_v H}{T\Delta_v V}$$

$$\because \Delta_v V = V^v - V^l = \frac{Z^v RT}{p^s} - \frac{Z^l RT}{p^s} = \frac{\Delta Z RT}{p^s}$$

$$\therefore \frac{dp^s}{dT} = \frac{\Delta_v H}{(RT^2/p^s)\Delta Z}$$

$$\frac{d\ln p^s}{d(1/T)} = -\frac{\Delta_v H}{R\Delta Z}$$

该式称为$ClCausius - Clapeyron$方程（克－克方程）

克－克方程把摩尔蒸发焓直接和蒸气压与温度曲线关联起来了。是一种严密的热力学关系，若知道了蒸气压和温度的关系，则可将它用于蒸发焓的计算。

描述蒸气压和温度关系的方程，被称为蒸气压方程。蒸气压方程很多，本章仅介绍简单的两种。有关蒸气压的估算方法请参见本书第八章。

令 $\dfrac{\Delta_v H}{R\Delta Z}=B$ 视为常数，积分克－克方程得：

$$\ln p^s = A - \frac{B}{T} \qquad \text{其中A为积分常数}$$

目前，工程计算中广泛使用的是Antoine （安托尼）方程，其形式为：

$$\ln p^s = A - \frac{B}{T + C}$$

$$\Delta Z = Z^v - Z^l = \frac{p}{RT}(V^v - V^l)$$

它可以用针对饱和汽、液均适用的状态方程计算，也可以用经验关联式计算。

$$\Delta Z = (1 - \frac{p_r}{T_r^3})^{1/2}$$

该式适用范围为$T < Tb$ 。近似计算时，也可假设$\Delta Z = 1$ 。有关ΔvH 详细的估算方法请参见第八章。

$$H^{R} = p \cdot \left[B - T \frac{dB}{dT} \right]_{T}$$

维里方程

$$S^{R} = -p \cdot \frac{dB}{dT}$$

状态方程法

$$H^{R} = pV - RT + \int_{V \to \infty}^{V} \left[T \left(\frac{\partial p}{\partial T} \right)_{V} - p \right]_{T} dV$$

立方型状态方程

$$S^{R} = \int_{V \to \infty}^{V} \left(\frac{\partial p}{\partial T} \right)_{V} dV + \int_{V \to \infty}^{V} R \frac{dV}{V}$$

普遍化维里系数法

$$\frac{H^{R}}{RT} = p_{r} \left[\frac{B^{(0)}}{T_{r}} - \frac{dB^{(0)}}{dT_{r}} + \omega \left(\frac{B^{(1)}}{T_{r}} - \frac{dB^{(1)}}{dT_{r}} \right) \right]$$

对应状态法

$$\frac{S^{R}}{R} = -p_{r} \left[\frac{dB^{(0)}}{dT_{r}} + \omega \frac{dB^{(1)}}{dT_{r}} \right]$$

普遍化压缩因子法

$$\frac{H^{R}}{RT_{c}} = \frac{\left(H^{R} \right)^{0}}{RT_{c}} + \omega \frac{\left(H^{R} \right)^{1}}{RT_{c}} \quad \frac{S^{R}}{R} = \frac{\left(S^{R} \right)^{0}}{R} + \omega \frac{\left(S^{R} \right)^{1}}{R}$$

例3-6 计算1-丁烯蒸气在478K，6.89MPa下的V、U、H和S。

假定1-丁烯饱和液体在273K(P^s=1.27×10⁵Pa)时的H和S值为

零。已知 T_c=419.5K p_c=4.02MPa, ω =0.187

C_p^{ig}=16.36+2.63×10⁻¹T-8.212×10⁻⁵T²(J.mol/K)

$\Delta_v H$=RT_C[(7.08)(1-T_r)$^{0.354}$+10.95 ω (1-T_r)$^{0.354}$)

解：

$$T_r = \frac{478}{419.5} = 1.139 \qquad P_r = \frac{6.89}{4.02} = 1.714$$

查图得： $Z^0 = 0.476, Z^1 = 0.135 \Rightarrow Z = Z^0 + \omega Z^1 = 0.501$

$$V = \frac{ZRT}{P} = \frac{0.501 \times 8.314 \times 478}{6.89 \times 10^6} = 2.89 \times 10^{-4} m^3 / mol$$

273K,0.127MPa

丁烯饱和液体始态

$$\Delta H, \Delta S$$

478K,6.89MPa

丁烯蒸汽

$$\Delta_v H$$
$$\Delta_v S$$

(a)

273K,0.127MPa

丁烯饱和蒸汽

$$H_2^R$$
$$S_2^R$$

(d)

(b)

$$-H_1^R$$
$$-S_1^R$$

273K,0.127MPa

理想气体状态丁烯

$$\Delta H^{ig}, \Delta S^{ig}$$

478K,6.89MPa

理想气体状态丁烯

(c)
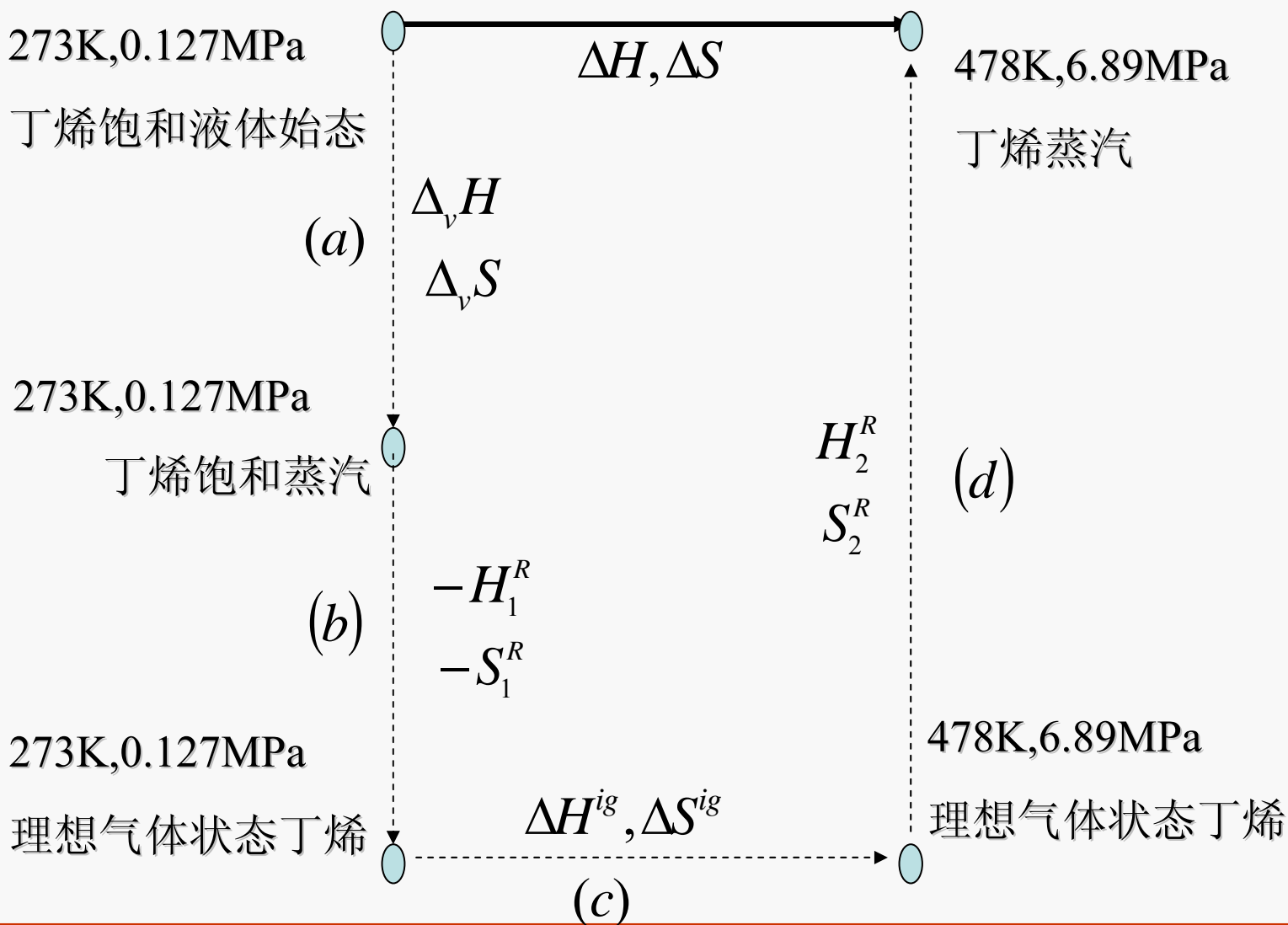
(a) 求 ΔH_v 和 ΔS_v

$$T_r = \frac{273}{419.5} = 0.65077$$

$$\Delta_v H = RT_C[(7.08)(1-T_r)^{0.354} + 10.95\omega(1-T_r)^{0.456}]$$

$$= 8.314 \times 419.5 \times [7.08 \times (1-0.65077)^{0.354}$$

$$+ 10.95 \times 0.187 \times (1-0.65077)^{0.456}]$$

$$= 21.5 \times 10^3 J/mol$$

$$\Delta S_v = \frac{\Delta H_v}{T} = \frac{21.5 \times 10^3}{273} = 78.6 J/mol \cdot K$$

(b)求H_1^R　　S_1^R

$$T_r = 0.65077 \qquad P_r = \frac{0.127}{4.02} = 0.0316$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.756 \qquad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} = 2.06$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.904 \qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} = 6.73$$

$$\frac{H_1^R}{RT} = P_r \left[\frac{B^0}{T_r} - \frac{dB^0}{dT_r} + \omega \left(\frac{B^1}{T_r} - \frac{dB^1}{dT_r} \right) \right]$$

$$= 0.0316 \left[\frac{-0.756}{0.65077} - 2.06 + 0.187 \times \left(\frac{-0.904}{0.65077} - 6.73 \right) \right]$$

$$= -0.14978$$

$$H_1^R = -0.14978 \times 8.314 \times 273 = -340 J/mol$$

$$\frac{S_1^R}{R} = -P_r \left(\frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right)$$

$$= -0.0316 \times (2.06 + 0.152 \times 6.73) = -0.1049$$

$$S_1^R = -0.1049 \times 8.314 = -0.872 J/(mol \cdot K)$$

(c) 求 ΔH^{ig} 和 ΔS^{ig}

$$\Delta H^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT = \int_{273}^{478} \left(16.36 + 2.63 \times 10^{-1} T - 8.212 \times 10^{-5} T^2\right) dT$$

$$= 16.36\left(478 - 273\right) + \frac{2.63 \times 10^{-1}}{2}\left(478^2 - 273^2\right)$$

$$- \frac{8.212 \times 10^{-5}}{3}\left(478^3 - 273^3\right)$$

$$= 21166 J/mol$$

(c) 求 ΔH^{ig} 和 ΔS^{ig}

$$\Delta S^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT - \int_{P_1}^{P_2} \frac{R}{P} dP$$

$$= \int_{273}^{478} \left(\frac{16.36}{T} + 2.63 \times 10^{-1} - 8.212 \times 10^{-5} T \right) dT - R \ln \frac{6.89}{0.127}$$

$$= \left[\begin{array}{l} 16.36 \ln \dfrac{478}{273} + 2.63 \times 10^{-1} \left(478 - 273 \right) \\[2mm] - \dfrac{8.212 \times 10^{-5}}{2} \left(478^2 - 273^2 \right) \end{array} \right] - 8.314 \ln \frac{6.89}{0.127}$$

$$= 23.55 J / \left(mol \cdot K \right)$$

(d)求H_2^R $\quad$ S_2^R

$T_r = 1.14$ $\quad\quad$ $P_r = 1.71$用普压法

$$\left(\frac{H^R}{RT_c}\right)^0 = -2.04 \qquad \left(\frac{H^R}{RT_c}\right)^1 = -0.51$$

$$\left(\frac{S^R}{R}\right)^0 = -1.34 \qquad \left(\frac{S^R}{R}\right)^1 = -0.58$$

$$\frac{H_2^R}{RT_c} = \left(\frac{H^R}{RT_c}\right)^0 + \omega\left(\frac{H^R}{RT_c}\right)^1 = -2.04 + 0.187(-0.51) = -2.14$$

$$\frac{S_2^R}{R} = \left(\frac{S^R}{R}\right)^0 + \omega\left(\frac{S^R}{R}\right)^1 = -1.34 + 0.187(-0.58) = -1.45$$

$$H_2^R = -2.14 \times 8.314 \times 419.5 = -7472 J/mol$$

$$S_2^R = -1.45 \times 8.314 = -12.1 J/(mol \cdot K)$$

$$H = \Delta H = \Delta H_v + \left(-H_1^R\right) + \Delta H^{ig} + H_2^R$$

$$= 21500 + 340.1 + 21166 - 7472 = 35534.1 J / mol$$

$$S = \Delta S = \Delta S_v + \left(-S_1^R\right) + \Delta S^{ig} + S_2^R$$

$$= 78.6 + 0.872 + 23.55 - 12.1 = 90.922 J / \left(mol \cdot K\right)$$

$$U = H - PV = 35534 - 6.89 \times 10^6 \times 2.89 \times 10^{-4}$$

$$= 33542.79 J / \left(mol \cdot K\right)$$

对化工过程进行热力学分析，对工程进行工艺与设备计算时，需要物质在各种状态下的焓、熵、比容等热力学参数的数据，人们将某些常用物质（如水蒸气、空气、氟里昂等）的焓、熵、比容和温度、压力的关系制成专用的图或表，常用的有水和水蒸气的热力学性质表（附录四），温熵图、压焓图、焓熵图，这些热力学性质图表使用极为方便。

由相律：自由度＝组分数-相数＋2

对单组分，平衡两相，自由度为：1
在两相平衡状态下，对任一平衡相态，只要知道一个热力学性质，其他的热力学性质既可求算。表现在二维图上应为一段曲线。
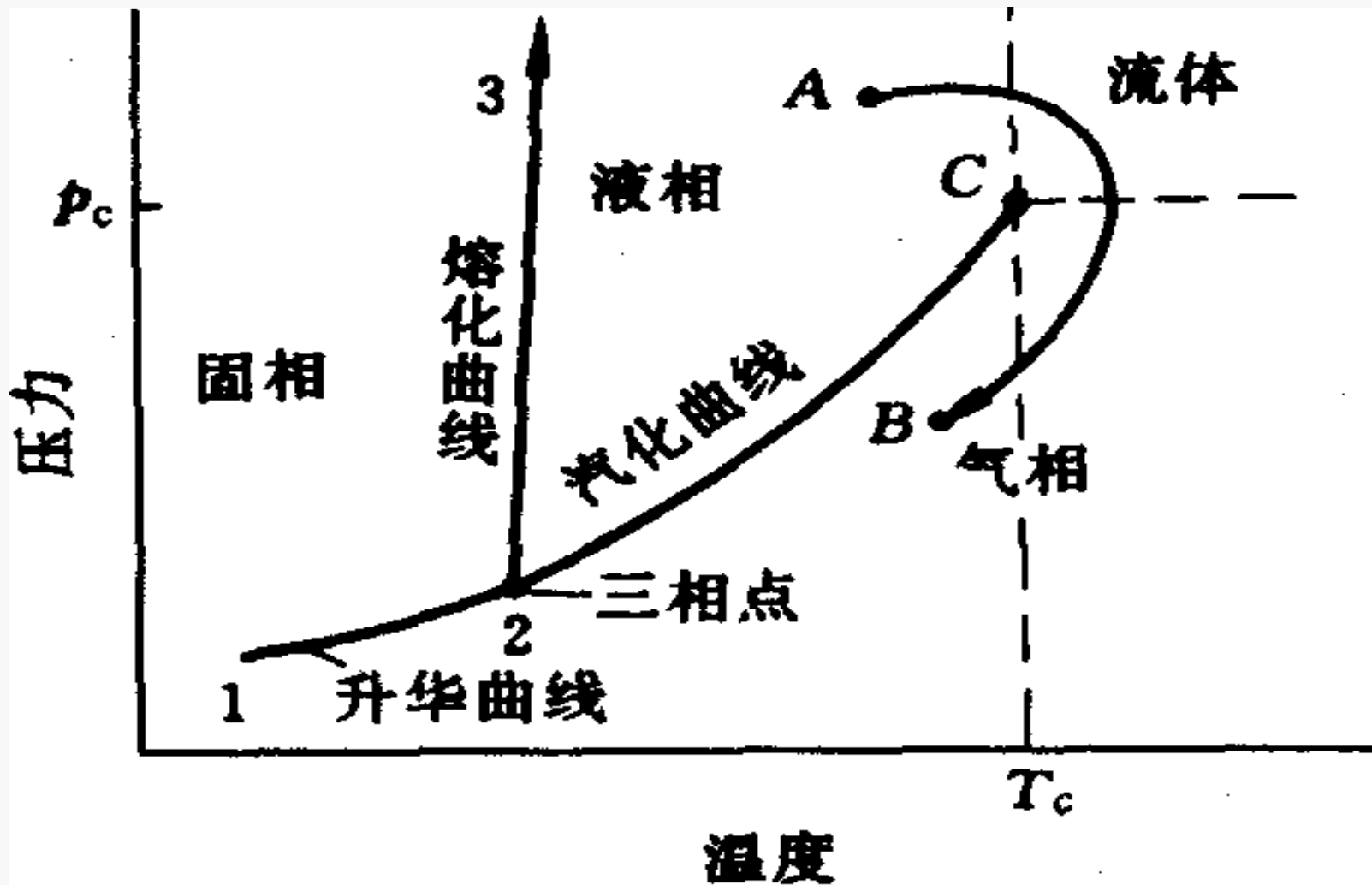
对于两相混合物的性质（两相共同体现出来的性质）与两相性质和相对量有关。

对两相混合物的广度性质应为两相的热力学性质与其摩尔分率（质量分率）乘积的加和。对汽液两相，定义x为β相的摩尔分率或质量分率。则：

$$M = M_{\alpha}(1 - x) + M_{\beta}x$$

对气液两相，x为干度。气液两相的热力学性质为：

$$U = U_1(1 - x) + U_g x$$

$$S = S_1(1 - x) + S_g x$$

$$H = H_1(1 - x) + H_g x$$

水蒸汽表

国际上规定，以液体水的三相点为计算基准。水的三相点参数为：

$$T = 273.16K$$

$$P = 611.2P_a$$

$$V = 0.00100022m^3 / kg$$

规定三相点时液体水内能和熵值为零。

$$H = U + PV = 0 + 611.2 \times 0.00100022 \times 10^{-3}$$

$$= 0.000614kJ / kg$$

热力学性质图在工程中经常遇到，如空气、氨、氟里昂等物质的热力学性质都制作成图，以便工程计算需要。热力学性质图的特点表现在：使用方便，易看出变化趋势，易于分析问题，但读数不如表格准确。常用热力学图包括：T-S图、H-S图、压-焓图（lnP-H）等。重点介绍T-S图。
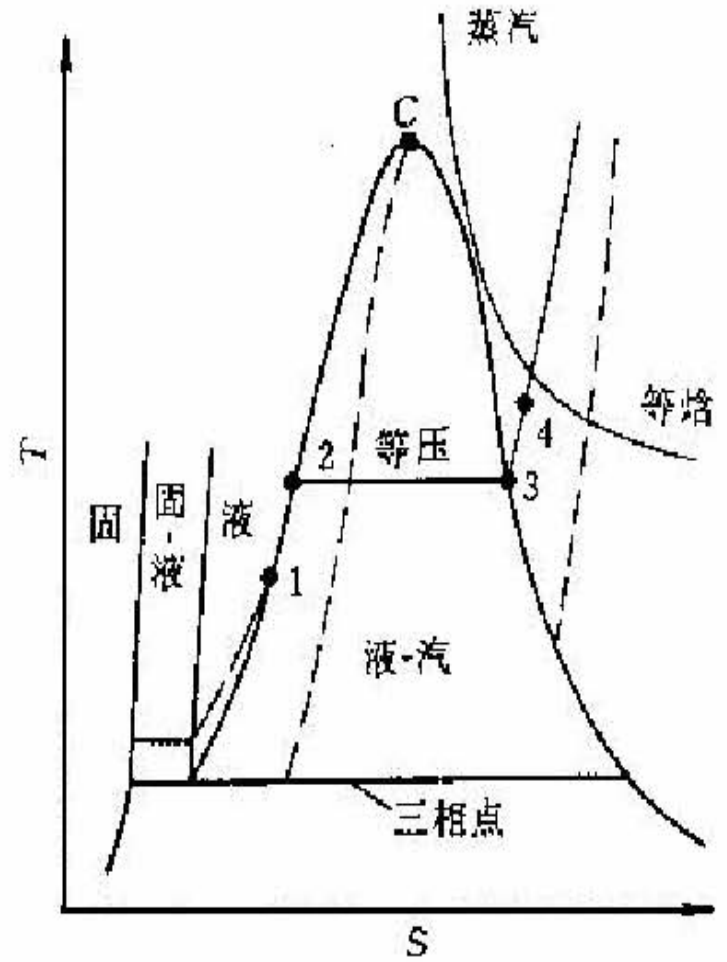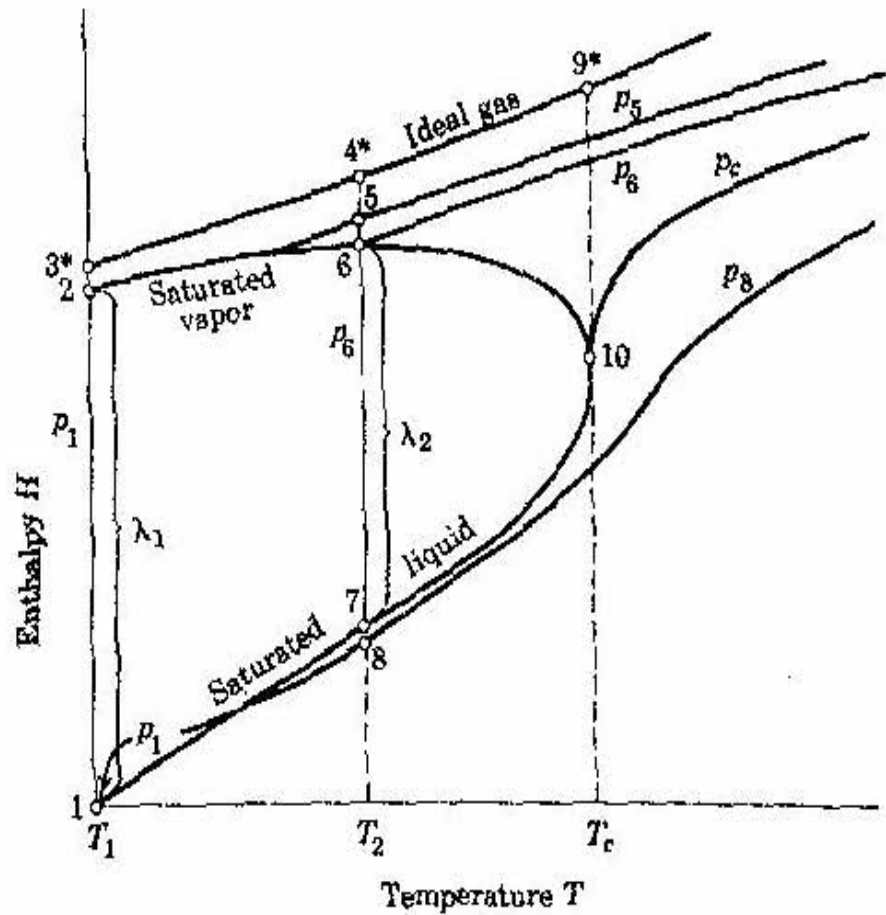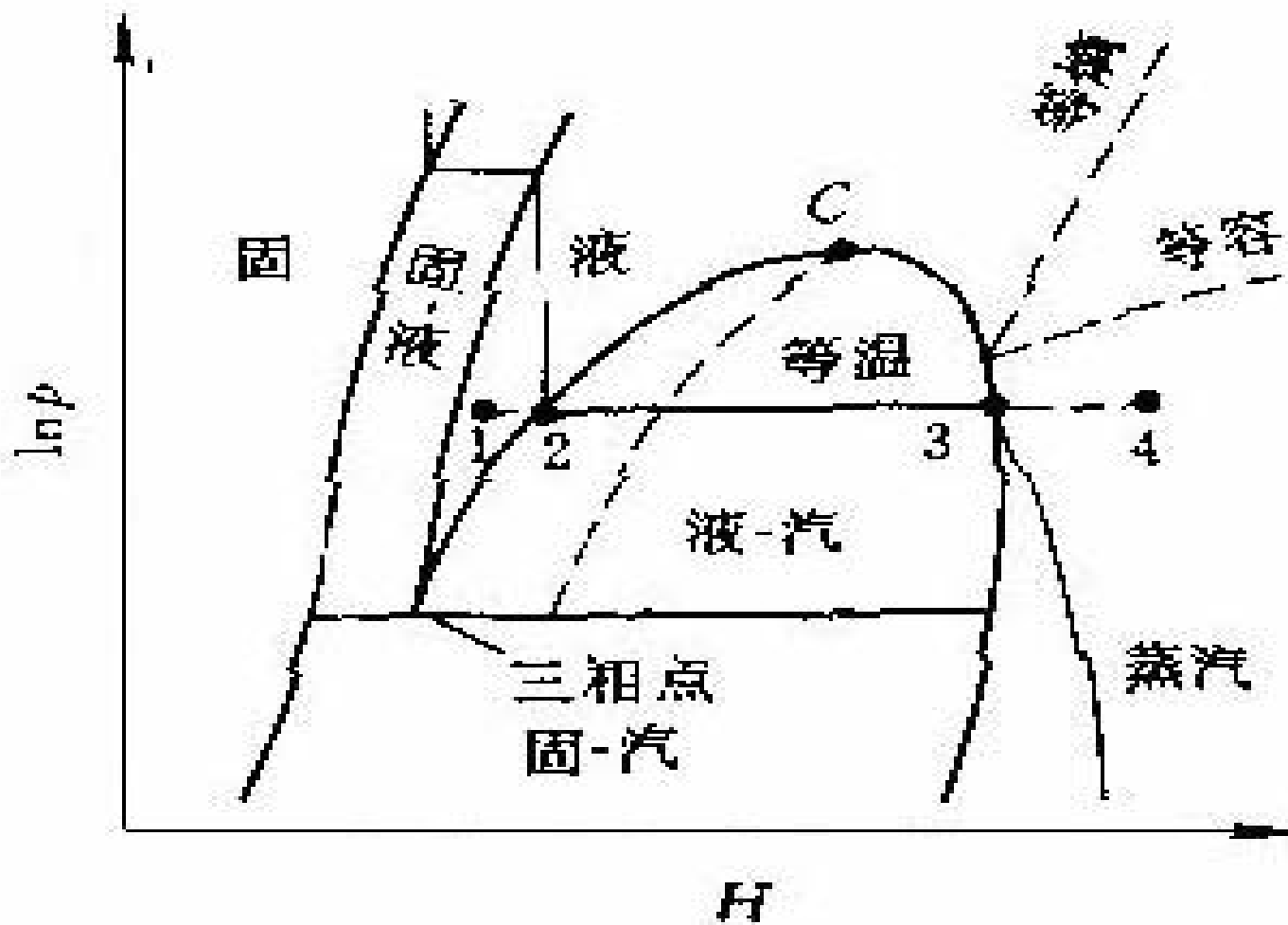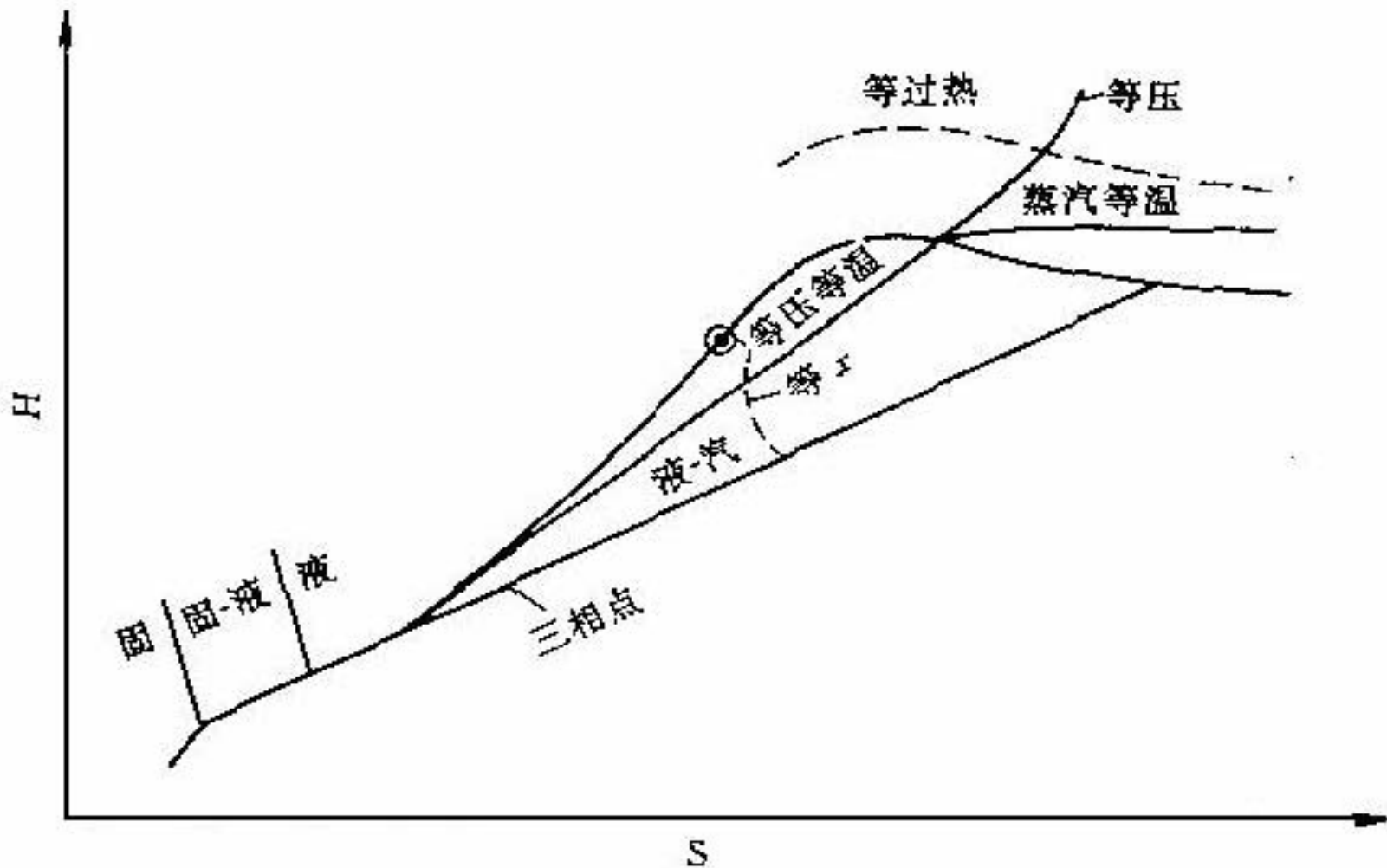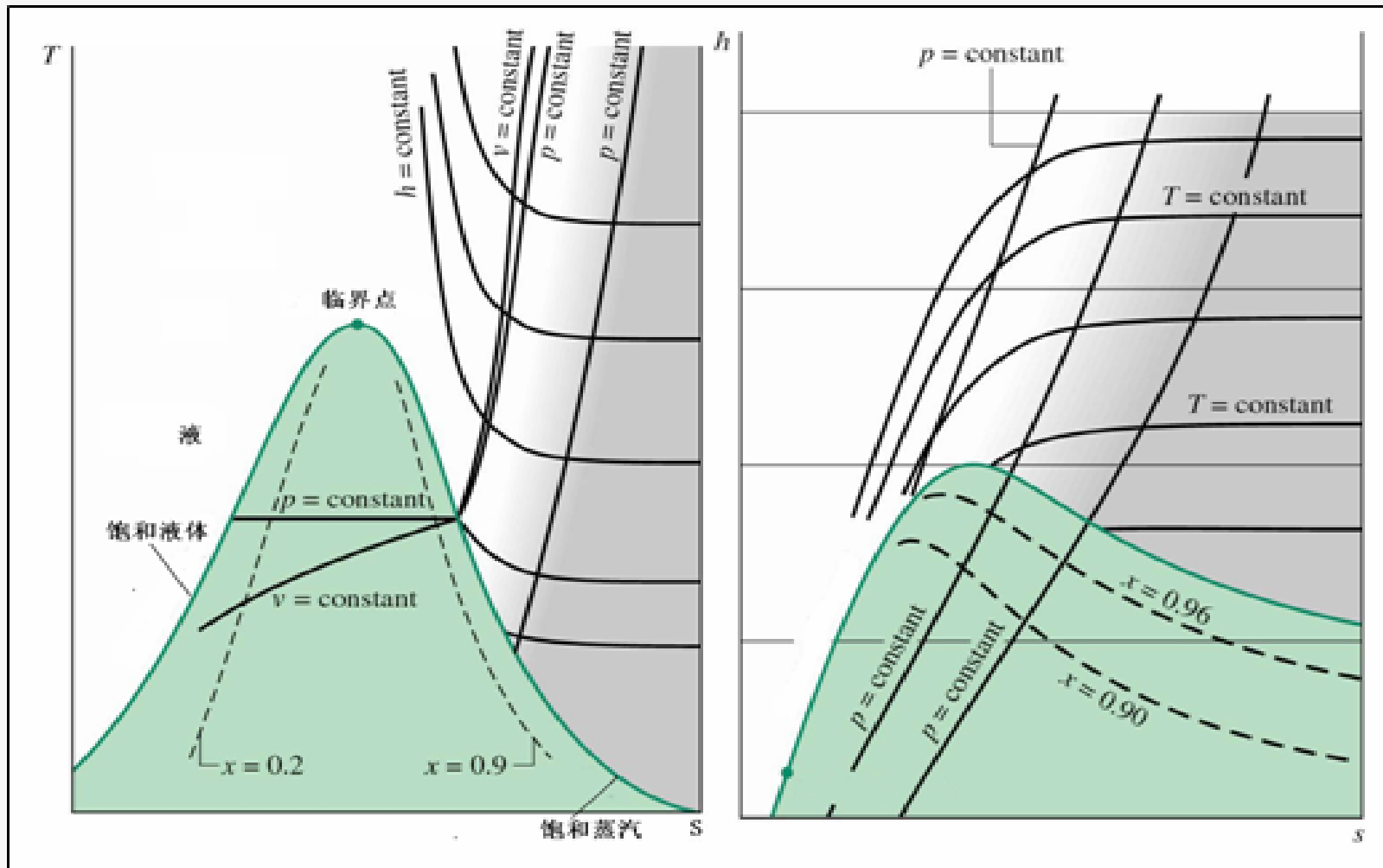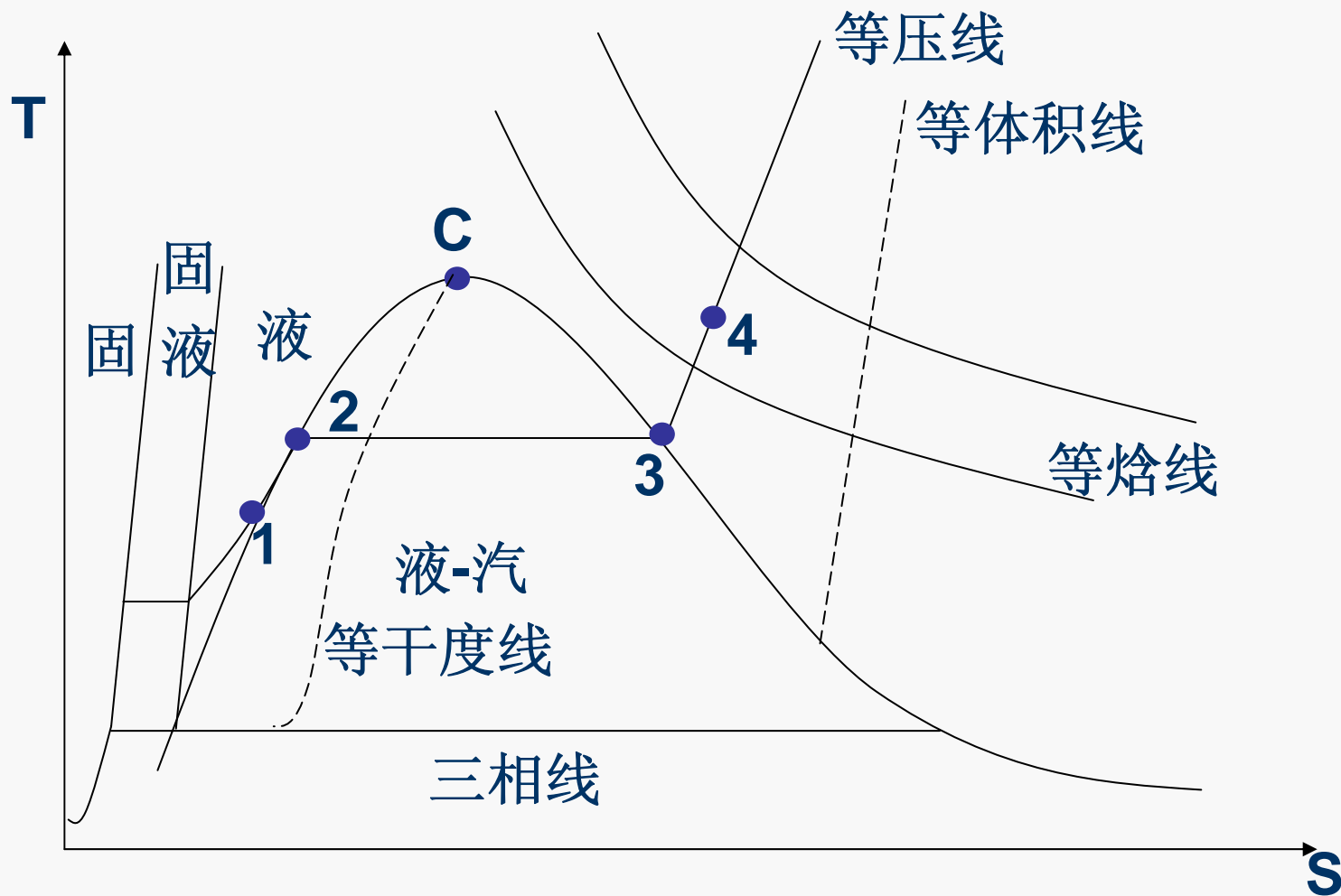
三相点在P-T图上是一个点，在T-S图上则是一条线；在P-T图上是一条线，则在T-S图上是一个面。

包含有饱和曲线、等压线、等容线、等焓线、等干度线以及等温线和等熵线等曲线。

等压线变化规律：

在一定温度下，熵值随压力增大而减小。

等焓线变化规律：

温度升高焓值增大，焓值大的等压线在上边。

2006年5月7日星期日
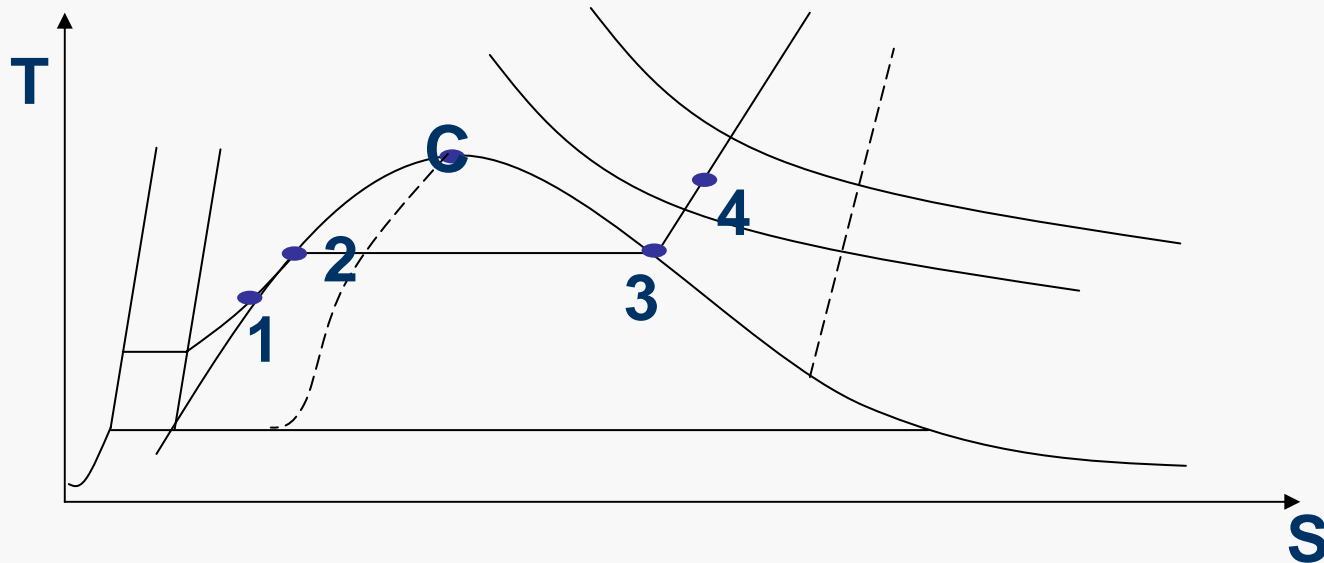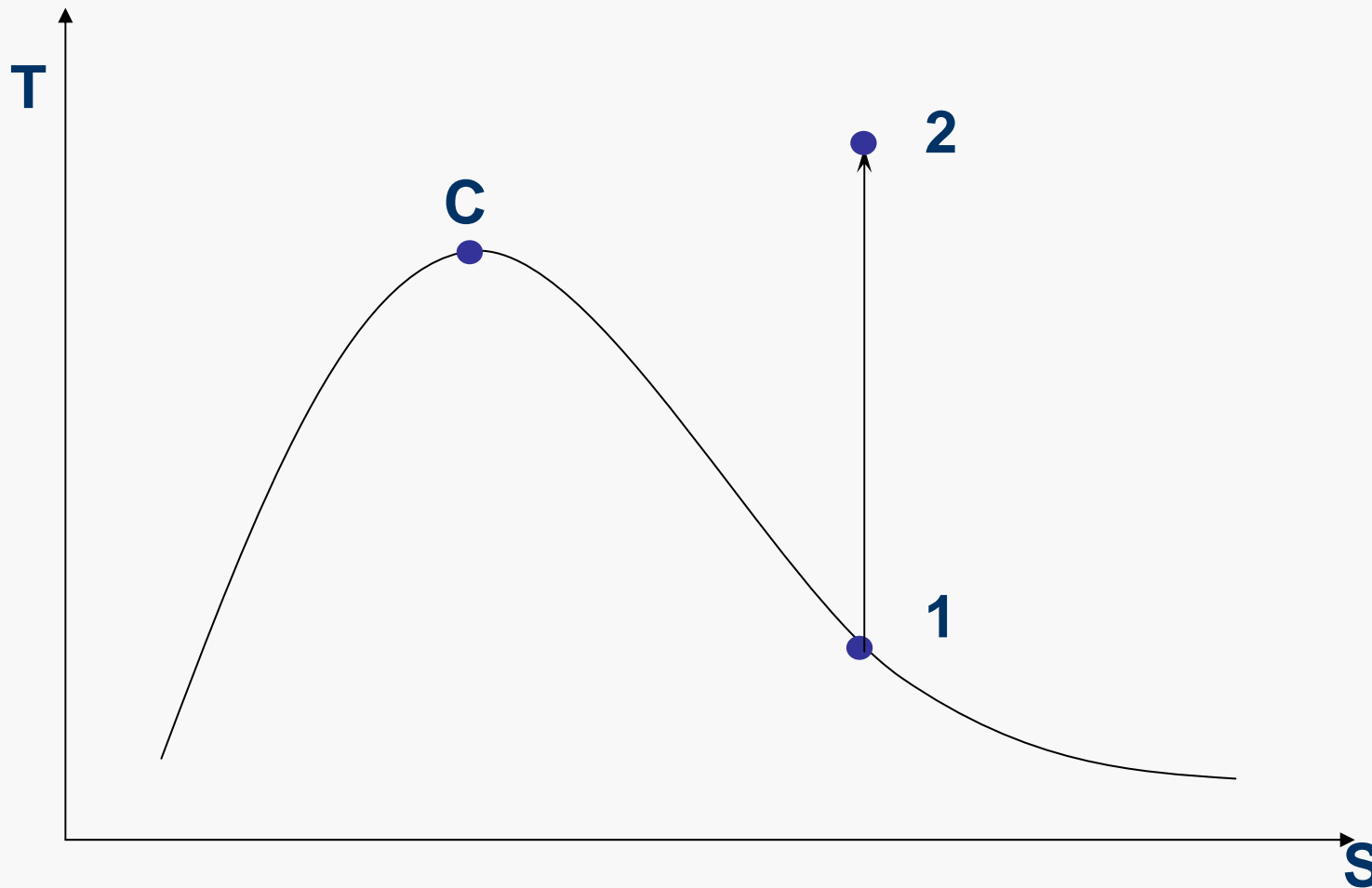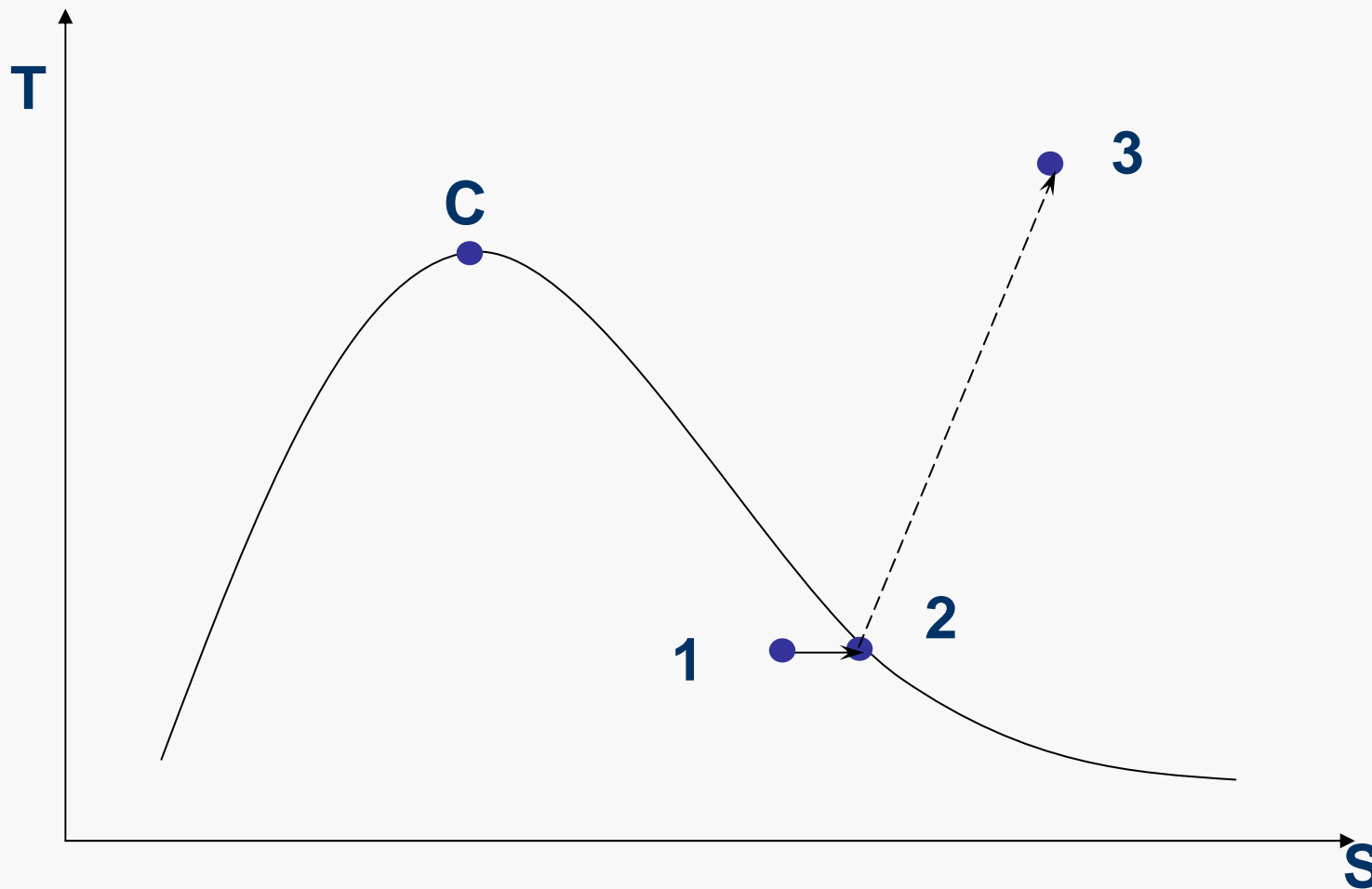
A.过热蒸气等压冷却、冷凝，冷却为过冷液体

B.饱和蒸气可逆绝热压缩至过热蒸气

C.接近饱和状态气体混合物，等容加热蒸发为过热蒸气

D.饱和液体分别等焓和等熵膨胀成湿蒸汽

E.过冷液体等压加热成过热蒸气

等压线

T

C

液

3

1

2

4

液-汽

三相线

S
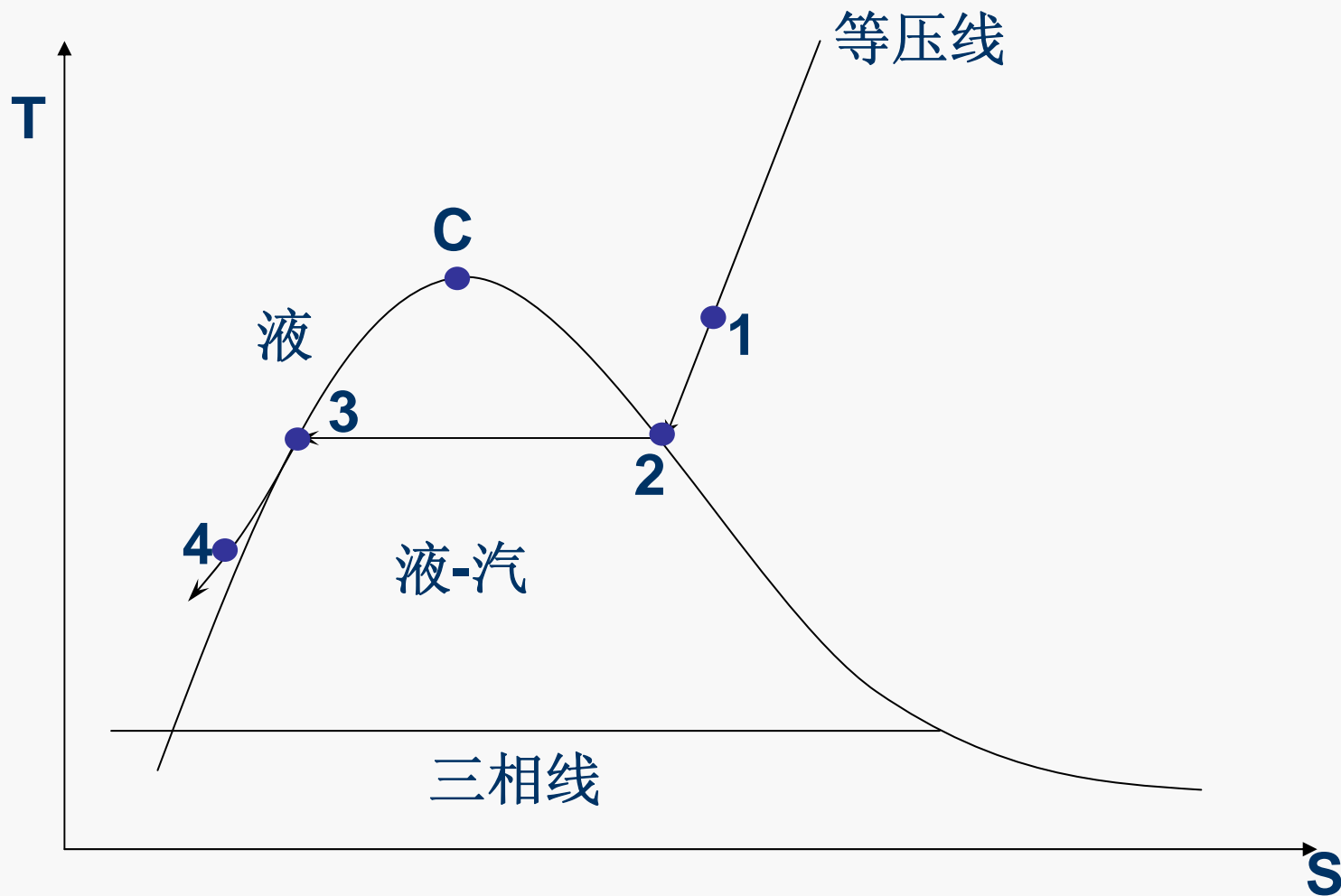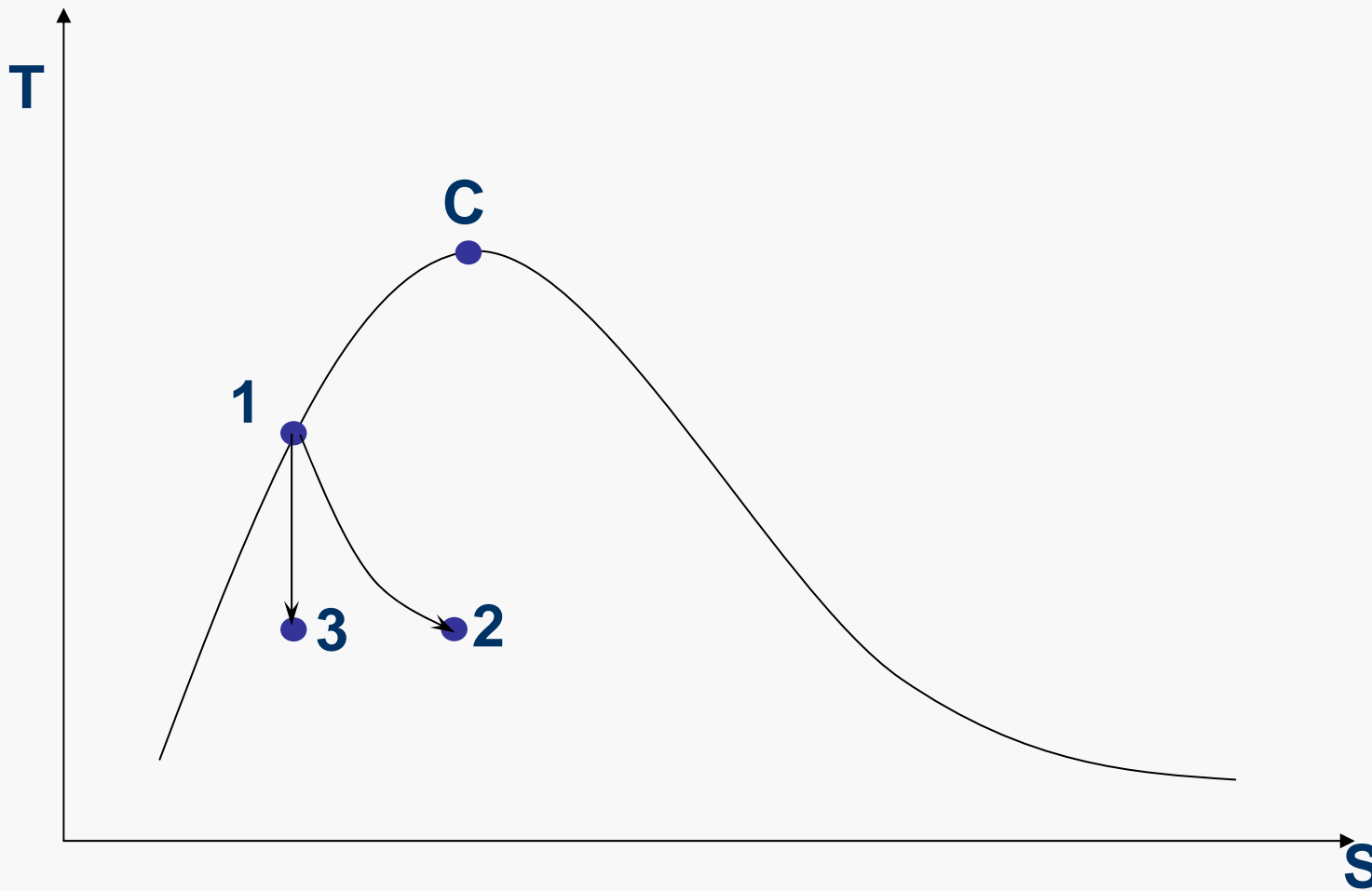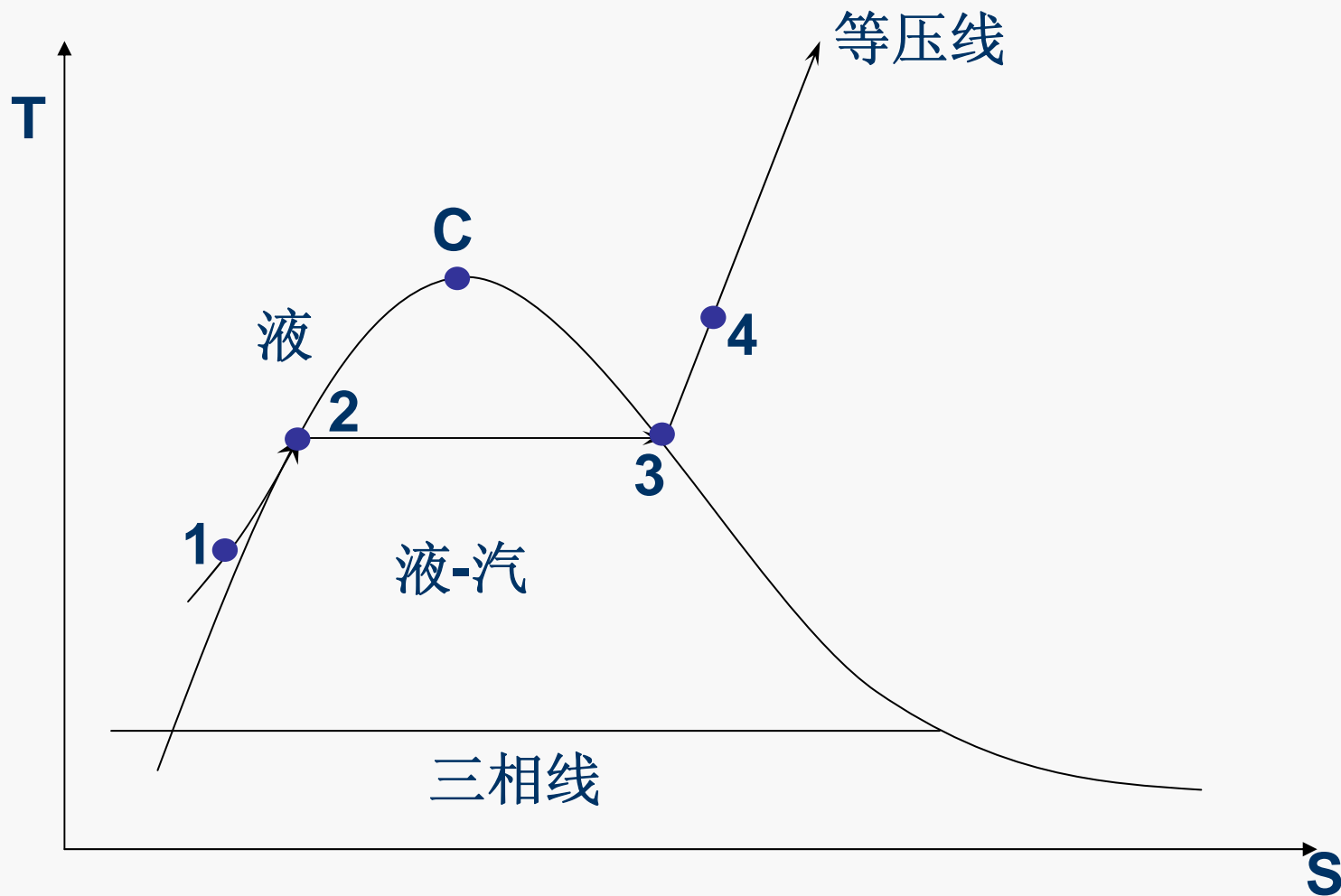
例3-9　1MPa,573K的水蒸气可逆绝热膨胀到0.1MPa,求蒸汽的干度。

T	S
280	7.0465
320	7.1962

$$\frac{299.85 - 280}{320 - 280} = \frac{S_1 - 7.0465}{7.1962 - 7.0465}$$

$$S_1 = 7.0465 + \frac{299.85 - 280}{320 - 280}(7.1962 - 7.0465)$$

$$= 7.1208 kJ / (kg \cdot K)$$

水蒸气由状态1绝热可逆膨胀到状态2为等熵过程，即S$_2$= S$_1$=7.1208kJ/(kg·K)。当P2=0.1MPa时

H	S
417.46	1.3026
2675.5	7.3594

$$S_2 = (1-x)S^l + S^g x$$

$$x = \frac{S_2 - S_l}{S_g - S_l} = \frac{7.1208 - 1.3026}{7.3594 - 1.3026} = 0.9606$$

$$H_2 = (1-x)H^l + H^g x$$

$$H_2 = 417.46 \times (1 - 0.96) + 2675.5 \times 0.95$$

$$H_2 = 2585.2 kJ \cdot kg^{-1}$$