热力学习题(1).

已知 α, β 为常数, $0^\circ C$ $1\,atm \to 10^\circ C$ $V=V(p,T)$

$$dV=\left(\frac{\partial V}{\partial T}\right)_p \cdot dT+\left(\frac{\partial V}{\partial p}\right)_T \cdot dp \leftarrow \text{全微分}$$

$$\alpha \equiv \frac{1}{V}\cdot\left(\frac{\partial V}{\partial T}\right)_p \qquad \beta \equiv \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \qquad k_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$dV = V\cdot\alpha\cdot dT - V\cdot k_T\cdot dp$$

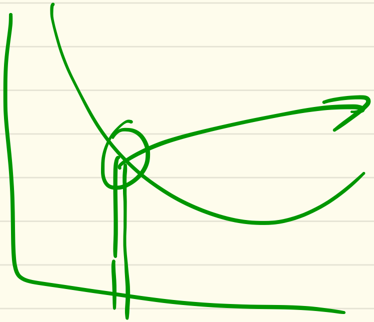
体积不变 $dV=0$

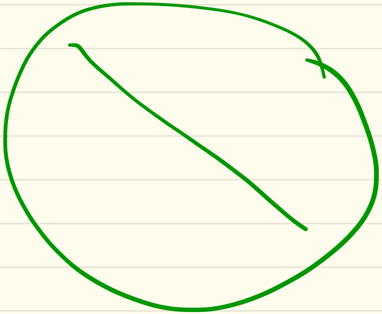
$$V\cdot\alpha\cdot \underbrace{dT}_{10K} = V\cdot k_T\cdot \underbrace{dp}_{\text{可求出}}.$$

(2).

$$dV = V \cdot \alpha \cdot \underbrace{dT}_{10K} - V \cdot k_T \cdot \underbrace{dP}_{100\ atm.}$$

$= \quad \cdots\cdots$





2. 已知 T, p, ρ, C_p, γ.

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

① $$C_V = \left(\frac{dQ}{dT}\right)_V$$

$$dQ = C_V \cdot dT$$ 在等容过程.

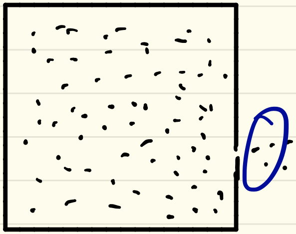
$$= \frac{C_p}{\gamma} \cdot dT$$

② $$C_p = \left(\frac{dQ}{dT}\right)_p$$

$$dQ = C_p \cdot dT$$

③ 容器有缝隙. $\Longrightarrow$ 分子数可变.

$\Longrightarrow$ 保证内外压强一致.



$$dQ = C_p(N) \cdot dT$$

现在容器内的分子数.

$$= C_p \cdot \frac{n}{n_0} dT$$

最初容器中的分子数.

理想气体方程. $PV = nRT$ $\quad PV = n_0 \cdot R T_0$

有 $\frac{n}{n_0} = \frac{T_0}{T}$

$$dQ = C_p \cdot \frac{T_0}{T} \cdot dT$$

$$\Delta Q = \int_{0°C}^{20°C} C_p \frac{T_0}{T} \cdot dT$$

$$= C_p \cdot T_0 \ln(T_1/T_0)$$

3. $pV = nRT.$

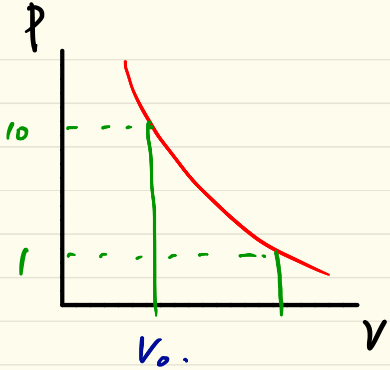
$$p = \frac{nRT}{V}$$

$$W' = \int_{V_0}^{\frac{V_0}{10}} p \cdot dV$$

$$= \int_{V_0}^{10 V_0} \frac{nRT}{V} \cdot dV$$

$$= nRT \ln 10$$

$$Q = W' = nRT \cdot \ln 10$$



理想气体温度不变

→ 内能不变

$$\Delta U = -W' + Q$$

4 $$dS = \frac{dQ}{T}$$

等容过程. $dQ = C_V \cdot dT$.

$$dS = C_V \cdot \frac{dT}{T}$$

$$\Delta S_V = C_V \cdot \ln(T_1/T_0)$$

等压过程. $dQ = C_p \cdot dT$.

... $\Delta S_p = C_p \cdot \ln(T_1/T_0)$.

$\gamma = \frac{C_p}{C_V} \Rightarrow \frac{\Delta S_p}{\Delta S_V}$ 即 $\Delta S_p = \gamma \cdot \Delta S_V$

$c_p - c_V$ $\qquad C_V \equiv \frac{dQ}{dT}$ 在等容过程.

把 $S = S(T.V)$ $\qquad \rightarrow T\left(\frac{\partial S}{\partial T}\right)_V$

全微分 $dS = \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T \cdot dV$

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

$\downarrow$ maxwell 关系

$$T \cdot dS = C_V \cdot dT + \left(\frac{\partial P}{\partial T}\right)_V \cdot dV \quad ①$$

同样 $S = S(p, T)$

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

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

Maxwell 关系

$$T \cdot dS = C_p \cdot dT - T\left(\frac{\partial V}{\partial T}\right)_p \cdot dp \quad ②$$

联立①②消去 $T \cdot dS$ 得

$$(C_p - C_v)\cdot dT = T\left(\frac{\partial p}{\partial T}\right)_V \cdot dV + T\left(\frac{\partial V}{\partial T}\right)_p \cdot dp$$

考虑等压过程 ($dp = 0$)

$$C_p - C_v = T\cdot\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

代入范式气体方程

证明 $\left(\frac{\partial S}{\partial p}\right)_H < 0$ 和 $\left(\frac{\partial S}{\partial V}\right)_U > 0$

焓的基本微分方程

$$dH = d(U+pV) = dQ - p\cdot dV + d(pV) = T\cdot dS + V\cdot dp$$

焓不变: $dH = 0.$ $\Rightarrow$ $T\cdot(dS)_H = -V\cdot(dp)_H$

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

$V>0.$
$T>0.$ 故 $\left(\frac{\partial S}{\partial p}\right)_H < 0$

$$dU = T \cdot dS - p \cdot dV$$

$$dU = 0 \Rightarrow T \cdot (dS)_U - p \cdot (dV)_U = 0$$

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

$p > 0$

$T > 0$.

$$\left(\frac{\partial S}{\partial V}\right)_U > 0$$