

# Solution Worksheet 1.

## • Maxwell's Velocity Distribution.

We have the probability density of finding a particle with a velocity  $v = |\vec{v}|$  goes:

$$f(\vec{v}) = f(v) = C e^{-\alpha \vec{v}^2} = C e^{-\alpha(v_x^2 + v_y^2 + v_z^2)}$$

The normalization constant  $C$  can be calculated considering that probability distributions;

$$\int_{\mathbb{R}^3} d\vec{v} f(\vec{v}) = 1.$$

Hence

$$\begin{aligned} \int_{\mathbb{R}^3} d^3\vec{v} f(\vec{v}) &= C \int_{\mathbb{R}^3} d^3\vec{v} \exp(-\alpha \vec{v}^2) \\ &= C \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dv_x dv_y dv_z \exp(-\alpha(v_x^2 + v_y^2 + v_z^2)) \\ &= C \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dv_x dv_y dv_z e^{-\alpha v_x^2} e^{-\alpha v_y^2} e^{-\alpha v_z^2} \\ &= C \left[ \int_{-\infty}^{\infty} dv_x e^{-\alpha v_x^2} \right] \left[ \int_{-\infty}^{\infty} dv_y e^{-\alpha v_y^2} \right] \left[ \int_{-\infty}^{\infty} dv_z e^{-\alpha v_z^2} \right] \end{aligned}$$

These 3 integrals are the same, so let us take

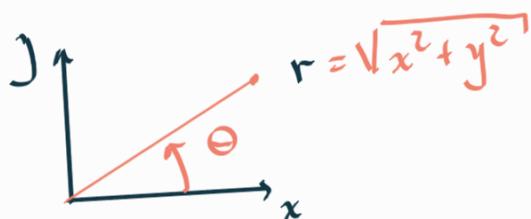
$$\int_{-\infty}^{\infty} dx e^{-\alpha x^2} \quad \text{and solve it.}$$

There is a trick to calculate this integral.

Take  $I = \int dx e^{-x^2}$

$$I^2 = \left[ \int_{-\infty}^{\infty} dx e^{-x^2} \right]^2 = \int_{-\infty}^{\infty} dx e^{-x^2} \int_{-\infty}^{\infty} dy e^{-y^2}$$
$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy e^{-(x^2+y^2)}$$

and consider polar coordinates;



$$dx dy = r dr d\theta$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy e^{-(x^2+y^2)} = \int_0^{\pi} \int_0^{\infty} dr d\theta r e^{-r^2}$$
$$= 2\pi \int_0^{\infty} dr r e^{-r^2} \quad u = -r^2$$
$$\frac{du}{2} = -r dr$$
$$= 2\pi \int_{-\infty}^0 \frac{du}{2} e^u = \pi (e^0 - e^{-\infty})$$
$$= \pi$$

finally

$$I^2 = \left[ \int_{-\infty}^{\infty} dx e^{-x^2} \right]^2 = \pi \longrightarrow I = \sqrt{\pi}$$

Hence

$$\int_{-\infty}^{\infty} dx e^{-ax^2}$$
 with the substitution  $u = \sqrt{a} x$ 
$$\frac{du}{\sqrt{a}} = dx$$

$$\int_{-\infty}^{\infty} dx e^{-\alpha x} = \frac{1}{\sqrt{\alpha}} I = \sqrt{\frac{\pi}{\alpha}}$$

Coming back to the Maxwell's distribution;

$$\int_{\mathbb{R}^3} d^3 \vec{r} f(\vec{v}) = C \left( \sqrt{\frac{\pi}{\alpha}} \right)^3 = 1.$$

$$C = \left( \frac{\alpha}{\pi} \right)^{3/2}$$

Now, taking the relation Temperature Kinetic Energy

$$\left( \frac{3}{2} \right) k_B T = \langle E \rangle = \frac{m}{2} \langle \vec{v}^2 \rangle$$

$$= m \langle \vec{v}^2 \rangle$$

$$= m \left( \frac{\alpha}{\pi} \right)^{3/2} \underbrace{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dv_x dv_y dv_z e^{-\alpha \vec{v}^2}}_{-a(v_x^2 + v_y^2 + v_z^2)}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dv_x dv_y dv_z (v_x^2 + v_y^2 + v_z^2) e^{-a(v_x^2 + v_y^2 + v_z^2)}$$

Notice that the integrals for  $v_x$ ,  $v_y$  and  $v_z$ , then we can use simply  $v_x$

$$= 3 \left[ \int_{-\infty}^{\infty} dv_x e^{-a v_x^2} \overset{C^{1/3}}{\cancel{C}} \int_{-\infty}^{\infty} dv_y e^{-a v_y^2} \overset{C^{1/3}}{\cancel{C}} \int_{-\infty}^{\infty} dv_z e^{-a v_z^2} v_z^2 \right]$$

$$\Rightarrow 3 \cancel{3} k_B T = 3 \left( \frac{\alpha}{\pi} \right)^{3/2} \cancel{\left( \frac{\alpha}{\pi} \right)} \int dv_x e^{-a v_x^2} v_x^2$$

Take  $v = v_x$

$$k_B T = m \left( \frac{a}{\pi} \right)^{1/2} \left[ \int_{-\infty}^{\infty} dv e^{-av^2} v^2 \right]$$

and like  $v$  goes  $(-\infty, \infty)$  and the function is symmetric

$$k_B T = m \left( \frac{a}{\pi} \right)^{1/2} \left[ 2 \int_0^{\infty} dv e^{-av^2} v^2 \right]$$

$$x = av^2 \quad dx = 2avv \, dv$$

$$\sqrt{\frac{x}{a}} = v \quad \frac{dx}{2av} = dv$$

Then

$$k_B T = m \left( \frac{a}{\pi} \right)^{1/2} \left[ \cancel{2} \int_0^{\infty} dx e^{-x} \sqrt{\frac{x}{a}} \frac{dx}{\cancel{a}} \right]$$

$$= m \left( \frac{a}{\pi} \right)^{1/2} \left[ \frac{1}{a\sqrt{a}} \int_0^{\infty} dx e^{-x} x^{1/2} \right]$$

$$= m \left( \frac{1}{a\sqrt{\pi}} \right) \left[ \int_0^{\infty} dx e^{-x} x^{1/2} \right]$$

identifying this integral with the  $\Gamma(z)$  function

$$\Gamma(z) = \int_0^{\infty} dx e^{-x} x^{z-1}$$

$$\Gamma(3/2) = \int_0^{\infty} dx e^{-x} x^{\frac{3}{2}-1} = \int_0^{\infty} dx e^{-x} x^{1/2}$$

and using  $\Gamma(3/2) = \frac{1}{2} \Gamma(1/2) = \frac{\sqrt{\pi}}{2}$

$$k_B T = \left( \frac{m}{\alpha \sqrt{\pi}} \right) \left[ \frac{\sqrt{\pi}}{2} \right]$$

$$= \left( \frac{m}{2a} \right) \Rightarrow 2a = \frac{m}{k_B T}$$

$$a = \frac{m}{2k_B T}$$

replacing  $a$  in  $C$

$$C = \left( \frac{m}{2\pi k_B T} \right)^{3/2}$$

So, the Maxwell Distribution goes

$$f(\vec{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{m \vec{v}^2}{2 k_B T} \right)$$

Exact and inexact differentials.

consider

$$\vec{F} \cdot d\vec{x} = (x^2 - y) dx + x dy.$$

$$= F_x dx + F_y dy.$$

and let us compute the mixed derivatives

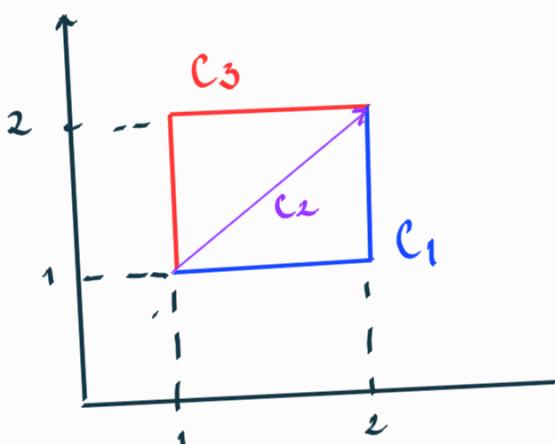
$$\left. \begin{array}{l} \frac{\partial F_x}{\partial y} = -1 \\ \frac{\partial F_y}{\partial x} = 1 \end{array} \right\} \frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = -1 - (1) = -2.$$

as this term doesn't vanish, then it is not an exact differential.

let us compute the line

integrals over  $C_1$ ,  $C_2$  and  $C_3$ .

Case  $C_1$



$$\int_{C_1} \vec{F} \cdot d\vec{x} = \int_1^2 F_x dx \Big|_{y=1} + \int_1^2 F_y dy \Big|_{x=1}$$

$$= \int_1^2 (x^2 - y) dx \Big|_{y=1} + \int_1^2 x dy \Big|_{x=2}$$

$$= \left( \frac{x^3}{3} - x \right) \Big|_1^2 + 2y \Big|_1^2 = \left( \frac{2^3}{3} - 2 \right) - \left( \frac{1^3}{3} - 1 \right) + 2(2 - 1)$$

$$= \frac{8}{3} - 2 - \frac{1}{3} + 1 + 2 - 2 = \frac{10}{3} \text{ h.}$$

case C<sub>2</sub>

let us define a parametric equation for C<sub>2</sub>.

$$C_2 = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} t \\ t^2 \end{pmatrix} \quad t \in [1, 2].$$

$$\begin{aligned} \int_{C_2} \vec{F} \cdot d\vec{x} &= \int_1^2 dt \left\{ t^2 - t + t^2 \right\} = \int_1^2 dt \cdot t^2 \\ &= \frac{t^3}{3} \Big|_1^2 = \frac{8}{3} - \frac{1}{3} = \frac{7}{3} h. \end{aligned}$$

case C<sub>3</sub>

$$\begin{aligned} \int_{C_3} \vec{F} \cdot d\vec{x} &= \int_1^2 x \, dy \Big|_{x=1} + \int_1^2 (x^2 - y) \, dx \Big|_{y=2} \\ &= y \Big|_1^2 + \left( \frac{x^3}{3} - 2x \right) \Big|_1^2 \\ &= \cancel{2-1} + \cancel{\frac{8}{3}} - \cancel{4} - \cancel{\frac{1}{3}} + \cancel{2} \\ &= \frac{7}{3} - 1 = \frac{4}{3} h. \end{aligned}$$

Again, as the differential is not exact, the result is path dependent.

let us find the integrating factor.

To do so, let us consider a function  $g(x, y)$  that completes the differential.

$$\frac{\partial}{\partial y} (F_x g(x, y)) - \frac{\partial}{\partial x} (F_y g(x, y)) = 0$$

**Ansatz** let us consider a separable function.

$$g(x, y) = X(x) Y(y)$$

thus

$$\frac{\partial}{\partial y} ((x^2 - y) X(x) Y(y)) - \frac{\partial}{\partial x} (x X(x) Y(y)) = 0$$

$$X(x) \left[ \frac{\partial}{\partial y} ((x^2 - y) Y(y)) \right] - Y(y) \left[ \underbrace{\frac{\partial}{\partial x} (x X(x))}_{\text{II}} \right] = 0$$

$$\text{I} = -1 \cdot Y(x) + (x^2 - y) \frac{\partial}{\partial y} Y(y)$$

$$\text{II} = X(x) + x \frac{\partial}{\partial x} X(x)$$

Then

$$-X(x)Y(y) + X(x)(x^2 - y) \frac{\partial}{\partial y} Y(y) - X(x)Y(y) - xY(y) \frac{\partial}{\partial x} X(x) = 0$$

$$X(x)(x^2 - y) \frac{\partial Y(y)}{\partial y} - x Y(y) \frac{\partial X(x)}{\partial x} = 2 X(x) Y(y)$$

taking  $X(x) Y(y) \neq 0$

$$(x^2 - y) \frac{1}{Y(y)} \frac{\partial Y(y)}{\partial y} - x \frac{1}{X(x)} \frac{\partial X(x)}{\partial x} = 2$$

and using that  $\frac{\partial}{\partial z} \log(f(z)) = \frac{1}{f(z)} \frac{\partial f(z)}{\partial z}$

$$(x^2 - y) \frac{\partial}{\partial y} \log(Y(y)) - x \frac{\partial}{\partial x} \log(X(x)) = 2$$

Note: this expression should vanish for all values of  $x$  and  $y$ , therefore

$$\frac{\partial}{\partial y} \log(Y(y)) = 0$$

so there is no contribution of the first term.

$$\log(Y(y)) = \text{const.}$$

so, with any lack of generality we can take  $Y(y) = 1$   
 so  $\log(Y(y)) = 0$ .

from the second term

$$\frac{d}{dx} \log(X(x)) = -\frac{2}{x}$$

and, using the logarithm properties.

$$\frac{d}{dx} \ln(x) = \frac{1}{x}$$

and

$$a \ln(x) = \ln(x^n),$$

$$\begin{aligned}\frac{d}{dx} (\log(X(x))) &= -2 \frac{d}{dx} (\log(x)) \\ &= \frac{d}{dx} (-2 \log(x)) \\ &= \frac{d}{dx} (\log(x^{-2}))\end{aligned}$$

$$X(x) = \frac{1}{x^2}$$

therefore

$$g(x, y) \vec{F} \cdot d\vec{x} = X(x) Y(y) \vec{F} \cdot d\vec{x} = \frac{1}{x^2} \vec{F} \cdot d\vec{x}$$

is now, an exact differential

$$\frac{1}{x^2} \vec{F} \cdot d\vec{x} = \left( 1 - \frac{y^2}{x^2} \right) dx + \frac{1}{x} dy$$

Equipartition theorem.

Every degree of freedom +  $\frac{k_B T}{2}$

case monoatomic gas

There are just contributions to the kinetic energy given by the translational degrees of freedom.

$$k_{\text{mono}} = \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

$v_x, v_y, v_z$

3 deg. of freedom

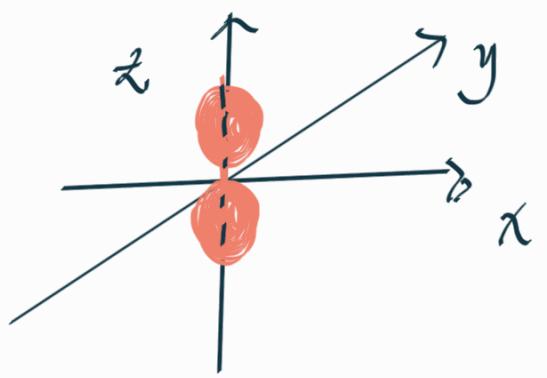
So, for a monoatomic gas of  $N$  particles.

$$E = 3N \frac{k_B T}{2}$$

Every particle has 3 deg. freedom.

case diatomic Gas

The difference now comes from the rotational degrees of freedom



The molecule has two axis of rotation

(Given one symmetry)

• Rotation around the z axis

• Rotation around ANY axis perpendicular to z

Then the energy for the diatomic Gas

$$E_{\text{diatomic}} = 5N \quad \frac{k_B T}{2}$$

D.o.F. = 3 translational + 3 Rotational - 1 Symmetry

$$\approx 5.$$

Now, if we compare two gases (mono- and diatomic) at the same temperature

$$\frac{E_{\text{di}}}{E_{\text{mono}}} = \frac{5}{3}$$

Here it is clear that, the inclusion of more deg. of freedom can change completely the energy added to any kind of system to bring them to certain temperature  $T$ .

This is also part of the reason why some materials are easier to heat up than others.

Then we should think about

Amount of energy required to heat up an element certain  $\Delta T$

$\equiv$  Heat Capacity

let us write the heat capacities.

$$\frac{\Delta U}{T} = C \frac{\Delta T}{T}$$

amount of energy      |      amount of temperature.  
heat capacity.

let us consider an isochoric process  $\Delta V=0$   
the 1st law of thermodynamics goes as  
 $\Delta U = \Delta W + \Delta Q = P \Delta V + \Delta Q$

$$dU = \delta q = C_V dT$$

$$\frac{dU}{dT} = C_V$$

Case monocatomic

$$\frac{dU_{\text{mono}}}{dT} = \frac{3}{2} N k_B \xrightarrow{\substack{dT \\ dT}} = \frac{3}{2} N k_B$$

and

$$C_P = N_A k_B + C_V$$

for a mole of material, for  $N$  particles  
gas

$$C_P = N k_B + C_V$$

$$= N k_B + \frac{3}{2} N k_B$$

$$= \frac{5}{2} N k_B$$

so

$$\gamma_{\text{mono}} = \frac{C_P}{C_V} = \frac{\cancel{\frac{5}{2} N k_B}}{\cancel{\frac{3}{2} N k_B}} = \frac{5}{3}$$

# Case Diatomic

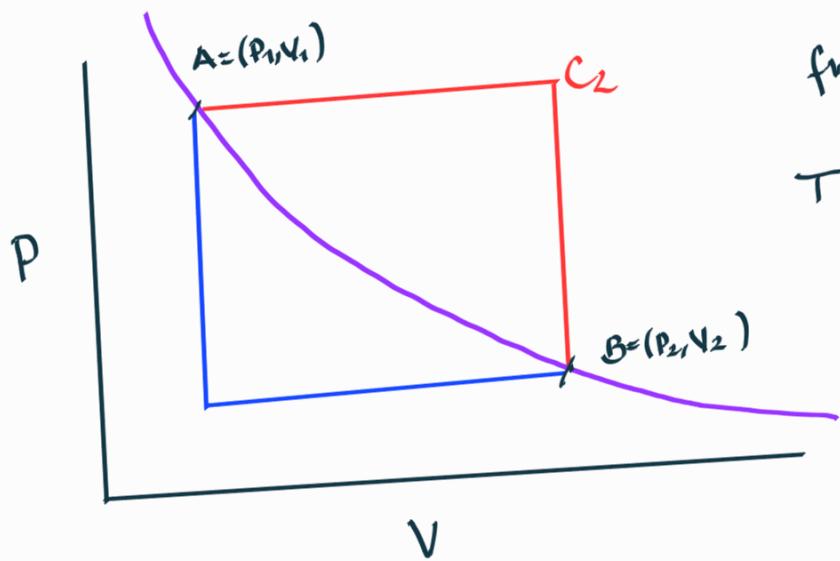
Similarly

$$\frac{dU_{di}}{dT} = \frac{5}{2} N k_B \quad \cancel{\frac{dT}{dT}} = C_V$$

$$C_P = N k_B + \frac{5}{2} N k_B = \frac{7}{2} N k_B$$

$$\gamma_{\text{diatomic}} = \frac{\frac{7}{2} N k_B}{\frac{5}{2} N k_B} = \frac{7}{5}$$

# Expansion / Compression of Gases



Let us consider several paths from A to B.

The equation of state goes

$$PV = N k_B T$$

and the first law

$$dU = \delta W + \delta Q$$

let us now make a small summary

- \* isochoric: Constant volume  $\delta W = P \delta V = 0$
- \* adiabatic: No heat exchange with the environment.  $\delta Q = 0$

$$\delta U = \delta Q = P \delta V = P(V_f - V_i)$$

- \* isobaric: Constant Pressure

$$\begin{aligned} dU &= \delta W + \delta Q = P dV + \delta Q \\ &= P dV + \left. \frac{\partial U}{\partial T} \right|_P dT \\ &= P dV + C_p dT. \end{aligned}$$

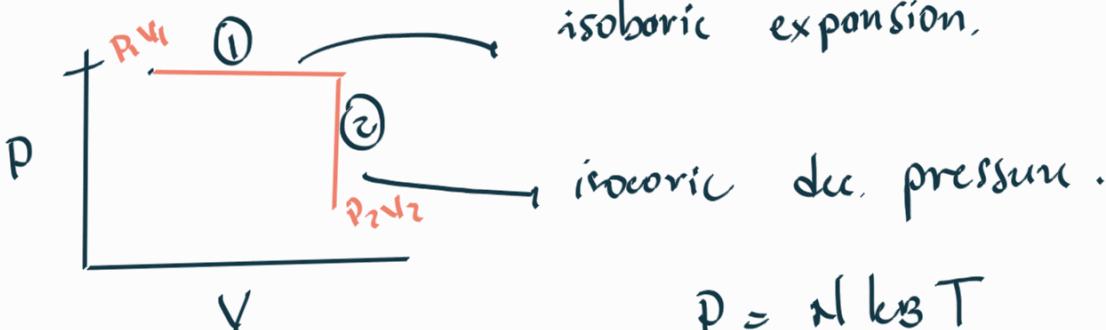
for a monoatomic ideal gas, we have that

$$C_p = \frac{5}{2} N k_B$$

thus

$$dU = P dV + \frac{5}{2} N dT.$$

Case C<sub>1</sub>



$$P = \frac{n k_B T}{V}$$

① work

$$\delta W_1 = P \delta V$$

$$\int_{①}^{②} \delta W_1 = \nu V_2 - \nu V_1 = \Delta W_{12} = -P_1 (V_2 - V_1)$$

The heat can be calculated with the amount of thermal energy getting in the system.

$\Rightarrow$  change of temperature.

$$T = \frac{PV}{Nk_B} \rightarrow \Delta T = \frac{P_1}{Nk_B} \Delta V = \frac{P_1}{Nk_B} (V_2 - V_1)$$

$$\Delta U = \frac{3}{2} Nk_B \Delta T$$

$$= \frac{3}{2} P_1 (V_2 - V_1)$$

$$\begin{aligned}\Delta Q &= \Delta U - \Delta W \\ &= P_1 (V_2 - V_1) \left( \frac{3}{2} + 1 \right) \\ &= \frac{5}{2} P_1 (V_2 - V_1).\end{aligned}$$

and for ②

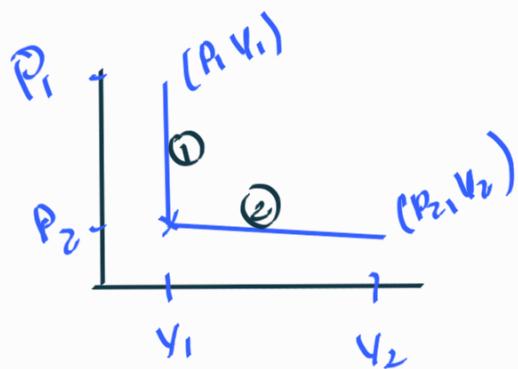
$$\Delta W = 0$$

$$\Delta U = \frac{3}{2} V_2 (P_2 - P_1)$$

$$\Delta Q = \Delta U - \Delta W = \frac{3}{2} V_2 (P_2 - P_1)$$

$$\begin{aligned}\Delta U_{\text{tot}} &= \frac{3}{2} V_2 (P_2 - P_1) + \frac{3}{2} P_1 (V_2 - V_1) \\ &= \frac{3}{2} (V_2 P_2 - V_2 P_1 + P_1 V_2 - P_1 V_1)\end{aligned}$$

case



Similarly, we will

①

$$\Delta U = \frac{3}{2} V_1 (P_2 - P_1)$$

$$\Delta Q = \Delta Q - \Delta W = \frac{3}{2} V_1 (P_2 - P_1)$$

$$\Delta W = 0$$

②

$$\Delta W = P_2 (V_2 - V_1)$$

$$\Delta U = \frac{3}{2} P_2 (V_2 - V_1)$$

$$\begin{aligned}\Delta Q &= P_2 (V_2 - V_1) \left( \frac{3}{2} + 1 \right) \\ &= \frac{5}{2} P_2 (V_2 - V_1)\end{aligned}$$

$$\Delta U_{\text{total}} = \frac{3}{2} V_1 (P_2 - P_1) + \frac{3}{2} P_2 (V_2 - V_1)$$

### Case 3

The case of the adiabatic expansion  $\Delta Q = 0$

then

$$\Delta u = \Delta w = \int_{V_1}^{V_2} P dV$$

but during adiabatic processes

$$PV^\gamma = \text{cte.}$$

now

$$P_1 V_1^\gamma = P_2 V_2^\gamma = k.$$

then

$$\Delta w = \int_{V_1}^{V_2} \frac{k}{V^\gamma} dV$$

$$= k \left[ \frac{V^{-\gamma+1}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$= \frac{k}{1-\gamma} \left( V_2^{1-\gamma} - V_1^{1-\gamma} \right)$$

$$= \frac{k}{1-\gamma} \left( V_2 V_2^{-\gamma} - V_1 V_1^{-\gamma} \right)$$

$$= \frac{1}{1-\gamma} \left[ V_2 (k V_2^{-\gamma}) - V_1 (k V_1^{-\gamma}) \right]$$

$$= \frac{1}{1-\gamma} (V_2 P_2 - V_1 P_1)$$

$$= \frac{1}{1-\gamma} [N k_B \Delta T] h.$$