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作业在课程主页 《汪志诚》的习题为主 周一收作业

《热力学·统计物理》

作业 30% 期中 30% 期末 40%

研究对象：宏观物体，大量微观粒子组成的系统

热学四大定律 第零定律 第一定律 能量守恒

热力学第二定律 方向 绝对零度不可到达

统计物理 从微观结构出发 等概率原理

第一章 ...

热力学系统 孤立系 闭系 开系

平衡态：不受外界影响下，系统的性质不随时间改变的状态

力学平衡 化学平衡 相平衡 热平衡

参量：几何：长度 面积 体积 应变张量

力学：压强 应力张量

化学：摩尔数 质量 浓度

电磁：电场 电极化 磁化强度

温度

广延量 强度量

绝热壁 透热壁 热平衡

温度 温标

看课件 理想气体温标

物态方程：给出温度和系统参量之间的函数关系的方程

[2.25] 简单系统 $f(p,V,T)=0$

定压膨胀系数 $\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ 定容压力系数 $\beta=\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$

定温压缩系数 $\kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ $\alpha=\beta\kappa_T p$

气体状态方程 $PV=nRT$ (理想气体)

范德瓦尔斯方程 $\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT$ $V_m=\frac{V}{n}$

简单固液 $V(T,p)\approx V(T_0,0)+\left(\frac{\partial V}{\partial T}\right)_p\Big|_{T=T_0,p=0}(T-T_0)+\left(\frac{\partial V}{\partial p}\right)_T\Big|_{T=T_0,p=0}p$

$V(T,p)=V(T_0,0)[1+\alpha(T-T_0)-\kappa_T p]$

顺磁性 ~~物质~~ $f(M,H,T)=0$ 顺磁性物质 $M=\frac{CH}{T}$

第二章 热力学第一定律 内能

$\Delta U=W+Q$

$W=-\int pdV$

准静态过程 磁化功 极化功

$dW=\sum_{i=1} Y_i dy_i$ Y_i广义力 y_i广义坐标

[2.29] 热统 4.17 集体

热容量 $C=\lim_{\Delta T\to 0}\frac{\Delta Q}{\Delta T}$ $C_m=\frac{C}{n}$ 摩尔热容量 (与过程有关)

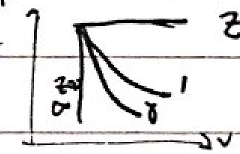
定容热容 C_V 定压热容 C_p $C_V=\left(\frac{\partial U}{\partial T}\right)_V$

$C_p=\frac{\Delta U+P\Delta V}{\Delta T}=\left(\frac{\partial(U+PV)}{\partial T}\right)_p$

稀薄气体的热容量 $C_V<C_p$ P大 C大 $\gamma=\frac{C_p}{C_V}>1$

焓 $H=U+PV$ $C_p=\left(\frac{\partial H}{\partial T}\right)_p$

多方 $pV^z=\mathrm{const}$

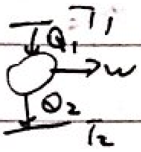


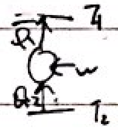
$z=0$ 等压 $z=1$ 等温 $z=\gamma$ 绝热 ($\Delta Q=0$) $z\to\infty$ 等容

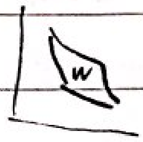
CO2 P31

理想气体 $U=U(T)$ $H=H(T)=U(T)+nRT$ $C_p-C_V=nR$

$C_V=\frac{nR}{\gamma-1}$ $C_p=\frac{\gamma nR}{\gamma-1}$

循环过程  $W=Q_1-Q_2$ $\eta=\frac{W}{Q_1}=1-\frac{Q_2}{Q_1}$

 $\eta'=\frac{Q_2}{W}=\frac{Q_2}{Q_1-Q_2}$

卡诺循环  $\eta=1-\frac{T_2}{T_1}$ ⊙ $\eta'=\frac{T_2}{T_1-T_2}$ ⊙

第二章 热力学第二定律 熵

时间反演不对称性

$\boxed{3.8}$ $\cancel{\oint\frac{\delta Q}{T}\le 0}$ $S_1-S_0\ge\int\frac{\delta Q}{T}$

熵增流

$S=k\ln W$

$\boxed{3.21}$ cos 单元系的相变

$(P,V)_{const}$ 物态由 $F=U-TS$ 最低决定

1. 力学体系  $\frac{\partial u}{\partial x}=0$ 平衡 $\frac{\partial^2 u}{\partial x^2}>0$ 稳定

2. 热力学 $(U,V)_{const}$(孤立系) S 最大

$\delta Q=du+\delta w$ $\delta Q\le Tds$

$Tds\ge du+\delta w=du+pdV \Rightarrow ds\ge 0$

$\delta' S=0$ $\delta'' S<0$

$T\ V$ const $\Rightarrow dF=d(U-TS)\le 0$

$\delta' F=0$ $\delta'' F>0$

$T\ P$ const $\Rightarrow dG=d(U-TS+pV)\le 0$

$\delta' G=0$ $\delta'' G>0$

V,S const $U\downarrow$ P,S const $H\downarrow$

期中复习 5/13 克劳修斯等式 吸热 dQ $\oint \frac{dQ}{T} \le 0$ ~~热~~ $du = dQ + pd(-V)$

$H = U + pV$ $\boxed{dU = TdS - pdV}$

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

$pV = nRT$ $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$

$f(M, H, T) = 0$ $M = \frac{C}{T}H$ 居里定律 顺磁性固体 总磁矩 $m = MV$

4.6 统计物理

4.14 三维自由粒子

复习 理想气体 $PV = NkT$ $\langle\varepsilon\rangle = \frac{3}{2}kT$ $V_m = \frac{V}{n}$

一. $P = \frac{RT}{V_m}\left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \cdots\right)$ B C 第二 三位力系数

极化功 $\delta W = Udq = ElAd\rho = EVd\rho$

介质 $\rho = \vec{D} = \varepsilon_0\vec{E} + \vec{P}$ $\delta W = Vd\frac{\varepsilon_0 E^2}{2} + VEdP$

磁化功 $\delta w = Udq = UIdt$ ~~U~~ $= (-N\frac{d}{dt}(AB) \cdot I dt)$

$\cdot \delta w_{外} = Nd(AB)\cancel{I}H = VHdB$

介质 $B = \mu_0(H + M)$ $\delta w = Vd\frac{\mu_0 H^2}{2} + \mu_0 VHdM$

$C_V = \frac{dQ}{dT}\Big|_V = \left(\frac{\partial U}{\partial T}\right)_V$ $C_p = \frac{dQ}{dT}\Big|_p = \left(\frac{\partial H}{\partial T}\right)_p$

$H = U + pV = U - (p \cdot V)$ $dH = TdS + Vdp$

理想气体 $U(T)$ $H(T)$ $U = \frac{3}{2}NkT$

$C_p - C_V = nR$ $\gamma(T) = \frac{C_p}{C_V}$ $C_V = \frac{nR}{\gamma - 1}$ $C_p = \frac{\gamma nR}{\gamma - 1}$

$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$ $\eta' = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$

熵 S, S_0 $\int \frac{dQ}{T}$ $\boxed{dS \ge \frac{dQ}{T}}$ $du = TdS + pd(-V)$

$S = k\ln W$ $F = U - TS$ $dF = -SdT - pdV$

$G = U - TS + pV$ $dG = -SdT + Vdp$

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

$\cancel{U=u(T)\cdot V \quad p=\frac{1}{3}u}$

平衡辐射场 $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \Rightarrow u(T) = \frac{T}{3}\frac{\partial u}{\partial T} - \frac{u}{3} \Rightarrow u = aT^4$

$\Rightarrow dS = \frac{4}{3}a\,d(T^3V) \quad S = \frac{4}{3}aVT^3 \Rightarrow G=0$

通量密度 $J = \frac{1}{4}cu$

磁介质热力学 $H \; m \; T$ 顺磁 $m = \frac{CV}{T}\cdot H \quad (m=VM)$

$dW = \mu_0 H dm \quad (p \Rightarrow \mu_0 H, \; -V \sim m)$

气体节流过程 绝热，存在功(通过多孔塞，等焓)

$\mu = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial H}{\partial p}\right)_T = \frac{V}{C_p}(T\alpha - 1)$ 理想气体 $\alpha = \frac{1}{T}$

条件 $\mu > 0$ 节流致冷

气体绝热膨胀 $\mu_S = \left.\frac{\partial T}{\partial p}\right|_S = \frac{VT\alpha}{C_p}$

热力学第三定律 $(\Delta S)_T \xrightarrow{T\to 0} 0$

四. 单元系相变 $\overset{d<0}{}$ $\delta = 0$ 平衡 $\delta^2 > 0$ 稳定 (对于↓趋势)

(U,V) $dS \geq 0$ $\delta S = 0$ $\delta^2 S < 0$

(T,V) $dF \leq 0$

1.2 $\delta S = \frac{\delta U + p\delta V}{T} \rightarrow$ 平衡 $T=T_0 \quad p=p_0$

$\delta^2 S = -\frac{C_V}{T^2}(\delta T)^2 + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T(\delta V)^2 \rightarrow C_V>0 \quad \kappa>0$

开系 $dU = TdS + pd(-V) + \mu dN$ μ化学势 $\therefore \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$

$J = U - TS - \mu N \quad dJ = -SdT - pdV + \mu dN$ 巨热力势

$G = U - TS + pV = N\mu$

单元复相平衡条件 34/119 由两相 α β 组成 $\cancel{\delta U^\alpha + \delta U^\beta}$

$\delta U = \delta U^\alpha + \delta U^\beta = 0 \quad \delta V = 0 \quad \delta n = 0 \quad \therefore \delta S = \delta U^\alpha\left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right) + \delta V^\alpha\left(\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}\right) - \delta n^\alpha\left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta}\right)$

相图平衡曲线上 $\delta^2 G = 0$ $\delta G = 0$ 中性平衡

克拉珀龙方程 $\mu = G_m \quad d\mu = -S_m dT + V_m^\beta dp \quad L = T(S_m^\beta - S_m^\alpha)$ 相变潜热

$\frac{dp}{dT} = \frac{S_m^\alpha - S_m^\beta}{V_m^\alpha - V_m^\beta} = \frac{L}{T(V_m^\alpha - V_m^\beta)}$ V_m忽略时 $= \frac{Lp}{RT^2}$

气液 二相 临界点 C $\left(\frac{\partial p}{\partial V_m}\right)_{T_c} \Rightarrow \left(\frac{\partial^2 p}{\partial V_m^2}\right)_c = 0$

液滴: 过液气 $\mu^\alpha\left(p' + \frac{2\sigma}{r}, T\right) = \mu^\beta(p', T)$

相变的分类 $\mu_1=\mu_2 \cdots$ $\frac{\partial \mu_1}{\partial T^{n-1}} = \frac{\partial^{n-1}\mu_2}{\partial T^{n-1}}$ $\frac{\partial^{n-1}\mu_1}{\partial p^{n-1}} = \frac{\partial^{n-1}\mu_2}{\partial p^{n-1}}$ $\partial^n \cdots \neq \partial^n \cdots$ n级相变

一级 $\mu_1=\mu_2$ $S_{m1}\neq S_{m2}$ $V_{m1}\neq V_{m2}$ 发现 相变潜热 L 和体积突变 ΔV_m

二级 $C_p = T\left(\frac{\partial S_m}{\partial T}\right)_p = -T\frac{\partial^2\mu}{\partial T^2}$ $\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = \frac{1}{V}\frac{\partial^2\mu}{\partial T\partial p}$ $\kappa_T = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial p}\right)_T = -\frac{1}{V}\frac{\partial^2\mu}{\partial p^2}$

五：多元系的复相平衡与化学平衡

$T^i=T^j$ $p^i=p^j$ $\mu^i=\mu^j$

化学平衡条件 一般形式 $\sum \nu_i A_i = 0$ $Q_p = \Delta H = \sum \nu_i h_i$

(T,p) $\delta G = 0$ $\sum \nu_i \mu_i = 0$ $\delta G = \delta n \sum \nu_i \mu_i \leq 0$ $n_i = n_i^0 + \nu_i \Delta n$

反应度 $\varepsilon = \frac{\Delta n - \Delta n_b}{\Delta n_a - \Delta n_b}$ ($\Delta n_a > \Delta n_b$)

混合理想气体的性质

道尔顿分压 $p = \sum p_i$ ...

理想气体化学平衡

$\ln K_p = -\sum \nu_i \varphi_i$ $K_p = \prod p_i^{\nu_i}$ $\Rightarrow$ $\prod x_i^{\nu_i} = p^{-\sum \nu_i} K_p$ 正向条件是 <

$\therefore \ln K_p = -\frac{A}{T} + C\ln T + B$

$\boxed{4.21}$ 系统，以粒子能量子态上的粒子数 (没有系统；配分函数的表述)

~~$U = \sum a_l \varepsilon_l = \sum \varepsilon_l w_l e^{-\alpha-\beta\varepsilon_l} =$~~

$Z_1 = \sum_l w_l e^{-\beta\varepsilon_l}$ $f_1 \triangleq -\ln Z_1$

$N = e^{-\alpha} Z_1$ $U = e^{-\alpha}\sum \varepsilon_l w_l e^{-\beta\varepsilon_l} = \frac{N}{Z_1}\left(-\frac{\partial}{\partial\beta}\right)Z_1 = N\frac{\partial}{\partial\beta}f_1$

$\boxed{4.25}$ $\sum a_l = N$ $\sum \varepsilon_l a_l = E$ $\Rightarrow \{a_l\}$

$\delta W =$ 广义力 δy 广义位移 $Y = \sum \frac{\partial\varepsilon_l}{\partial y} a_l = e^{-\alpha}\left(-\frac{1}{\beta}\frac{\partial}{\partial y}\right)\sum w_l e^{-\beta\varepsilon_l} = \frac{N}{\beta}\frac{\partial}{\partial y}f_1$

$\delta W = \sum a_l d\varepsilon_l$ $\delta Q = dU - \delta W = \sum \varepsilon_l da_l$

$\boxed{5.5}$ 刘维尔定理公式

5.9 ε_l 上的 f_s 量子态平均粒子数

$$f_s = \begin{cases} e^{-\beta(\varepsilon_l-\mu)} & \text{M-B} \\ \frac{1}{e^{\beta(\varepsilon_l-\mu)}+1} & \text{F-D} \\ \frac{1}{e^{\beta(\varepsilon_l-\mu)}-1} & \text{B-E} \end{cases}$$

$\varepsilon_l(q,p)$ 色散关系

$D(\varepsilon)d\varepsilon$ 态密度

书4.1 求配分函数

M-B: $\Xi = Z_1^{N}$ $\quad Z_1 = \sum_{\mu\text{空间}} e^{-\beta\varepsilon(s)}$

B-E: $\Xi = \prod_l \left[1-e^{-\beta(\varepsilon_l-\mu)}\right]^{-\omega_l}$

F-D: $\Xi = \prod_l \left[1+e^{-\beta(\varepsilon_l-\mu)}\right]^{-\omega_l}$

$\boxed{\text{复习}}$

六 $\quad \frac{N!}{\prod a_l!}\prod \omega_l^{a_l} \qquad \prod \frac{(\omega_l+a_l-1)!}{a_l!(\omega_l-1)!} \qquad \prod \frac{\omega_l!}{a_l(\omega_l-a_l)!} \qquad \sum a_l = N \quad \sum \varepsilon_l a_l = E$

$\ln m! = m(\ln m - 1) \qquad \delta\ln\Omega - \alpha\delta N - \beta\delta E = 0$

$\Rightarrow a_l = \omega_l e^{-\alpha-\beta\varepsilon_l} \qquad \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\mp 1}$

七 $\quad Z_1 = \sum_l \omega_l e^{-\beta\varepsilon_l} \qquad N = \sum a_l = \sum \omega_l e^{-\alpha-\beta\varepsilon_l} = e^{-\alpha} Z_1$

$U = -N\frac{\partial}{\partial\beta}\ln Z_1 \qquad p = \frac{N}{\beta}\frac{\partial}{\partial V}\ln Z_1 \qquad S = Nk\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right) \underbrace{-k\ln N!}$

$F = -NkT\ln Z_1 \quad \underbrace{+kT\ln N!}$

$I(n) = \int_0^{\infty}\frac{x^{n-1}}{e^x-1}dx \qquad I(2) = \frac{\pi^2}{6} = 1.645 \quad I(3) = 2.404 \quad I(4) = 6\times\frac{\pi^4}{90}$

$I(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}\times 2.612 \qquad I(\frac{5}{2}) = \frac{3\sqrt{\pi}}{4}\times 1.341$

$\int_0^{\infty}\frac{x\,dx}{e^x+1} = \frac{\pi^2}{12}$

$\Gamma(n+1) = n\Gamma(n) \quad \Gamma(1) = 1 \quad \Gamma(\frac{1}{2}) = \sqrt{\pi} \qquad \Gamma(n) = \int_0^{+\infty} x^{n-1}e^{-x}dx$

$I(n) = \int_0^{+\infty} e^{-\alpha x^2}x^n dx \qquad I(0) = \frac{\sqrt{\pi}}{2\alpha^{\frac{1}{2}}} \quad I(1) = \frac{1}{2\alpha} \quad I(2) = \frac{\sqrt{\pi}}{4\alpha^{\frac{3}{2}}} \quad I(3) = \frac{1}{2\alpha^2} \quad I(4) = \frac{3\sqrt{\pi}}{8\alpha^{\frac{5}{2}}}$

$\sum \omega e^{-\alpha-\beta\varepsilon_l} = N \Rightarrow \int \frac{V}{h^3}e^{-\alpha-\beta\frac{1}{2m}(p_x^2+p_y^2+p_z^2)}dp_x dp_y dp_z = N \qquad e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}$

能量均分: 平方项 $\frac{1}{2}kT$, 推广 $x_i\frac{\partial\varepsilon}{\partial x_j} = \delta_{ij}kT$

$\frac{1}{2m}(p_x^2+p_y^2+p_z^2) + \frac{1}{2I}\left(p_\theta^2 + \frac{1}{\sin^2\theta}p_\varphi^2\right) + \frac{1}{2m_\mu}p_r^2 + u(r) \quad \left(+\frac{1}{2}m_\mu\omega^2 r^2\right)$

$M = \frac{N}{\beta}\frac{\partial}{\partial B}\ln Z_1 \qquad M = \chi H \qquad B = \mu H$

八 $\quad$ 巨$\Xi = \prod\left[1-e^{-\alpha-\beta\varepsilon_l}\right]^{-\omega_l} \qquad \prod\left[1+e^{-\alpha-\beta\varepsilon_l}\right]^{\omega_l}$

$\ln\Xi = -\sum\omega_l\ln(1-e^{-\alpha-\beta\varepsilon_l}) \qquad \ln\Xi = \sum\omega_l\ln(1+e^{-\alpha-\beta\varepsilon_l})$

$\bar{N} = -\frac{\partial}{\partial\alpha}\ln\Xi$

$U = -\frac{\partial}{\partial\beta}\ln\Xi \qquad Y = -\frac{1}{\beta}\frac{\partial}{\partial y}\ln\Xi \qquad p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln\Xi \qquad \alpha = -\frac{\mu}{kT} \qquad \beta = \frac{1}{kT}$

$S = k\left(\ln\Xi - \alpha\frac{\partial}{\partial\alpha}\ln\Xi - \beta\frac{\partial}{\partial\beta}\ln\Xi\right) \qquad J = -kT\ln\Xi \qquad J = U - TS - \bar{N}\mu$

f_c $S = k\ln\Omega(N\,E\,V)$ $\quad dE = TdS - pdV$ $\quad T\ p\ \mu$

$N\ V\ T$

$Z = \sum_s e^{-\beta E_s} = \sum_l \Omega_l e^{-\beta E_l}$ $\quad U = -\frac{\partial}{\partial\beta}\ln Z$ $\quad Y = -\frac{1}{\beta}\frac{\partial}{\partial y}\ln Z$ $\quad S = k(\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z)$

$F = U - TS = -kT\ln Z$ $\quad (\mu = \frac{\partial F}{\partial N} = -kT\ln\frac{Z_1}{N})$

$$\overline{(E-\bar{E})^2} = \overline{E^2} - \bar{E}^2 = -\frac{\partial\bar{E}}{\partial\beta} = kT^2\frac{\partial\bar{E}}{\partial T} = kT^2C_V$$

$\mu\ V\ T$

$\Xi = \sum_{N=0}^{\infty}\sum_s e^{-\alpha N - \beta E_s}$ $\qquad \sum_N \frac{e^{-\alpha N}}{N!h^{Nr}}\int e^{-\beta E(q,p)}d\Omega$

$\bar{N} = -\frac{\partial}{\partial\alpha}\ln\Xi$ $\quad U = \bar{E} = -\frac{\partial}{\partial\beta}\ln\Xi$ $\quad Y = -\frac{1}{\beta}\frac{\partial}{\partial y}\ln\Xi$

$S = k(\ln\Xi - \alpha\frac{\partial}{\partial\alpha}\ln\Xi - \beta\frac{\partial}{\partial\beta}\ln\Xi)$

$$\overline{(N-\bar{N})^2} = -\left(\frac{\partial\bar{N}}{\partial\alpha}\right)_{\beta y} = kT\left(\frac{\partial\bar{N}}{\partial\mu}\right)_{TV} = \frac{kT}{V}\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{kT}{V}\kappa_T$$

$$\overline{(a_l-\bar{a}_l)^2} = -\frac{\partial\bar{a}_l}{\partial\alpha}\left[= \bar{a}_l\left(1 \pm \frac{\bar{a}_l}{\omega_l}\right)\right]$$