$\boxed{\text{Thermodynamics of an ideal gas}}$

eqn. of state for ideal gas: $p = \rho R T$
T in °K

comes from experiments showing

$$p\,dV + V\,dp = R\,dT$$ where V is

the volume of a unit mass, R is a constant, dT can be in °C or °K
with °K = °C + 273

integrate to get $pV = RT$ where T is in °K so that the integration constant is zero

$$\Rightarrow \quad p = \rho R T \qquad \rho = \frac{1}{V}$$

$$R = c_p - c_v$$

c_p = specific heat at constant pressure

$$c_p \equiv \left.\frac{\partial h}{\partial T}\right|_p \qquad h = \hat{u} + p/\rho$$

$\hat{u}$ = internal energy per unit mass

p = pressure = the (compressive) normal stress on a fluid at rest

h = enthalpy per unit mass

c_v = specific heat at constant volume

$$c_v \equiv \left.\frac{\partial \hat{u}}{\partial T}\right|_v$$

How can we understand c_p and c_v?
<u>idealized situation</u>

c_p is the amount of energy required to raise the temperature of a unit mass by 1°K, keeping pressure fixed

$$c_p = \left[\frac{\text{energy}}{\text{mass} \cdot {}^\circ K}\right]$$

1st Law of Thermodynamics

is $\delta Q = d\hat{u} + \delta W$

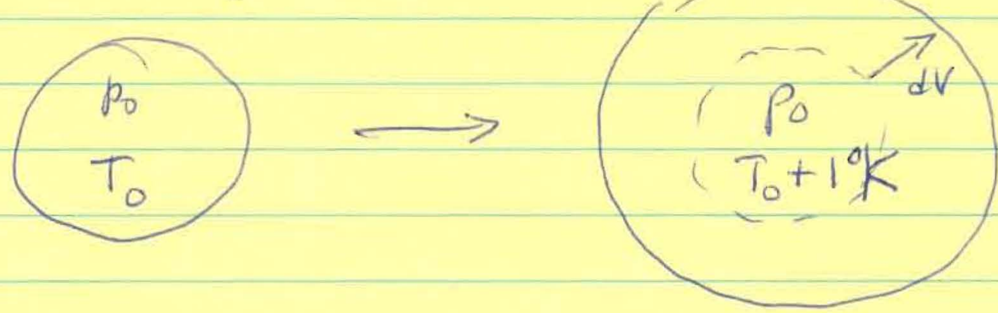
where δQ is small amount of heat added to the system

δW is " " of work done by the system

$d\hat{u}$ is the change in internal energy

[δQ, δW are path-dependent]

ballon of gas



To heat the gas inside, keeping p_0 fixed, some energy goes into expanding the balloon, doing work against the atmosphere

$$\delta Q = d\hat{u} + p\,dV$$

defining $h = \hat{u} + pV = \hat{u} + P/\rho$

Then $c_p = \left.\frac{\partial h}{\partial T}\right|_p$

Alternatively, keeping volume fixed

$$\begin{matrix} p_0 \\ T_0 \end{matrix} \longrightarrow \begin{matrix} p_1 \\ T_0 + 1^\circ K \end{matrix}$$

$\delta Q = d\hat{u}$

then $\quad C_V = \left.\dfrac{\partial \hat{u}}{\partial T}\right|_V$

Note that heat is a form of energy

temperature is a measure of equilibrium

Heat depends on how much mass there is,
temperature does not

Heat and work are not functions
internal energy is a function

Ok, how do we get $R = c_p - c_v$

[obviously $c_p > c_v$]

ideal gas law in differential form:

$$p\,dV + V\,dp = R\,dT$$

By definition $h = \hat{u} + pV$

$$\Longrightarrow \quad dh = d\hat{u} + p\,dV + V\,dp$$

$$= d\hat{u} + R\,dT \quad \text{using ideal gas law above}$$

Also by definition

$$dh\big|_p = c_p\,dT$$

$$\Longrightarrow \quad c_p\,dT = d\hat{u} + R\,dT$$

Also by definition $\partial\hat{u}\big|_v = c_v\,dT$

IF $\hat{u} = \hat{u}(T)$ is only a function of temperature, **then**

$$C_p\,dT = C_v\,dT + R\,dT$$

or $C_p = C_v + R$

It remains to show that $\hat{u} = \hat{u}(T)$ for an ideal gas

To show $\hat{u} = \hat{u}(T)$ use

ideal gas law $\quad V\,dp + p\,dV = R\,dT$

1^{st} and 2^{nd} Laws of Thermo

$$\delta Q = d\hat{u} + p\,dV = T\,dS$$

$S =$ entropy (a function)

Manipulations

$$\delta q = d\hat{u} + R\,dT - V\,dp = T\,dS$$

$$\Rightarrow \quad dS = \frac{d\hat{u}}{T} + R\frac{dT}{T} - \frac{V\,dp}{T}$$

$$= \frac{d\hat{u}}{T} + R\,d(\ln T) - \frac{R}{p}\,dp$$

$$= \frac{d\hat{u}}{T} + R\,d(\ln T) - R\,d(\ln p)$$

$$= \frac{d\hat{u}}{T} + R\,d\left[\ln T - \ln p\right]$$

$$= \frac{d\hat{u}}{T} + R\,d\left[\ln (T/p)\right]$$

$$= \frac{d\hat{u}}{T} + d\left[R\ln(T/p)\right] \qquad R \text{ constant}$$

$$\Rightarrow \quad \frac{d\hat{u}}{T} = d\left[S - R\ln(T/p)\right]$$

$$= dG \qquad \left[\text{exact differential}\right]$$

$$\frac{d\hat{u}}{T} = dG(p,T)$$ bc. two thermodynamic quantities p, T determine S

$$\frac{1}{T}\frac{\partial \hat{u}}{\partial p}dp + \frac{1}{T}\frac{\partial \hat{u}}{\partial T}dT = \frac{\partial G}{\partial p}dp + \frac{\partial G}{\partial T}dT$$

$$\Rightarrow \frac{1}{T}\frac{\partial \hat{u}}{\partial p} = \frac{\partial G}{\partial p} \qquad \frac{1}{T}\frac{\partial \hat{u}}{\partial T} = \frac{\partial G}{\partial T}$$

Now since $\dfrac{\partial^2 G}{\partial T \partial p} = \dfrac{\partial^2 G}{\partial p \partial T}$

$$\Rightarrow \frac{\partial}{\partial T}\left[\frac{1}{T}\frac{\partial \hat{u}}{\partial p}\right] = \frac{\partial}{\partial p}\left[\frac{1}{T}\frac{d\hat{u}}{dT}\right]$$

$$-\frac{1}{T^2}\frac{\partial \hat{u}}{\partial p} + \cancel{\frac{1}{T}\frac{\partial^2 \hat{u}}{\partial T \partial p}} = \cancel{\frac{1}{T}\frac{\partial^2 \hat{u}}{\partial p \partial T}}$$ cancel out

$$\Rightarrow \frac{\partial \hat{u}}{\partial p} = 0$$ QED

$$\Rightarrow \hat{u} = \hat{u}(T)$$ only