Chapter 8

heat and work — in a Reservoir: τ = const regardless of addition or extraction of heat

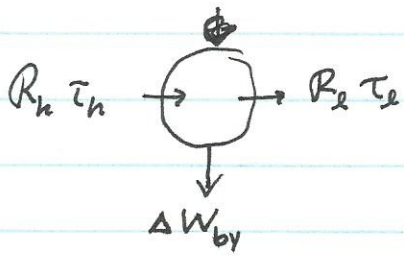
1st Law $\tilde{Q} = dU - \tilde{W}$ $\quad (= dU + pdV$ gas$) \quad = \tau d\sigma)$

$$\therefore \tilde{Q} = \tau d\sigma$$

$$\Delta Q = \int \tilde{Q} \qquad \Delta W_{on} = \int \tilde{W} \qquad \Delta U = \int dU$$

$$\boxed{\Delta U = 0 \Rightarrow \Delta Q_{abs} = -\Delta W_{on}} \quad (\text{cycle: } \oint dU = 0 \text{ \underline{always}})$$

heat → work (engines)



1st Law $\Delta Q_{abs} = -\Delta W_{on} = +\Delta W_{by} \quad (\Delta U = 0)$

$$\Delta Q_{abs} = \underbrace{Q_h}_{\text{heat in}} - \underbrace{Q_\ell}_{\text{heat out}}$$

$$\Delta W_{by} = Q_h - Q_\ell = \tau_h \sigma_h - \tau_\ell \sigma_\ell$$

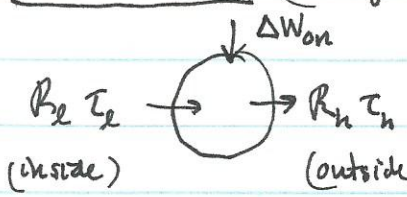
2nd Law $\sigma_\ell \geq \sigma_h$ (can't destroy entropy)

$$\Delta W_{by} \leq (\tau_h - \tau_\ell)\sigma_h = \left(\frac{\tau_h - \tau_\ell}{\tau_h}\right) Q_h \equiv \eta_c Q_h$$

$$\left(\frac{\text{work out}}{\text{heat in}}\right) = \left(\frac{\Delta W_{by}}{Q_h}\right) \leq \eta_c < 1 \qquad \eta = \eta_c$$

$\eta_c = 1$ only for $\tau_\ell = 0$ which is (3rd Law) unattainable (like speed of light)

Work → heat (refrigerators)



1st $-\Delta W_{on} = \underbrace{Q_\ell}_{\text{in } \Delta Q_{abs}} - \underbrace{Q_h}_{\text{out}} = \tau_\ell \sigma_\ell - \tau_h \sigma_h \quad (\Delta U = 0)$

$$\therefore \Delta W_{on} = \tau_h \sigma_h - \tau_\ell \sigma_\ell$$

2nd $\sigma_h \geq \sigma_\ell$

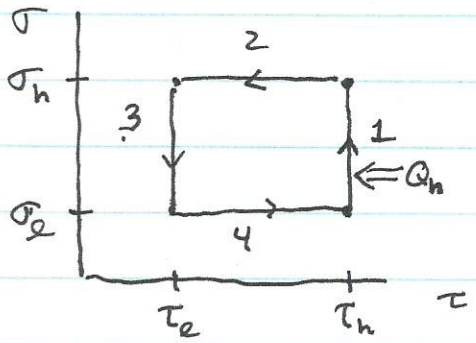
$$\Delta W_{on} \geq (\tau_h - \tau_\ell)\sigma_\ell = \left(\frac{\tau_h - \tau_\ell}{\tau_\ell}\right) Q_\ell$$

$$\left(\frac{\text{heat extracted}}{\text{work in}}\right) = \left(\frac{Q_\ell}{\Delta W_{on}}\right) \leq \frac{\tau_\ell}{\tau_h - \tau_\ell} \equiv \gamma_c \qquad (0 < \gamma_c < \infty!)$$

$$\gamma \leq \gamma_c$$

heat pump: (inside) ⟷ (outside)

Carnot cycle



1st Law

$$\Delta U = 0 = \oint dU$$

$$\oint \tilde{Q} = -\oint \tilde{W} = \Delta W_{by}$$

$$\Delta W_{by} = \oint \tau \, d\sigma = \tau_h(\sigma_h - \sigma_\ell) + \tau_\ell(\sigma_\ell - \sigma_h)$$

$$= (\tau_h - \tau_\ell)(\sigma_h - \sigma_\ell) \quad \text{(area of rect.)}$$

$$Q_h = \tau_h(\sigma_h - \sigma_\ell) = \text{heat in}$$

$$\therefore \left(\frac{\text{work out}}{\text{heat in}}\right) = \left(\frac{\tau_h - \tau_\ell}{\tau_h}\right) = \eta_c$$

max. efficiency : cyclic processes never truly reversible

Ideal gas cycle : $\eta = \eta_c$

$$dU = \tilde{W} + \tilde{Q}$$

When can we write $\tilde{Q} = dQ$ ~~exact~~ or $\tilde{W} = dW$?

If $\tilde{Q} = dQ$ $\boxed{\text{or}}$ $\tilde{W} = dW$ then If $\tilde{Q}$ is exact so is $\tilde{W}$, and if $\tilde{W}$ is exact so is $\tilde{Q}$

1. $dU = \tilde{W} + dQ \Rightarrow \tilde{W} = d(U-Q) \equiv dW$ (i.e. if one is exact, so is the other!)

   or $\boxed{\tilde{W} \text{ and } \tilde{Q} \text{ are both exact}}$

   $dU = dW + \tilde{Q} \Rightarrow \tilde{Q} = d(U-W) \equiv dQ$

2. $\Delta Q = \int_1^2 \tilde{Q} = Q_2 - Q_1$ and $\Delta W = \int_1^2 \tilde{W} = W_2 - W_1$

3. $\oint \tilde{Q} = 0$ <u>and</u> $\oint \tilde{W} = 0$

<u>Isothermal work</u>

$$\tilde{Q}_\tau = \tau d\sigma = d(\tau\sigma) = dQ_\tau \Rightarrow dW = d(U - Q_\tau) = (dF)_\tau$$

$\therefore$ F = isothermal work, for τ = const. $\quad (dU)_\tau = (dF)_\tau + (dQ)_\tau$

$\boxed{\text{ideal gas}: (dU)_\tau = 0 \Rightarrow (dF)_\tau = -(dQ)_\tau}$

<u>Isobaric work</u>

$$-pdV = -d(pV) = d\Omega \quad (\Omega \equiv F - \mu N)$$

$$\tilde{W} = -pdV + \tilde{W}' \quad (\tilde{W}' \equiv f_i dX_i) \quad \tilde{W}_p = -d(pV) + \tilde{W}_p' = d\Omega + \tilde{W}_p'$$

↑ other forms of work

$$\boxed{(dU)_p = \tilde{W}' - d(pV) + (\tilde{Q})_p} \text{ or } (d(U+pV))_p \equiv \boxed{(dH)_p = \tilde{W}' + \tilde{Q}_p}$$

$H \equiv$ enthalpy $\quad \boxed{\tilde{W}' = 0 \Rightarrow (dH)_p = \tilde{Q}_p}$ ← (evaporation from open vessel)

at constant p, change in H = $\tilde{W}' + \tilde{Q}_p$ is independent of volume-related work

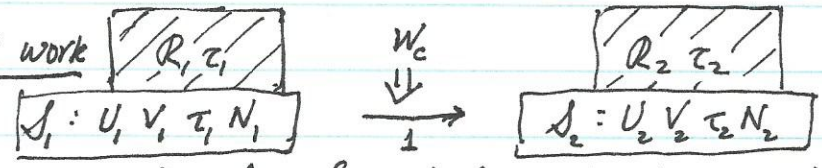
<u>Isobaric, isothermal work</u>

$$\tilde{Q} = d(\tau\sigma) = dQ_\tau \qquad (d(U+pV))_{p\tau} = \tilde{W}' + dQ_\tau$$

$$\tilde{W}_p = -d(pV) + \tilde{W}_p' \qquad \Rightarrow \tilde{W}' = (d(U + pV - Q_\tau))_{\tau p} = (d(U + pV - \tau\sigma))_{\tau p}$$

$\boxed{\text{chemical reactions}}$ $\quad \boxed{\tilde{W}' = (dG)_{\tau p} = \sum_i \mu_i dN_i}$

Chemical work



transfer one particle from $\mathcal{S}_1$ to $\mathcal{S}_2$ with (V_1, V_2) both constant, (τ_1, τ_2) const.

$$W_c = \mu_1(-1) + \mu_2(+1) = \mu_2 - \mu_1 = \text{chemical work done per particle}$$

$$\tilde{W}_c = \mu\, dN = (dG)_{\tau,p}$$

Systems at constant volume - chemical, magnetic, electrical work per unit volume

$$\tilde{w} = \frac{\tilde{W}'}{V} = \mu\, d\left(\frac{N}{V}\right) + \tilde{w}_{mag} + \tilde{w}_{elec} \quad (\text{volume-independent work/vol.})$$

$$\tilde{w}_{mag} = d\left(\tfrac{1}{2}\mu_0 H^2\right) + \mu_0 \vec{H}\cdot d\vec{M} = \vec{H}\cdot d\vec{B} \qquad \vec{B} \equiv \mu_0(\vec{H}+\vec{M})$$

$$\tilde{w}_{elec} = d\left(\tfrac{1}{2}\epsilon_0 E^2\right) + \vec{E}\cdot d\vec{P} = \vec{E}\cdot d\vec{D} \qquad \vec{D} \equiv \epsilon_0\vec{E} + \vec{P}$$

$(\vec{H}, \vec{E} \equiv$ applied fields$)$

$$d\left(\frac{U}{V}\right) \equiv du = \tilde{Q}/V + \tilde{W}'/V = \tau\, ds + \mu\, dn + \vec{H}\cdot d\vec{B} + \vec{E}\cdot d\vec{D}$$

$$\left(s \equiv \frac{\sigma}{V}\right)$$

$$F/V = f = u - \tau s$$

$$df = -s\, d\tau + \mu\, dn + \vec{H}\cdot d\vec{B} + \vec{E}\cdot d\vec{D}$$

Constant n, magnetic field case

$$df = -s\, d\tau + \vec{H}\cdot d\vec{B}$$

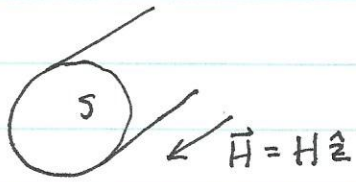
Control $\vec{H}$ (applied) not $\vec{B}$ so use

$$g \equiv f - \vec{H}\cdot\vec{B} \qquad dg = df - d(\vec{H}\cdot\vec{B}) = -s\, d\tau - \vec{B}\cdot d\vec{H}$$

$$s = -\left(\frac{\partial g}{\partial \tau}\right)_H \qquad \vec{B} = -\left(\frac{\partial g}{\partial \vec{H}}\right)_\tau$$

Example: superconductor in a magnetic field

$\vec{B} = \mu_0(\vec{H} + \vec{M}) = 0$ in S (Meissner effect)



superconducting cylinder in axial field

(to avoid demag factors)

For $H=0$, S $\rightarrow$ normal state at $\tau = \tau_c$.

At $H_c(\tau)$ S $\rightarrow$ normal state

Measurements: $H_c(\tau) = H_c(0)\left[1 - \left(\frac{\tau}{\tau_c}\right)^2\right]$

1. What is the decrease in energy upon going into the S state?
2. How does the specific heat behave at and below τ_c?

$\boxed{\text{Just by knowing } H_c(\tau) \text{ we can answer } \underline{\text{both}} \text{ of these questions}}$

$\tau = \text{constant}$

$$g(\tau, H) - g(\tau, 0) = -\int_0^H B(H')\,dH'$$

In normal (n) state $\vec{B} = \mu_0 \vec{H}$ $(\vec{M} = 0)$

$$g_n(\tau, H) - g_n(\tau, 0) = -\tfrac{1}{2}\mu_0 H^2 \qquad (1)$$

In superconducting (s) state, $\vec{B} = 0$ $(\vec{M} = -\vec{H})$ so

$$g_s(\tau, H) - g_s(\tau, 0) = 0 \qquad (2)$$

At $H = H_c(\tau)$, n and S are in phase equilibrium:

$$g_s(\tau, H_c) = g_n(\tau, H_c) = g_n(\tau, 0) - \tfrac{1}{2}\mu_0 H_c^2 \qquad \text{by (1)}$$

$$g_s(\tau, H_c) = g_s(\tau, 0) \qquad \text{by (2)}$$

$$\therefore \quad g_s(\tau, 0) = g_n(\tau, 0) - \tfrac{1}{2}\mu_0 H_c^2$$

since $f_{s,n}(\tau, 0) = g_{s,n}(\tau, 0)$, can also write

$$f_s(\tau, 0) = f_n(\tau, 0) - \tfrac{1}{2}\mu_0 H_c^2$$

free energy is <u>lower</u> in s state by $\frac{1}{2}\mu_0 H_c^2$ $\equiv$ "condensation energy"

$$= \tfrac{1}{2}\mu_0 H_c(0)^2 \left[1 - \left(\tfrac{\tau}{\tau_c}\right)^2\right]^2$$

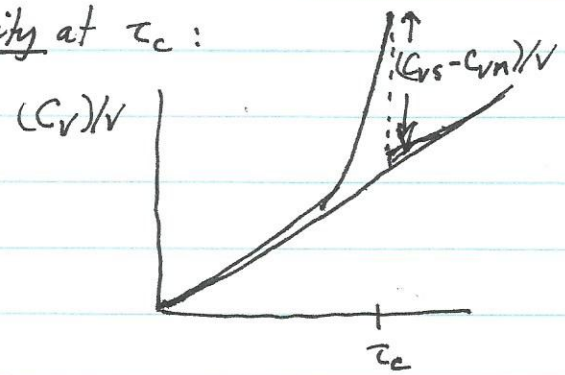
$$s_s(\tau,0) - s_n(\tau,0) = -\frac{\partial}{\partial\tau}\left(f_s(\tau,0) - f_n(\tau,0)\right) = \mu_0 H_c(\tau)\frac{dH_c}{d\tau}$$

$$C_V = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_V \Rightarrow V\tau\mu_0\left[\left(\frac{dH_c}{d\tau}\right)^2 + H_c(\tau)\frac{dH_c}{d\tau}\right] = C_{Vs} - C_{Vn}$$

There is a jump in specific heat <u>at all</u> $\tau > 0$.

At $\tau = \tau_c$ $\quad C_{Vs} - C_{Vn} = \left(V\tau\mu_0 H_c(0)^2 \frac{4\tau^2}{\tau_c^4}\right)_{\tau_c} = 4V\mu_0 H_c(0)^2/\tau_c$

Specific heat <u>discontinuity</u> at τ_c :



Also

$$g_s(\tau,H) = g_s(\tau,0) = g_n(\tau,0) - \tfrac{1}{2}\mu_0 H_c^2$$

$$\Rightarrow \quad g_s(\tau,H) - g_n(\tau,H) = g_n(\tau,0) - \tfrac{1}{2}\mu_0 H_c^2 - g_n(\tau,H)$$

$$= \tfrac{1}{2}\mu_0(H^2 - H_c^2)$$

so, for $H \neq 0$

$$s_s - s_n = s_s(\tau H) - s_n(\tau,H) = \mu_0 H_c \frac{dH_c}{d\tau}$$

$$\Rightarrow \quad C_H/V = \tau\left(\frac{\partial s}{\partial\tau}\right)_H \Rightarrow (C_{sH} - C_{nH})/V = \mu_0\tau\left[\left(\frac{dH_c}{d\tau}\right)^2 + H_c\frac{d^2H_c}{d\tau^2}\right]$$

so there is a <u>jump in specific heat</u> at <u>all values of H</u> (for $\tau \neq 0$): The

$$\left((C_{sH} - C_{nH})/V = \mu_0\tau\left[\left(\frac{-2H_{c0}\tau}{\tau_c^2}\right)^2 + H_c(0)\left[1 - \left(\frac{\tau}{\tau_c}\right)^2\right]\left(\frac{-2H_{c0}}{\tau_c^2}\right)\right]\right)$$

jump only depends on τ (cf. diagram above)

Exam 2: 18 April – Friday

Chemical Equilibria in Gases

$G = U + PV - \tau\sigma = F + PV$

$dG = dU + d(PV) - d(\tau\sigma) = \tau d\sigma - pdV + \sum_j \mu_j dN_j + d(PV) - d(\tau\sigma)$

In equilibrium, G is min $\Rightarrow dG = 0$, so

$$(dG)_{\tau p} = 0 = \sum_j \mu_j dN_j \quad \text{(sum over all species present)}$$

$(dU)_{\tau p} = \tau d\sigma - pdV + \sum_j \mu_j dN_j = d(\tau\sigma) - d(PV) + \sum_j \mu_j dN_j \quad (dG)_{\tau p} = \sum_j \mu_j dN_j = 0$

Consider

$$aA + bB \rightleftharpoons cC + dD$$

Stoichiometry requires

$$\Delta N_A = \frac{a}{b}\Delta N_B = -\frac{a}{c}\Delta N_C = -\frac{a}{d}\Delta N_D$$

$$\therefore \quad \mu_A \Delta N_A + \mu_B \Delta N_B + \mu_C \Delta N_C + \mu_D \Delta N_D = 0$$

Take $\Delta N_A = 1$. Then

$$\Rightarrow \quad a\mu_A + b\mu_B - c\mu_C - d\mu_D = 0$$

For an ideal gas

$$\mu_j = \tau \ln\left(\frac{n_j}{C_j}\right) \qquad C_j \equiv n_{Qj} Z_j(\text{int}) = n_{Qj}\, e^{-F_j(\text{int})/\tau}(2S_j+1)$$

$$n_{Qj} \equiv \left(\frac{m_j \tau}{2\pi\hbar^2}\right)^{3/2}$$

$$\sum_j \mu_j \nu_j = \sum_j \tau \ln\left[\left(\frac{n_j}{C_j}\right)^{\nu_j}\right] = 0$$

$$\Rightarrow \prod_j \left(\frac{n_j}{C_j}\right)^{\nu_j} = 1 \quad \text{or} \quad \prod_j n_j^{\nu_j} = \prod_j C_j^{\nu_j} \equiv K(\tau)$$

$$\therefore \boxed{\prod_j (n_j)^{\nu_j} = K(\tau)} \quad \text{"Law of mass action"}$$

$U = \tau\sigma - PV + \sum_j \mu_j dN_j$

$dU = \tau d\sigma - pdV + \sum_j \mu_j dN_j \quad \Rightarrow \quad \sigma d\tau - Vdp + \sum_j N_j d\mu_j = 0$

$dG = dU + d(PV) - d(\tau\sigma) = -\sigma d\tau + Vdp + \sum_j \mu_j dN_j = \sum_j d(\mu_j N_j)$ ✓

$\cancel{\tau(\sigma_2 - \sigma_1)d\tau + (V_1 - V_2)dp + \sum_j (\mu_j^{(2)} - \mu_j^{(1)})dN_j}$

Dissociation of diatomic H_2

$$AB \rightleftharpoons A + B$$

$$H_2 \rightleftharpoons 2H$$

$$\nu_{H_2} = 1 \qquad \nu_H = -2$$

$$\frac{n_{H_2}}{(n_H)^2} = K(T) \qquad n_H \equiv [H] \quad n_{H_2} = [H_2]$$

$$\Rightarrow \frac{[H]}{[H_2]} = \frac{1}{[H_2]^{1/2} K(T)^{1/2}}$$

lower $[H_2] \Rightarrow$ higher $\frac{[H]}{[H_2]}$ $\therefore$ lower density of $[H_2]$ favors higher ratio $\frac{[H]}{[H_2]}$ (as in interstellar space)

Skip

pH

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\frac{[H_2O]}{[H^+][OH^-]} = K(T) = \frac{[H_2O]}{10^{-14}\,(\text{mol}^2/\ell^2)} \quad \text{room } T$$

pure H_2O $\quad [H^+] = [OH^-] = 10^{-7}\,\frac{\text{mol}}{\ell}$

$$pH \equiv -\log_{10}[H^+] \qquad \begin{cases} pH < 7 & \text{acid} \\ pH > 7 & \text{base} \end{cases}$$

apples $pH \sim 3$ $\qquad$ human blood plasma $pH \sim 7.3$ to 7.5

Detailed Balance

$$A + B \rightleftharpoons AB \qquad \frac{dn_{AB}}{dt} = \underset{\substack{\uparrow \\ \text{collision rate}}}{C} n_A n_B - \underset{\substack{\uparrow \\ \text{decay rate}}}{D} n_{AB}$$

Equilibrium $\frac{dn_{AB}}{dt} = 0 \Rightarrow \frac{n_A n_B}{n_{AB}} = \frac{D}{C}$ $\left(\text{e.g. } \frac{[H]^2}{[H_2]} = \frac{D}{C} = \frac{1}{K(T)}\right)$

$C n_A n_B = D n_{AB}$ $\leftarrow$ principle of detailed balance

Nuclear abundances in early universe

$$Z_x\ p\text{'s} + N_x\ n\text{'s} \rightleftharpoons \text{nucleus } X : A_x \equiv Z_x + N_x$$

$$Z_x \mu_p + N_x \mu_n = \mu_x$$

$$\mu_p = \tau \ln\left(\frac{n_p}{n_{Qp} Z_p(\text{int})}\right) \quad \mu_n = \tau \ln\left(\frac{n_n}{n_{Qn} Z_n(\text{int})}\right) \quad \mu_x = \tau \ln\left(\frac{n_x}{n_{Qx} Z_x(\text{int})}\right)$$

$$Z_p(\text{int}) = 2 e^{-m_p c^2/\tau} \quad Z_n(\text{int}) = 2 e^{-m_n c^2/\tau} \quad Z_x(\text{int}) = (2S_x+1) e^{-M_x c^2/\tau}$$

$$\left(\frac{n_p}{n_{Qp}}\right)^{Z_x} \left(\frac{n_n}{n_{Qn}}\right)^{N_x} Z_p^{-Z_x} Z_n^{-N_x} = \frac{n_x}{n_{Qx}} Z_x^{-1}$$

or

$$\underline{n_x} = n_{Qx} Z_x Z_p^{-Z_x} Z_n^{-N_x} \left(\frac{n_p}{2n_{Qp}}\right)^{Z_x} \left(\frac{n_n}{2n_{Qn}}\right)^{N_x} \qquad (S_p = S_n = \tfrac{1}{2})$$

$$= (2S_x+1)\, n_{Qx}\, e^{-E_0^x/\tau} \left(\frac{n_p}{2n_{Qp}}\right)^{Z_x} \left(\frac{n_n}{2n_{Qn}}\right)^{N_x}$$

$$E_0^x \equiv M_x c^2 - Z_x m_p c^2 - N_x m_n c^2 = \text{nuclear binding energy}$$

$\underline{\tau = 1\,\text{MeV}}$

$$\underline{\frac{n_p}{2n_{Qp}} = e^{-11.6}} \qquad \underline{\frac{n_n}{2n_{Qn}} = e^{-7.6}}$$

gives observed n_x up to $A_x \sim 60$ to 70 (to Cu or Zn)

For heavier elements n_x is <u>too</u> <u>small</u> compared to observed value.