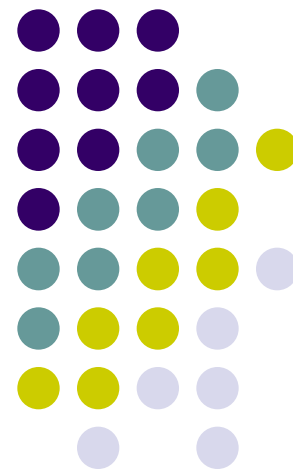


## 3.2.2.2 剩余性质的计算

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# 学习目标

- 计算的基本方程
- 实验数据法
- 状态方程法
- 普遍化方法

$T_0, P_0$   
理想气体  
(参考态)

$H_0^{ig}$   
 $S_0^{ig}$

$\Delta H, \Delta S$

$H$   
 $S$   
( $T, P$ )  
真实气体

①

$\Delta H_{P_0}$   
 $\Delta S_{P_0}$

$T, P_0$   
理想气体

②

$\Delta H_T$   
 $\Delta S_T$

$T, P$   
理想气体

$H^{ig}$   
 $S^{ig}$

③

$$H = H_0^{ig} + \Delta H_{P_0} + \Delta H_T + H^R$$

$$S = S_0^{ig} + \Delta S_{P_0} + \Delta S_T + S^R$$

剩余性质 Residual  
Property

$H^R$   
 $S^R$

# 剩余性质的计算

## 1、计算的基本方程

$$1) V^R = V - V^{ig} = V - \frac{RT}{P}$$

$$2) H^R = H - H^{ig}$$

$T$ 一定下, 对  $P$  求导

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

$$\int_{H_0^R}^{H^R} dH^R = \int_{P_0}^P \left[ V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

当  $P_0 \rightarrow 0$ , 状态  $\rightarrow$  理想气体

$$H_0^R \rightarrow 0$$

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

$$3) S^R = S - S^{ig}$$

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

## 2. $H^R$ 和 $S^R$ 压缩因子表达式

吉祥如意

用压缩因子表示

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

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

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

$$H^R = -RT^2 \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

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

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

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

$$= -RT^2 \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

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

$$= -R \int_0^P \left[ (Z - 1) + T \left( \frac{\partial Z}{\partial T} \right)_p \right] \frac{dp}{P}$$

## 1、实验数据（繁琐）

利用式子3-36,37,38,39图解积分

## 2、状态方程法

*Virial*方程, *RK*, *SRK*, *PR*

## 3、普遍化方法

### ① 普遍化压缩因子法

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

### ② 普遍化维里系数法

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1$$

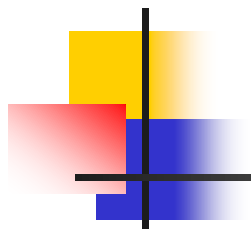


- 1.由气体PVT实验数据计算——图解积分法

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- 要点:

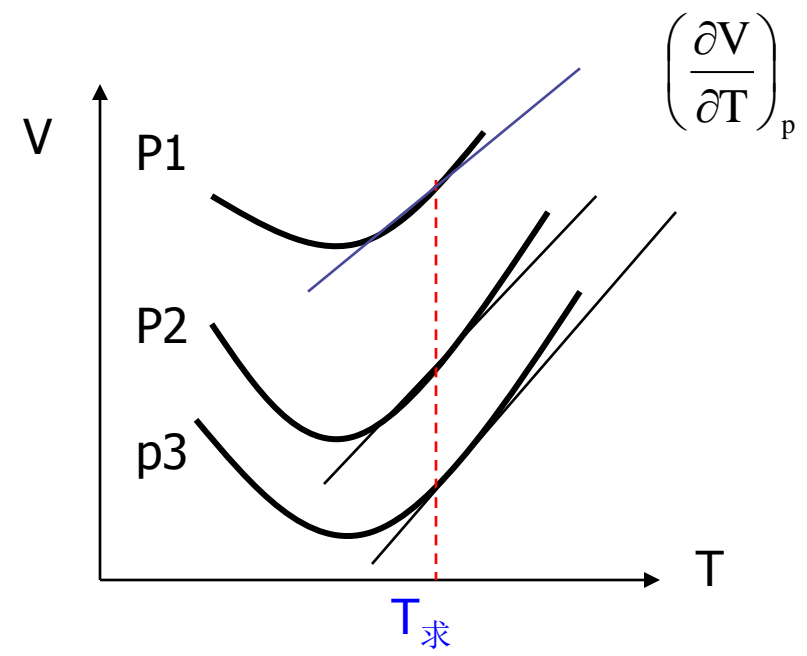
- 要有PVT实验数据
- 作图量面积



➤作V—T的等压线，并计算  
给定T下的等压线斜率

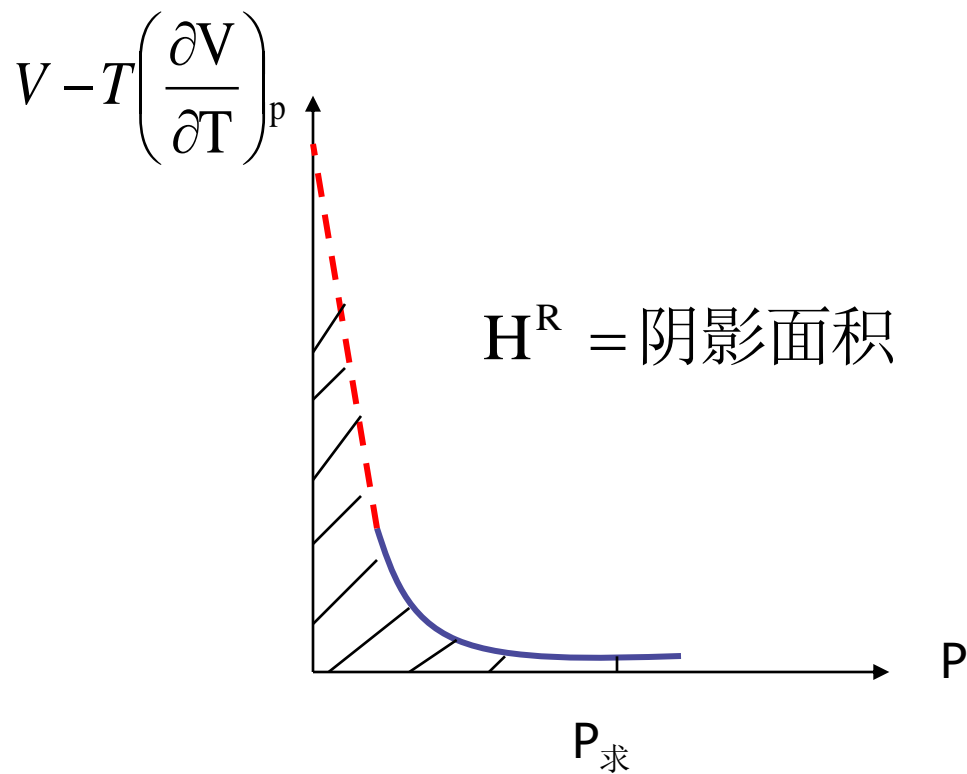
$$H^R = \int_0^P \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

(恒T)





作  $\left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] \sim P$  的曲线，曲线下的面积为  $H^R$  的值





## 利用剩余体积 $V^R$ 图解积分法

- 积分式的求取

$$V^R = V - V^* \quad V = V^* + V^R = \frac{RT}{P} + V^R$$

$$\text{微分:} \quad \left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P} + \left( \frac{\partial V^R}{\partial T} \right)_P$$

将上式代入用PVT表示的剩余焓和剩余熵的计算式中，得：

$$H^R = \int_0^P V^R dp + T \int_0^P \left( \frac{\partial V^R}{\partial T} \right)_P dP \quad (\text{恒}T)$$

$$S^R = \int_0^P \left( \frac{\partial V^R}{\partial T} \right)_P dP \quad (\text{恒}T)$$

以上内容仅为本文档的试下载部分，为可阅读页数的一半内容。如要下载或阅读全文，请访问：<https://d.book118.com/808043122075006024>