第六章
热力学微分关系式及实际气体的性质

Thermodynamic differential relation and the property of real gas

§ 6-1 研究热力学微分关系式的目的

√ 确定 $\Delta u, \Delta h, \Delta s$ 与可测参数（p,v,T,c_p)之间的关系，便于编制工质热力性质表。

√ 确定 c_p, c_v 与 p,v,T 的关系，用以建立实际气体状态方程。

√ 确定 c_p 与 c_v 的关系，由易测的 c_p 求得 c_v。

√ 热力学微分关系式适用于任何工质，可用其检验已有图表、状态方程的准确性。

§6-2 特征函数

简单可压缩系统，两个独立变量。

$$u = f(p, v) \qquad u = f(T, v)$$

$$\boxed{u = f(s, v)} \qquad u = f(s, p) \qquad \cdots$$

其中只有某一个关系式有这样的特征，当这个关系式确定，其它参数都可以从这个关系式推导得到，这个关系式称为“**特征函数**”。

u的特征函数

$u = f(s,v)$ 是特征函数

$Tds = du + pdv$

状态参数的性质

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

$du = Tds - pdv$

$$du = \left(\frac{\partial u}{\partial s}\right)_v d$$

$$h = u + pv = u - \left(\frac{\partial u}{\partial v}\right)_s v$$

$$T = \left(\frac{\partial u}{\partial s}\right)_v \qquad p = -\left(\frac{\partial u}{\partial v}\right)_s$$

h的特征函数

$$Tds = dh - vdp$$

热力学恒等式

$$h = f(s, p)$$

$$T = \left(\frac{\partial h}{\partial s}\right)_p$$

$$dh = Tds + vdp$$

$$v = \left(\frac{\partial h}{\partial p}\right)_s$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$$

$$u = h - pv = h - p\left(\frac{\partial h}{\partial p}\right)_s$$

$h = f(s, p)$ 是特征函数

$u = f(s, v)$ 是特征函数

亥姆霍兹函数（Holmhotz Function）

$$du = Tds - pdv = d(Ts) - sdT - pdv$$

$$d(u - Ts) = -sdT - pdv$$

令 $f = u - Ts$ 亥姆霍兹函数 $F = U - TS$

$$df = -sdT - pdv$$

*f*的物理意义: *f*的减少＝可逆等温过程的膨胀功，或者说，*f*是可逆等温条件下内能中能转变为功的那部分，也称亥姆霍兹自由能

f 的特征函数

$$df = -s\,dT - p\,dv$$

$$f = f(T, v)$$ 是特征函数

$$df = \left(\frac{\partial f}{\partial T}\right)_v dT + \left(\frac{\partial f}{\partial v}\right)_T dv$$

$$s = -\left(\frac{\partial f}{\partial T}\right.$$

$$h = u + pv = f - T\left(\frac{\partial f}{\partial T}\right)_v - v\left(\frac{\partial f}{\partial v}\right)_T$$

$$u = f + Ts = f - T\left(\frac{\partial f}{\partial T}\right)_v$$

吉布斯函数（Gibbs Function）

$$dh = Tds + vdp = d\left(Ts\right) - sdT + vdp$$

$$d\left(h - Ts\right) = -sdT + vdp$$

令 $g = h - Ts$ 吉布斯函数 $G = H - TS$

$dg = -sdT + vdp$ $g = g(T, p)$ 是特征函数

g的物理意义：g的减少＝可逆等温过程对外的技术功，或者说，g是可逆等温条件下焓中能转变为功的那部分，也称吉布斯自由焓

$$dg = -s\,dT + v\,dp$$

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

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

State equation

四个特征函数（吉布斯方程）
Gibbs equation

$$du = Tds - pdv \qquad u = f(s,v)$$

$$dh = Tds + vdp \qquad h = h(s,p)$$

$$df = -sdT - pdv \qquad f = f(T,v)$$

$$dg = -sdT + vdp \qquad g = g(T,p)$$

§ 6-3 数学基础

点函数 $z = f(x, y)$ —— 状态参数

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

全微分欧拉定义

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

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

全微分条件

Total differential

热量是不是满足全微分条件?

可逆过程 $\delta q = du + pdv$

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

$$du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_v dT$$

$$\delta q = \left[p + \left(\frac{\partial u}{\partial v}\right)_T\right] dv + \left(\frac{\partial u}{\partial T}\right)_v dT = Mdv + NdT$$

$$\left(\frac{\partial M}{\partial T}\right)_v = \left(\frac{\partial p}{\partial T}\right)_v + \frac{\partial^2 u}{\partial T \partial v} \neq \left(\frac{\partial N}{\partial v}\right)_T = \frac{\partial^2 u}{\partial v \partial T}$$

δq 不是状态参数　热量不是状态参数

常用的状态参数间的数学关系

倒数式
Reciprocity relation

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

循环式
Cyclic relation

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

常用的状态参数间的数学关系

链式

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w \left(\frac{\partial z}{\partial x}\right)_w = 1$$

不同下标式

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

四个特征函数（吉布斯方程）Gibbs equation

$$du = Tds - pdv \qquad u = f(s,v)$$

全微分条件 $$\left(\frac{\partial M}{\partial v}\right)_s = \left(\frac{\partial N}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

Maxwell 关系式

四、麦克斯韦关系

据$z = z(x, y)$则

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

$$du = Tds - pdv \qquad \left(\frac{\partial u}{\partial s}\right)_v = T, \left(\frac{\partial u}{\partial v}\right)_s = -p \qquad \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$dh = Tds + vdp \qquad \left(\frac{\partial h}{\partial s}\right)_p = T, \left(\frac{\partial h}{\partial p}\right)_s = v \qquad \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

$$df = -sdT - pdv \qquad \left(\frac{\partial f}{\partial T}\right)_v = -s, \left(\frac{\partial f}{\partial v}\right)_T = -p \qquad \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$dg = -sdT + vdp \qquad \left(\frac{\partial g}{\partial T}\right)_p = -s, \left(\frac{\partial g}{\partial p}\right)_T = v \qquad \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

吉布斯方程

麦克斯韦关系(Maxwell relations)

Maxwell关系式

- 这些关系式将不能直接测量的或由状态方程计算的量与实验上可以直接测量的量（如C_p、C_v、p、T、V等)及状态方程联系起来

四个 Maxwell ralation

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s \qquad \left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

八个偏导数

$$\left(\frac{\partial u}{\partial s}\right)_v = T = \left(\frac{\partial h}{\partial s}\right)_p \qquad \left(\frac{\partial u}{\partial v}\right)_s = -p = \left(\frac{\partial f}{\partial v}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_s = v = \left(\frac{\partial g}{\partial p}\right)_T \qquad \left(\frac{\partial f}{\partial T}\right)_v = -s = \left(\frac{\partial g}{\partial T}\right)_p$$

四个特征函数（吉布斯方程）

只需记住

$$du = Tds - pdv$$

$$dh = Tds + vdp$$

$$df = -sdT - pdv$$

$$dg = -sdT + vdp$$

§6-4 热系数

P，*v*，*T* 可测，实际测量是让一个参数不变，测量其它两个参数的变化关系

1. 定容压力温度系数（弹性系数）

$$\alpha_v = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v \qquad [K^{-1}]$$

定容下，压力随温度的变化率

§6-4 热系数

2. 定压热膨胀系数 Volume expansivity

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad [K^{-1}]$$

3. 定温压缩系数 Isothermal compressibility

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad [P_a^{-1}]$$

§6-4　热系数

4.　绝热压缩系数

Coefficient of adiabatic compressibility

$$\beta_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s \qquad [P_a{}^{-1}]$$

热系数间的关系

循环式

$$\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_T = -1$$

$$\alpha_v = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v \quad [K^{-1}]$$

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \quad [K^{-1}]$$

$$\beta_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s \quad [P_a^{-1}]$$

$\alpha_v p$ $\quad$ $1/\alpha_p v$ $\quad$ $-v\beta_T$

$$\alpha_p = \alpha_v \cdot \beta_T \cdot p$$

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

热系数应用举例

用实验方法测熵变，组织一个实验

Maxwell关系

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p = -v\alpha_p$$

$$\Delta s_T = \int -\left(\frac{\partial v}{\partial T}\right)_p dp = \int -v\alpha_p dp$$

§ 6-5 熵、内能和焓的微分关系式

$p, v, T \rightarrow ds, du, dh$ **Generalized relations**

一、熵

理想气体

$$s = f(T, v) \qquad ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

$$s = f(T, p) \qquad ds = c_p \frac{dT}{T} - R\frac{dp}{p}$$

$$s = f(p, v) \qquad ds = c_v \frac{dp}{p} + c_p \frac{dv}{v}$$

熵的微分关系式

一般工质

熵的第一微分关系式

$$s = f(T, v) \qquad ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv$$

普适式

理想气体 $pv = RT$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

熵的微分关系式（普适式）

$$s = f(T, p)$$

$$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_p dp$$

熵的第二微分关系式

$$s = f(p, v)$$

$$ds = \left[\frac{c_p}{T}\left(\frac{\partial T}{\partial p}\right)_v - \left(\frac{\partial v}{\partial T}\right)_p\right] dp + \frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p dv$$

熵的第三微分关系式

内能的微分关系式（普适式）

$$du = Tds - pdv$$

三个*ds*的微分关系式分别代入：

$$ds = c_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v dv$$

$$u = f(T, v)$$

$$du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv$$

*u*的第一微分关系式

内能的微分关系式（普适式）

$$u = f(T, p)$$

$$du = \left[c_p - p\left(\frac{\partial v}{\partial T}\right)_p\right]dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_T\right]dp$$

u的第二微分关系式

$$u = f(p, v)$$

$$du = \left[c_p\left(\frac{\partial T}{\partial p}\right)_v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp + \left[c_p\left(\frac{\partial T}{\partial v}\right)_p - p\right]dv$$

u的第三微分关系式

内能的微分关系式（普适式）

u的第一微分关系式，最常用

$$du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv$$

理想气体： $pv = RT$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = T \cdot \frac{R}{v} - p = p - p = 0$$

$$du = c_v dT$$

焓的微分关系式（普适式）

$$dh = Tds + vdp$$

三个*ds*的微分关系式分别代入：

$$h = f(T, v)$$

$$dh = \left[c_v + v\left(\frac{\partial p}{\partial T}\right)_v\right]dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v + v\left(\frac{\partial p}{\partial v}\right)_T\right]dv$$

*h*的第一微分关系式

焓的微分关系式（普适式）

$$h = f(T, p)$$

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp$$

最常用

h的第二微分关系式

$$h = f(p, v)$$

$$dh = c_p \left(\frac{\partial T}{\partial v}\right)_p dv + \left[c_p \left(\frac{\partial T}{\partial p}\right)_v - T\left(\frac{\partial v}{\partial T}\right)_p + v \right] dp$$

h的第三微分关系式

§6-6 比热容的微分关系式

ds , du , dh 的微分关系式都有c_p , c_v

c_p , c_v 与 p , v , T 的关系？

c_p， c_v 表达式的用途

c_p 与 c_v的关系

定容比热容的微分关系式

熵的第一微分关系式

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

$$ds = c_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v \cancel{dv} \Rightarrow c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

全微分关系 $\Rightarrow$

$$\frac{\partial}{\partial v}\left[\left(\frac{c_v}{T}\right)\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial p}{\partial T}\right)_v\right]_v$$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

定压比热容的微分关系式

熵的第二微分关系式

$$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_p \cancel{dp} \;\Rightarrow\; c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

全微分关系 $\Rightarrow$

$$\frac{\partial}{\partial p}\left[\left(\frac{c_p}{T}\right)\right]_T = \frac{\partial}{\partial T}\left[-\left(\frac{\partial v}{\partial T}\right)_p\right]_p$$

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

比热容的微分关系式的用途

1、已知状态方程 $f(p, v, T) = 0$

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

对状态方程微分两次，再对压力积分

$$c_p - c_p^* = -\left[\int_{p\to 0}^{p} T\left(\frac{\partial^2 v}{\partial T^2}\right)_p dp\right]_T$$

理想气体c_p^*+状态方程 $\longrightarrow$ 实际气体c_p

比热容的微分关系式的用途

HFC-32的理想气体比定压热容

$$C_p^* / R = d_0 + d_1 T_r + d_2 T_r^2 + d_3 T_r^3$$

$$d_0 = 4.424901$$

$$d_1 = -2.661170$$

$$d_2 = 5.580232$$

$$d_3 = -1.680558$$

偏差<0.1%

比热容的微分关系式的用途

2、检验状态方程的准确性

$$f(p, v, T) = 0$$

对状态方程微分两次，得到c_p

对比实际测量的c_p

比热容的微分关系式的用途

3、建立状态方程

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

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

$$\boxed{v} = \left[-\iint \frac{\boxed{\left(\frac{\partial c_p}{\partial p}\right)_T}}{T} dT^2\right]_p + T\boxed{\varphi(p)} + \cancel{\varphi'(p)}$$

0

$\frac{RT}{p}$

$\frac{R}{p}$

实验数据确定

$p \to 0$ 理想气体

定压比热容与定容比热容的关系式

c_p易测，由$c_p \longrightarrow c_v$

由熵的第一和第二关系式可得

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

已知状态方程即可

固体、液体 $\left(\frac{\partial v}{\partial T}\right)_p \approx 0 \longrightarrow c_p \approx c_v$

Specific heat of incompressible substance

§ 6-7 克拉贝龙方程和焦汤系数

由微分关系，可导出两个非常有用的关系

一、克拉贝龙方程 Clapeyron equation

相变时，饱和压力和饱和温度一一对应

$$\left(\frac{dp}{dT}\right)_{相变}$$

克拉贝龙方程的推导

$$Maxwell: \quad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{相变}$$

相变时 → $p = f(T)$

相变过程的熵，通过 p, v, T 测量得到

积分

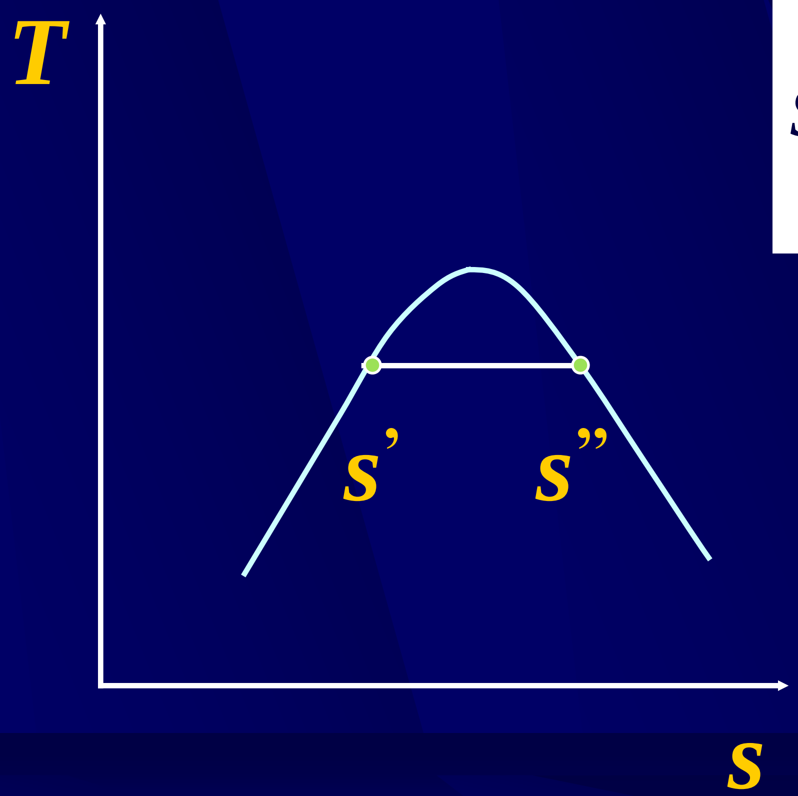
饱和液

饱和气

$$s'' - s' = \left(\frac{dp}{dT}\right)_{相变}\left(v'' - v'\right)$$

克拉贝龙方程的表达式

$$s'' - s' = \left(\frac{dp}{dT}\right)_{相变} (v'' - v')$$



$$s'' - s' = \frac{h'' - h'}{T_s} = \frac{\gamma}{T_s}$$

$$\left(\frac{dp}{dT}\right)_{相变} = \frac{\gamma}{T_s(v'' - v')}$$

克拉贝龙方程

广义克拉贝龙方程

气液相变时
$$\left(\frac{dp}{dT}\right)_{相变}=\frac{\gamma}{T_s(v''-v')}$$

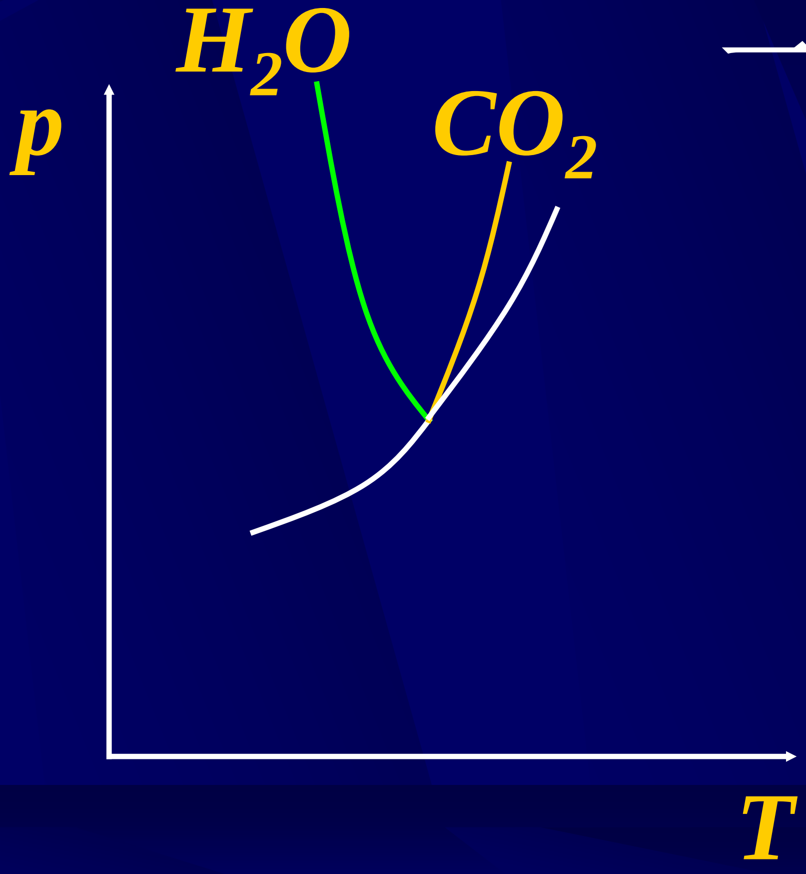
一般相变时
$$\left(\frac{dp}{dT}\right)_{相变}=\frac{\gamma}{T(v^{\beta}-v^{\alpha})}$$

α 初态，β 终态，T 相变时温度

γ
- 液 → 气 → 汽化潜热
- 固 → 液 → 融解热
- 固 → 气 → 升华热

克拉贝龙方程

$$\left(\frac{dp}{dT}\right)_{相变} = \frac{\gamma}{T(v^{\beta} - v^{\alpha})}$$



一般物质 $v^{液} - v^{固} > 0$

$$\left(\frac{dp}{dT}\right)_{相变} > 0$$

水 $v^{液} - v^{固} < 0$

$$\left(\frac{dp}{dT}\right)_{相变} < 0$$

克拉贝龙方程的用途

$$\left(\frac{dp}{dT}\right)_{相变} = \frac{\gamma}{T_s(v'' - v')} = \frac{\gamma}{T_s v''} = \frac{\gamma}{T_s \dfrac{RT_s}{p_s}}$$

1、估算低压下 γ

低压下 $v' << v''$

气相接近理想气体 $p_s v'' = RT_s$

$$\gamma = -R\frac{d\ln p_s}{d\ln\left(\dfrac{1}{T_s}\right)}$$

克拉贝龙方程的用途

2、预测p_s与T_s关系

$$\left(\frac{dp}{dT}\right)_{相变} = \frac{\gamma}{T_s(v'' - v')}$$

$$\gamma = -R\frac{d\ln p_s}{d\ln\left(\frac{1}{T_s}\right)}$$

低压时

T_s变化不大时

$$\gamma \approx Const$$

$$\ln p_s = -\frac{\gamma}{RT_s} + A \rightarrow \ln p_s = A - \frac{B}{T_s}$$

克拉贝龙方程的用途

$$\ln p_s = A - \frac{B}{T_s}$$

虽误差大，但基本形式确定

$$\ln p_s = A - \frac{B}{T_s + C}$$

$$\ln p_s = A - \frac{B}{T_s + C} + DT_s + E\ln T_s$$

***A*, *B*, *C*, *D*, *E*由实验数据拟合**

克拉贝龙方程的用途举例

HFC-32的饱和蒸气压方程

$$\ln p_r = (a_0 + a_1\tau^{1.89} + a_2\tau^{5.67})\ln T_r$$

$$p_r = p / p_c, T_r = T / T_c, \tau = 1 - T / T_c$$

$$a_0 = 7.232768$$

$$a_1 = 9.609696$$

$$a_2 = 20.851410$$

最大偏差<0.2%