Lecture 6

Tuesday, September 24, 2024 09:56

Midterm Location Change

MacKinnon 318

Time / Date are the same

(October 17, 10:00am – 11:15am)

Practice Problems

Consider a perfect gas inside a cylinder fitted with a piston.
Let the initial state be T, V_i and the final state be T, V_f. Calculate w, q, and ΔU for the following:

a) Free expansion against zero external pressure.

b) Reversible, isothermal expansion.

<u>Solution</u> : a) Temperature is constant.

$\Delta U = C_V \Delta T$; $\Delta T = 0$, so $\boxed{\Delta U = 0}$.

Expansion against no opposing force: no work is done; $dw = -\vec{F} \cdot d\vec{s}$, so $\boxed{w = 0}$. For heat, $\underbrace{\Delta U}_{0} = q + \underbrace{w}_{0}$,

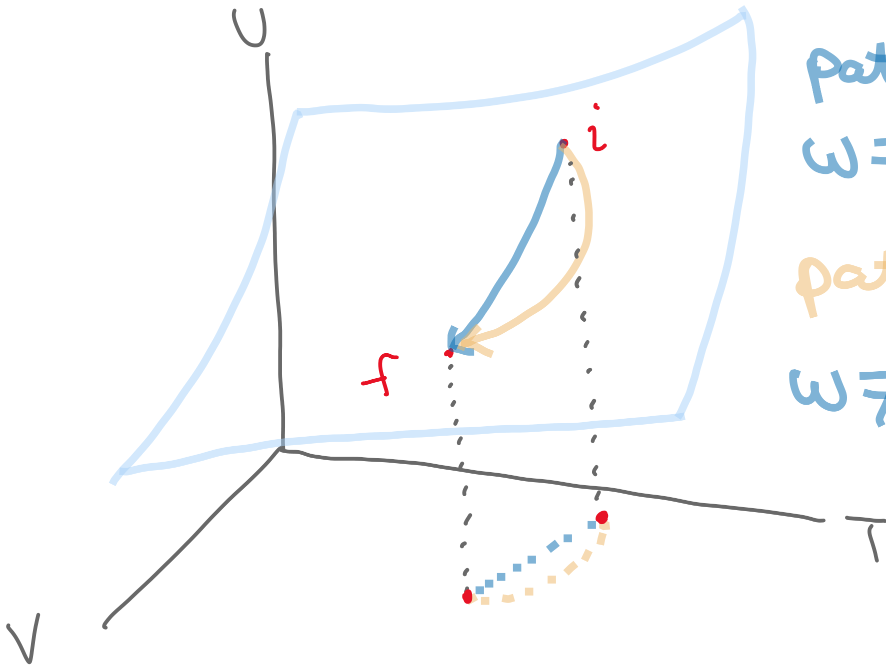
and $\boxed{q = 0}$ as well.

b) We still have an isothermal process, so $\boxed{\Delta U = C_V \Delta T = 0}$. For work, we use the previously derived expression $\boxed{w = -nRT \ln \frac{V_f}{V_i}}$. As for heat, we the First Law: $\Delta U = q + w$, therefore

$$\boxed{q = +nRT \ln \frac{V_f}{V_i}}.$$

<u>Topic 2D : State Functions and Exact</u>

Differentials



path 1:

$w \neq 0, q = 0$

path 2:

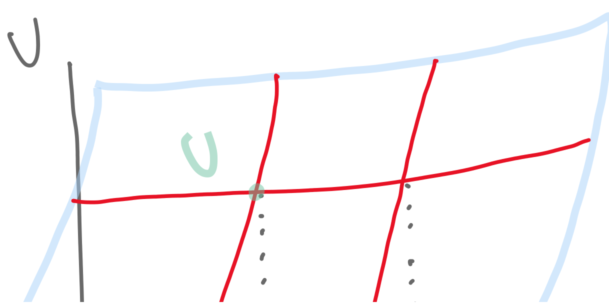
$w \neq 0, q \neq 0$

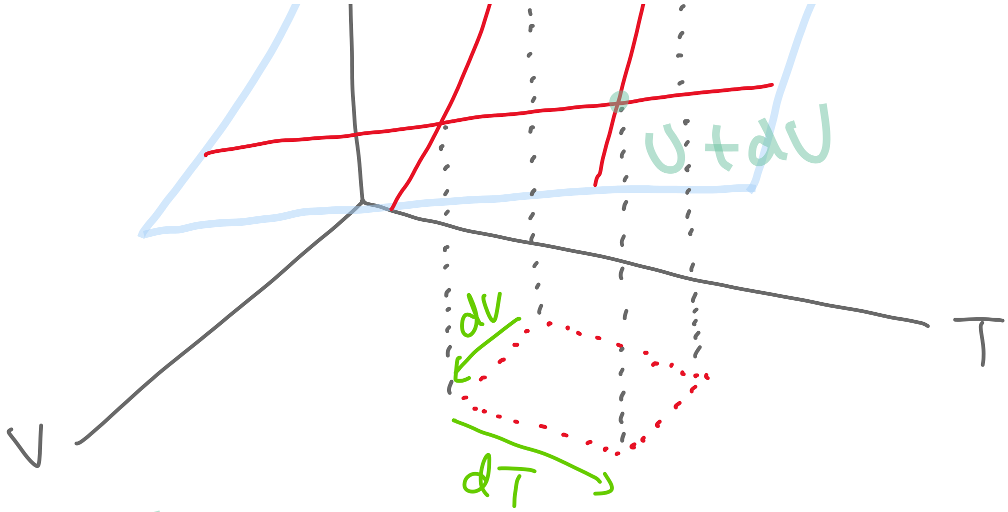
For state functions, the following expression is exact:

$$df(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$U(T,V)$



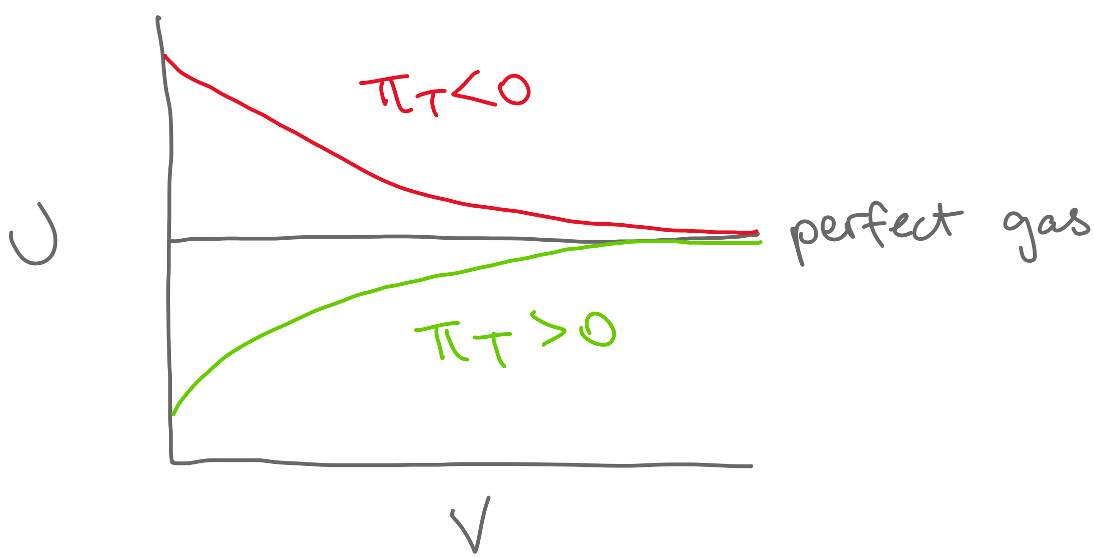


$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV$$

Define internal pressure to be

$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$; same units as pressure

$$\boxed{dU = C_V\, dT + \pi_T\, dV}$$



Changes in internal energy at constant pressure

$$dU = C_V dT + \pi_T dV$$

divide by dT

$$\frac{dU}{dT} = C_V + \pi_T \frac{dV}{dT}$$

impose the condition of constant pressure

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \pi_T \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{V \cdot \alpha}$$

Define expansion coefficient α :

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

α represents the fractional change in volume that accompanies a rise in temperature.

For example, $\alpha = 2.1 \times 10^{-4}\ K^{-1}$ for water, and $8.61 \times 10^{-5}\ K^{-1}$ for lead at 298 K.

A related quantity is the isothermal compressibility, κ_T:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

κ_T is a measure of the fractional change in volume when the pressure is increased.

For example, $\kappa_T = 4.90 \times 10^{-5}\ \text{bar}^{-1}$ for water and $2.18 \times 10^{-6}\ \text{bar}^{-1}$ for lead (at 1 bar of pressure).

Therefore,

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V}$$

useful, general eque

can measure in
different experiments

For a perfect gas, $\pi_T = 0$, so

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_p} = C_V \quad \text{and} \quad \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

Now, we can find the relation between C_p and C_V for a perfect gas.

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V = \left(\frac{\partial U}{\partial T}\right)}$$

$H = U + pV$

$$= \left(\frac{\partial \boxed{H}}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p$$

$$= \left(\frac{\partial (U + pV)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p$$

$pV = nRT$

$$= \cancel{\left(\frac{\partial U}{\partial T}\right)} + \left(\frac{\partial \boxed{(pV)}}{\partial T}\right) - \cancel{\left(\frac{\partial U}{\partial T}\right)}$$

$$\cancel{\left(\partial T\right)_p} + \left(\partial T\right)_p - \cancel{\left(\partial T\right)_p}$$

$$= \left(\frac{\partial (nRT)}{\partial T}\right)_p$$

$$\boxed{C_p - C_V = nR}$$

perfect gas

divide by n

$$\boxed{C_{p,m} - C_{V,m} = R}$$

$$\boxed{C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}}$$

general result

Practice Problem

The molar volume of water at 298 V_m is $1.81 \times 10^{-5}\ m^3 \cdot mol^{-1}$. From befo[re]

α is $2.1 \times 10^{-4}\ K^{-1}$ and κ_T is

$4.90 \times 10^{-10}\ Pa^{-1}$. Find the differe[nce] between C_p and C_V under these conditions.

$$C_p - C_V = \frac{\alpha^2 T V}{\kappa_T}$$

$$= \frac{(2.1 \times 10^{-4}\ K^{-1})^2 \cdot 298\ K \cdot 1.81 \times 10^{-5}\ m^3}{4.90 \times 10^{-10}\ Pa^{-1}}$$

$$dw = -\vec{F} \cdot d$$

$$= \underbrace{0.485}\ Pa\ m^3\ K^{-1}$$

round to two significant figures at the last step

$$\boxed{C_p - C_V = 0.49\ J \cdot K^{-1}}$$