THERMODYNAMICS OF SLOW EXPANSIONS (QUASI STATIC CHANGES OF STATES)

1ST law thermodynamics

$$dU = dQ + dW$$

- dU: change in internal energy of a gas
- dQ: change in heat (added or withdrawn)
- dW: work done upon the gas by expansion or contraction

Quasistatic $\rightarrow$ reversible processes

$dW = -PdV$, ie: a change of volume required a mechanical work on the gas dW

$$\Rightarrow \quad dQ = dU + PdV$$

2ND law of thermodynamics $\qquad dQ = T\,dS$ (for quasi-static changes of states)

- dQ: Heat increment
- dS: variation in entropy

$$\Rightarrow \quad T\,dS = dU + PdV$$

to calculate the change of entropy between two states of equilibrium.

But $U = U(V,T) \rightarrow dU = \frac{\partial U}{\partial V}\Big|_T dV + \frac{\partial U}{\partial T}\Big|_V dT$

$$\Rightarrow \quad dS = \frac{1}{T}\left[\frac{\partial U}{\partial V}\Big|_T + P\right] dV + \frac{1}{T}\frac{\partial U}{\partial T}\Big|_V dT$$

for a quasi static change of state of the gas

But $S = S(V,T) \rightarrow dS = \frac{\partial S}{\partial V}\Big|_T dV + \frac{\partial S}{\partial T}\Big|_V dT$

Since $\frac{\partial}{\partial T}\frac{\partial S}{\partial V} = \frac{\partial}{\partial V}\frac{\partial}{\partial T}$ (the order is not important)

Taking the second derivatives and comparing

$$\frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\frac{\partial U}{\partial V}\Big|_T + P\right] dV\right\} + \frac{\partial}{\partial V}\left\{\frac{1}{T}\frac{\partial U}{\partial T}\Big|_V dT\right\} = \frac{\partial^2 S}{\partial T \partial V} dV + \frac{\partial^2 S}{\partial T \partial V} dT$$

equal

$$\Rightarrow \quad \boxed{\frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\frac{\partial U}{\partial V}\Big|_T + P\right]\right\} = \frac{\partial}{\partial V}\left[\frac{1}{T}\frac{\partial U}{\partial T}\Big|_V\right]}$$

INTEGRABILITY CONDITION.

For a non-degenerate gas (ideal gas law) $PV = \underbrace{\frac{R}{\mu}}T$ w/ R molar gas constant $= \frac{K}{m_H}$

$R = 8.314 \times 10^7$ erg/mole/K

gas constant for 1 g of gas, depending on composition

$$dQ = dU + PdV = \frac{dU}{dT}dT + PdV \quad \text{w/ } U = U(T)$$

Let's define SPECIFIC HEAT $C_\alpha := \left(\frac{dQ}{dT}\right)_\alpha$

i.e.: rate of heat addition per unit rise in temperature all the time keeping α constant, w/ α function of physical variables.

$\Rightarrow dQ = F_1\, dT + F_2\, d\alpha$ after changing from the variables $(T,V) \longrightarrow (T,\alpha)$

w/ $F_1 = F_1(T,\alpha)$
$F_2 = F_2(T,\alpha)$ $\Rightarrow$ $\boxed{F_1 = C_\alpha}$

SPECIFIC HEAT @ a constant volume $\boxed{c_V := \left(\frac{dQ}{dT}\right)_V = \frac{dU}{dT}}$

i.e. when the gas particles have no excited states (e.g. an ionized gas) the internal energy is the kinetic energy of translation & C_V = const.

From $PV = \frac{R}{\mu}T \xrightarrow{\text{differentiating both side}} PdV + VdP = \frac{R}{\mu}dT$

$\Rightarrow dQ = \left(\frac{dU}{dT} + \frac{R}{\mu}\right)dT - VdP$ <—> similar form of $dQ = F_1 dT + F_2 d\alpha$

$R = k/m_H = 8.314 \times 10^7 \frac{erg}{mole\ K}$

$\Rightarrow$ For a perfect nondegenerate gas

$$\boxed{c_P = c_V + \frac{R}{\mu}}$$ specific heat at constant pressure.

$\rightarrow R/\mu$ for a perfect gas

For a non perfect gas [ie; $U = U(V,T)$] $\Rightarrow$ $c_P - c_V = \left[\frac{\partial U}{\partial V}\Big|_T + P\right] \frac{\partial V}{\partial T}\Big|_P$

useful in regions of partial ionization.

Let's define $\gamma := \frac{c_P}{c_V}$ $\quad$ γ depends on the # of degrees of freedom associated w/ the gas molecules & on temperature.

$\gamma = 1 + \frac{2}{f}$ $\quad$ w/ f # of unfrozen degrees of freedom (translational, rotational, vibrational) of a molecule.

In stellar interiors, gas is made of ionized particles w/ 3 translational degrees of freedom

$\Rightarrow$ $\gamma = \gamma_{\text{perfect monoatomic gas}} = \frac{5}{3}$

Using $PV = \frac{R}{\mu} T$ & $c_V = \frac{dU}{dT}$, we can write the 1st law as

$$dQ = c_V\, dT + \frac{RT}{\mu V}\, dV$$

Adiabatic change $\Leftrightarrow$ $dQ = 0$ $\Rightarrow$ $c_V \frac{dT}{T} + (c_P - c_V)\frac{dV}{V} = 0$

$c_P - c_V = \frac{R}{\mu}$ $\quad$ IDEAL GAS

For an ideal gas, $c_P = \text{const}$, $c_V = \text{const}$ $\quad$ $\Rightarrow$ integrating the eq. $\quad$ $\boxed{TV^{\gamma-1} = \text{const}}$

$PV^{\gamma} = \text{const}$

$\Leftrightarrow$ eq. $\quad P^{1-\gamma} T^{\gamma} = \text{const}$

Radiation pressure is important only for temperatures high enough so that matter is essentially completely ionized ($T \simeq 3.6 \times 10^7 \rho^{1/3}$ when $P_g = P_{rad}$). Also, P_{rad} not important except for densities low enough for e^- gas to be nondegenerate.

$\Rightarrow$ we can evaluate the effect of P_{rad} by considering adiabatic expansion of an ideal non-degenerate monoatomic gas plus P_{rad}.

$$\Rightarrow P = P_g + P_r = \frac{K\rho T}{\mu m_H} + \frac{1}{3} a T^4 = \frac{KT}{\mu m_H V} + \frac{1}{3} a T^4 \quad (*)$$

$V = \frac{1}{\rho}$

$$\Rightarrow \underbrace{U}_{\substack{\text{internal}\\ \text{energy}\\ \text{per gram}}} = \underbrace{a T^4}_{\substack{\text{energy}\\ \text{density}}} V + \frac{1}{\mu m_H}\left(\frac{3}{2} K T\right)$$

$V = \frac{1}{\rho}$ volume of 1 g of gas

Kinetic energy for monoatomic particles

From 1st thermodynamic law $\quad dQ = \left.\frac{\partial U}{\partial T}\right|_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV + P dV$

$$\text{w/} \quad \left.\frac{\partial U}{\partial V}\right|_T = a T^4 \qquad \left.\frac{\partial U}{\partial T}\right|_V = 4 a T^3 V + \frac{3}{2}\frac{K}{\mu m_H}$$

$$\Rightarrow dQ = \left(4 a T^3 V + \frac{3}{2}\frac{K}{\mu m_H}\right) dT + \left(\frac{4}{3} a T^4 + \frac{KT}{\mu m_H V}\right) dV \quad (\square)$$

For $dQ = 0 \iff$ adiabatic change

Following Chandrasekhar, let's define Γ_1, Γ_2 & Γ_3 adiabatic exponents:

for generic gas $\leftarrow$
$$\begin{cases} \dfrac{dP}{P} + \Gamma_1 \dfrac{dV}{V} = 0 \\[2mm] \dfrac{dP}{P} + \dfrac{\Gamma_2}{1-\Gamma_2}\dfrac{dT}{T} = 0 \\[2mm] \dfrac{dT}{T} + (\Gamma_3 - 1)\dfrac{dV}{V} = 0 \end{cases}$$

For a perfect non-degenerate particle gas
$\Gamma_1 = \Gamma_2 = \Gamma_3 = \gamma$

The adiabatic exponents are functions of the thermodynamic state, hence not immediately integrable. They demand

$$\Gamma_3 - 1 = \frac{(\Gamma_2 - 1)\Gamma_1}{\Gamma_2}$$

From (*) $dP = \left(\frac{4}{3}aT^4 + \frac{k}{\mu m_H}\frac{T}{V}\right)\frac{dT}{T} - \frac{k}{\mu m_H}\frac{T}{V}\frac{dV}{V} =$

differentiating w/ respect of dT & dV

$$= (4P_r + P_g)\frac{dT}{T} - P_g\frac{dV}{V} \quad (\star)$$

Replacing $\frac{dP}{P}$ into $\frac{dP}{P} + \Gamma_1\frac{dV}{V} = 0$

$$\Rightarrow (4P_r + P_g)\frac{dT}{T} + \left[\Gamma_1(P_r + P_g) - P_g\right]\frac{dV}{V} = 0$$

Eq. (□) can be written for $dQ = 0$ $\quad dQ = (12P_r + \frac{3}{2}P_g)\frac{dT}{T} + (4P_r + P_g)\frac{dV}{V} = 0$ $\quad (\Delta)$

Comparing these last two equations $\Rightarrow$ $\frac{\Gamma_1(P_r + P_g) - P_g}{4P_r + P_g} = \frac{4P_r + P_g}{12P_r + \frac{3}{2}P_g}$

Placing $\beta P = P_g$ $\quad (1-\beta)P = P_r$ $\Rightarrow$ $\boxed{\Gamma_1 = \frac{32 - 24\beta - 3\beta^2}{24 - 21\beta}}$

For $\beta = 1$ (particle gas) $\Rightarrow \Gamma_1 = \gamma = 5/3$

For $\beta = 0$ (photon gas) $\Rightarrow \Gamma_1 = 4/3$

Similarly, substituting $\frac{dP}{P}$ from ($\star$) into $\frac{dP}{P} + \frac{\Gamma_2}{1-\Gamma_2}\frac{dT}{T} = 0$ & comparing w/ (Δ)

$$\Rightarrow \frac{12(1-\beta) + \frac{3}{2}\beta}{4 - 3\beta + \Gamma_2/(1-\Gamma_2)} = -\frac{4 - 3\beta}{\beta}$$

$$\Rightarrow \boxed{\Gamma_2 = \frac{32 - 24\beta - 3\beta^2}{24 - 18\beta - 3\beta^2}} \quad \& \quad \boxed{\Gamma_3 = \frac{32 - 27\beta}{24 - 21\beta}}$$

NOTE: Each adiabatic exponent decreases monotonically from $\frac{5}{3}$ $(\beta = 1)$ to $\frac{4}{3}$ $(\beta = 0)$. (6)

NOTE: Stellar instability occurs when Γ_1, when averaged over a star, gets smaller than $\frac{4}{3}$.
Radiation pressure cannot (in the absence of $e^{\pm}$ e^- pair production or ionization) reduce Γ below $4/3$.
Stars dominated internally by Prad have $\Gamma \approx 4/3$.

From ($\square$) $C_V := \left.\frac{dQ}{dT}\right|_V = 4aT^3 V + \frac{3}{2}\frac{k}{\mu m_H} = \frac{3}{2}\frac{k}{\mu m_H}\left(1 + \frac{8aT^4/3}{Tk/\mu m_H V}\right)$

$$= c_V\left(1 + \frac{8P_r}{P_g}\right) = c_V\left[1 + \frac{8(1-\beta)}{\beta}\right] = c_V\frac{8-7\beta}{\beta}$$

where $c_V = \frac{3}{2}\frac{k}{\mu m_H}$ the specific heat of the particle gas alone

$$\Rightarrow \quad C_V = c_V\frac{8-7\beta}{\beta}$$

$$C_P = c_V\frac{32-24\beta-3\beta^2}{3\beta^2}$$

For a enclosure w/ ideal monatomic gas & radiation

NOTE: $\frac{C_P}{C_V} = \frac{\Gamma_1}{\beta}$

From 2ND law of thermodynamics, $dQ/T = dS$. From ($\square$)

$$dS = \left(4aT^2V + \frac{3k}{2\mu m_H T}\right)dT + \left(\frac{4}{3}aT^3 + \frac{k}{\mu m_H V}\right)dV$$

which can be integrate $\Rightarrow$

$$\boxed{S = \text{const} + \underbrace{\frac{k}{\mu m_H}\ln\frac{T^{3/2}}{\rho}}_{\text{entropy per gram of an ideal nondegenerate monatomic gas}} + \overbrace{\frac{4a}{3}\frac{T^3}{\rho}}^{\text{entropy per gram of photon component}}}$$

$\Leftrightarrow$ eq.

$$\boxed{S = \text{const} + \frac{k}{\mu m_H}\left(\ln\frac{T^{3/2}}{\rho} + 4\frac{P_r}{P_g}\right) = \text{const} + \frac{k}{\mu m_H}\left(\ln\frac{T^{3/2}}{\rho} + 4\,\frac{1-\beta}{\beta}\right)}$$

$$\Rightarrow \Delta S = \frac{k}{\mu m_H}\left\{\ln\left[\left(\frac{T_f}{T_i}\right)^{3/2}\frac{\rho_i}{\rho_f}\right] + 4\left[\frac{1-\beta_f}{\beta_f} - \frac{1-\beta_i}{\beta_i}\right]\right\}$$

increase in entropy of the final state f over that of the initial state i,

If a portion of the stellar interior is allow to expand (or contract) w/o exchanging heat with the surroundings $\Rightarrow \Delta S = 0$

$\Rightarrow$ ADIABATIC CHANGE.

<u>Ex:</u>
- gravitational contraction of a stellar core following exhaustion of a nuclear fuel supply
- expansion of a rising convective mass of gas.

In general

$$\boxed{S = \text{const} + S_{ion} + S_{e^-} + S_{rad}}$$

entropy per gram

S_{ion}: perfect non-degenerate gas

S_{e^-}: degenerate electrons

$$= \text{const} + \frac{k}{\mu_i m_H}\ln\frac{T^{3/2}}{\rho} + \frac{4a}{3}\frac{T^3}{\rho} + S_{e^-}$$

$$\text{w/ } S_{e^-} = \frac{k}{\mu_e m_H}\left[\frac{5}{3}\frac{F_{3/2}(\alpha)}{F_{1/2}(\alpha)} + \alpha\right]$$

(only for non-relativistic e^-s)