Ministry of Higher Education and Scientific Research
AL-Mustaqbal University College of Science
Department of Biochemistry

Physical chemistry

Lecture 8

Relation between Cp & Cv

By

Dr. Assel Amer Hadi

Relation between C_P & C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

Recall:
$H \equiv U + PV$

$$C_P - C_V = \left(\frac{\partial (U + PV)}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

Can be related

Relation between C_P & C_V

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

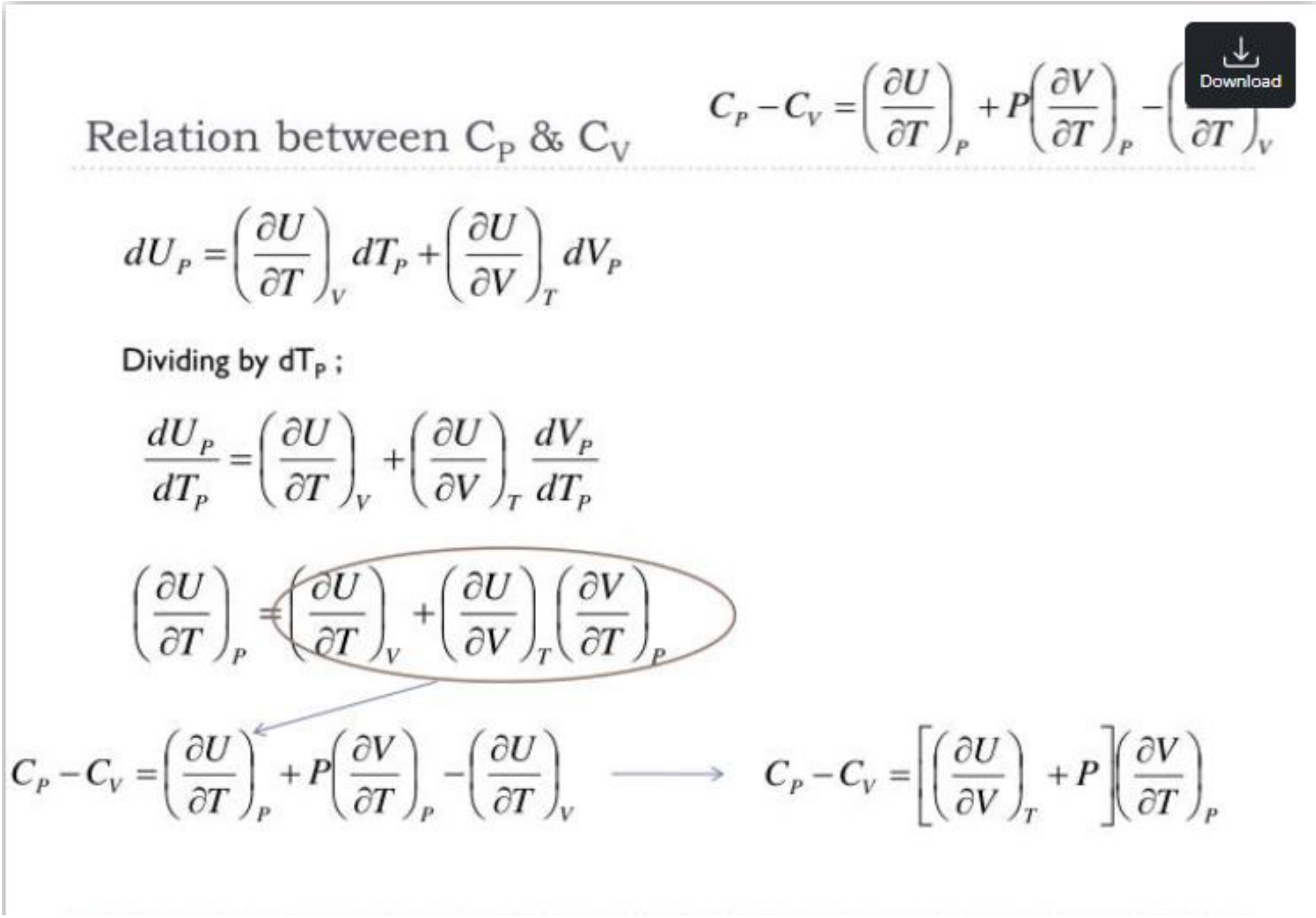
$\left(\frac{\partial U}{\partial T}\right)_V \longrightarrow$ U is a function of T and V

Thus;

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

At constant P;

$$dU_P = \left(\frac{\partial U}{\partial T}\right)_V dT_P + \left(\frac{\partial U}{\partial V}\right)_T dV_P$$



Relation between C_P & C_V

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{}{\partial T}\right)_V$$

$$dU_P = \left(\frac{\partial U}{\partial T}\right)_V dT_P + \left(\frac{\partial U}{\partial V}\right)_T dV_P$$

Dividing by dT_P ;

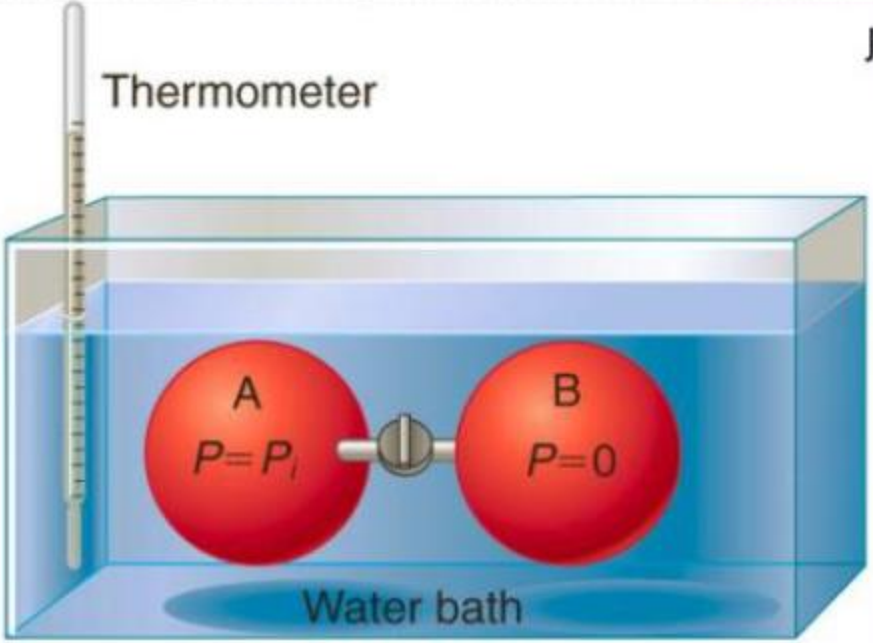
$$\frac{dU_P}{dT_P} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV_P}{dT_P}$$

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

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \longrightarrow C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

Joule Experiment

To determine $\left(\frac{\partial U}{\partial V}\right)_T$



Joule coefficient, μ_J

$$\mu_J = \left(\partial T / \partial V\right)_U$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = -C_V \mu_J}$$

Joule experiment gave $\mu_J = 0$ and $\left(\partial U / \partial V\right)_T = 0$

because the changes in temperature that occurred were too small to be measured by the thermometer.

Joule-Thomson experiment

$$\Delta U = U_2 - U_1 = q + w$$

Adiabatic process

$$= 0 + w$$

$$w = w_{left} + w_{right}$$

$$= -\int_{V_1}^{0} P_1 dV - \int_{0}^{V_2} P_2 dV$$

$$= P_1V_1 - P_2V_2$$

$$U_2 - U_1 = P_1V_1 - P_2V_2$$

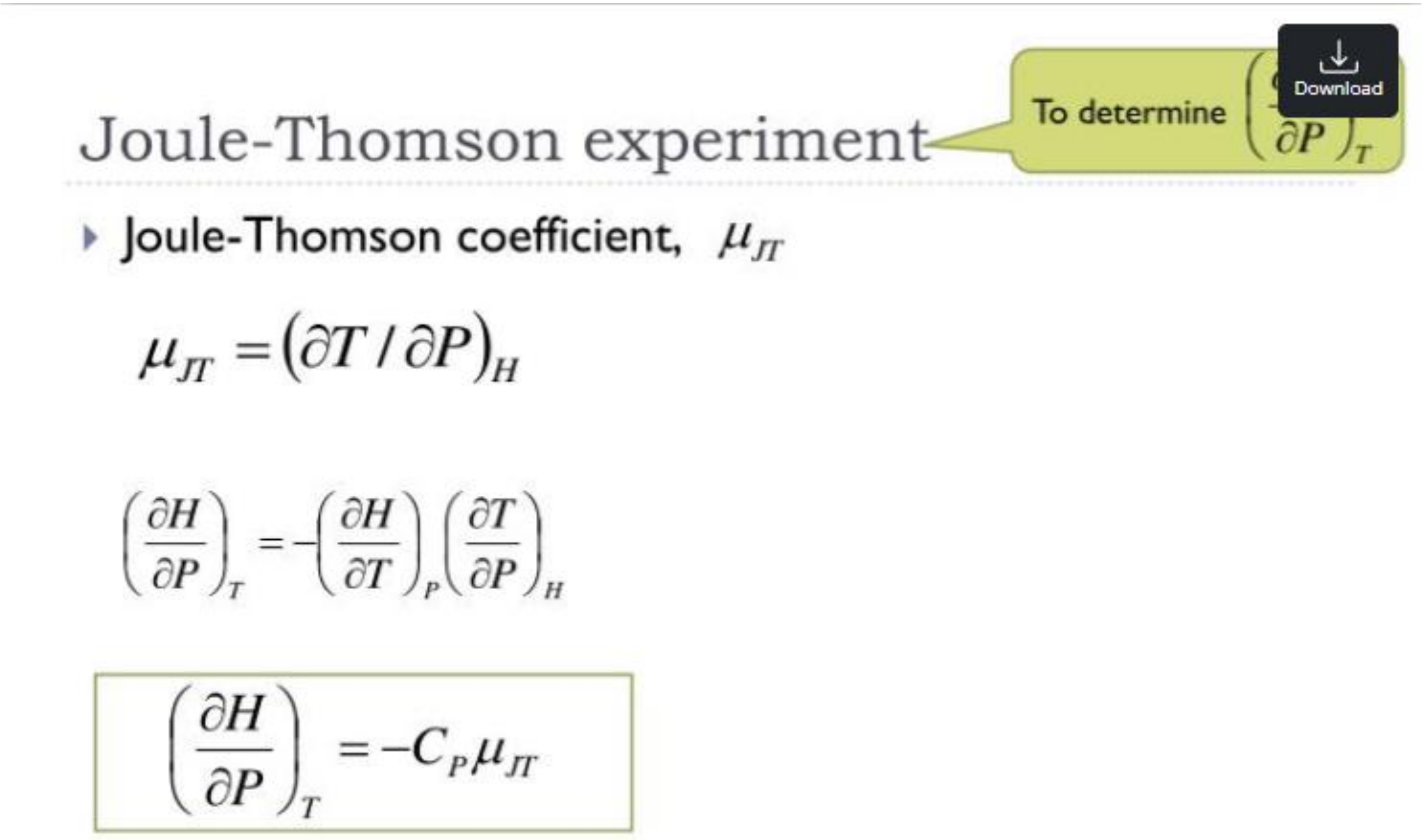
Rearranging;

$$\underline{U_2 + P_2V_2} = \underline{U_1 + P_1V_1}$$

$$H_2 = H_1$$

$$\Delta H = 0$$

Isenthalpic process



Joule-Thomson experiment

To determine $\left(\frac{\quad}{\partial P}\right)_T$

- Joule-Thomson coefficient, μ_{JT}

$$\mu_{JT} = \left(\partial T / \partial P\right)_H$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{JT}}$$

Perfect Gases

- Perfect gas: one that obeys both of the following:

$$PV = nRT$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

U is not change with V at constant T

If we change the volume of an ideal gas (at constant T), we change the distance between the molecules. Since intermolecular forces are zero, this distance change will not affect the internal energy.

Perfect Gases

- For perfect gas, internal energy can be expressed as a function of temperature (**depends only on T**):

$$U = U(T)$$

- An infinesimal change of internal energy,

$$dU = C_V dT$$

From $C_V = \left(\frac{\partial U}{dT}\right)_V$

(slide 19)

Perfect Gases

- For perfect gas, **enthalpy depends only on T**;

$$H \equiv U + \underset{\downarrow}{\underline{PV}}$$

$$H \equiv U + nRT$$

This shows that H depends only on T for a perfect gas

- Thus;

$$H = H(T)$$

- An infinesimal change of enthalpy,

$$dH = C_p dT$$

From $C_P = \left(\frac{\partial H}{dT}\right)_P$

(slide19)

Perfect Gases

- The relation of C_P and C_V for perfect gas;

$$C_P - C_V = \left[\underline{\left(\frac{\partial U}{\partial V}\right)_T} + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

From slide 24

Perfect gas

$$= [0 + P]\left(\frac{\partial V}{\partial T}\right)_P = P\underline{\left(\frac{\partial V}{\partial T}\right)_P}$$

PV=nRT, thus $\left(\frac{\partial V}{\partial T}\right)_P = nR/P$

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

or

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

Perfect Gases

- For perfect gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \mu_J \longrightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{JT} \longrightarrow \left(\frac{\partial H}{\partial P}\right)_T = 0$$

- Since U & H depend only on T.

Perfect gas and First Law

First law;

$$dU = dq + dw$$

For perfect gas;

$$\underset{\big\downarrow}{\underline{dU}} = dq + \underset{\big\downarrow}{\underline{dw}}$$

$$C_V dT = dq - PdV$$

Perfect gas, rev. process, P-V work only

Reversible Isothermal Process in a Perfect Gas

- First law:

$$\Delta U = q + w$$

- Since the process is **isothermal,** $\Delta T=0$;
- Thus, $\Delta U = 0$

$$dU = C_V \cancelto{0}{dT}$$

$$= 0$$

- First law becomes;

$$0 = q + w$$

Reversible Isothermal Process in a Perfect Gas

- Since $q + w = 0$, thus:

$$w = -q$$

- Work done;

$$w = -\int_1^2 P dV$$

$$= -\int_1^2 \frac{nRT}{V} dV = nRT - \int_1^2 \frac{1}{V} dV$$

$$= -nRT\left(\ln \frac{V_1}{V_2}\right) \quad \text{OR} \quad = -nRT\left(\ln \frac{P_2}{P_1}\right)$$

rev. isothermal process, perfect gas

Reversible Adiabatic Process in Perfect Gas

- First law,

$$dU = dq + dw$$

- Since the process is **adiabatic**, $dq = 0$

$$dU = dw$$

- For perfect gas, $dU = dw$ becomes,

$$\begin{aligned} C_V dT &= dW \\ &= -PdV \\ &= -\left(\frac{nRT}{V}\right)dV \end{aligned}$$

Since $dU = C_V dT$

Reversible Adiabatic Process in Perfect Gas

- If $C_{V,m}$ is constant, $\int_1^2 \frac{C_{V,m}}{T} dT = R \ln \frac{V_1}{V_2}$ becomes;

$$\ln \frac{T_2}{T_1} = \frac{R}{C_{V,m}} \ln \frac{V_1}{V_2}$$

$$= \ln \left(\frac{V_1}{V_2} \right)^{\frac{R}{C_{V,m}}}$$

OR

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{R}{C_{V,m}}}$$

rev. adiabatic
process, perfect gas

Reversible Adiabatic Process in Perfect Gas

- Alternative equation can be written instead of

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}}$$

- Consider $P_1V_1/T_1=P_2V_2/T_2$

$$P_2V_2/P_1V_1=\underline{T_2/T_1}$$

$$\downarrow$$

$$P_2V_2/P_1V_1=\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}}$$

$$P_1V_1^{1+R/C_{V,m}}=P_2V_2^{1+R/C_{V,m}}$$

Reversible Adiabatic Process in Perfect Gas

$$P_1V_1^{1+R/C_{V,m}} = P_2V_2^{1+R/C_{V,m}}$$

$$1+R/C_{V,m} = \left(C_{V,m}+R\right)/C_{V,m}$$

$$= C_{P,m}/C_{V,m}$$

Since
$C_{P,m} - C_{V,m} = R$

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

rev. adiabatic process,
perfect gas, C_V constant

where $\gamma = C_{P,m}/C_{V,m}$

Reversible Adiabatic Process in Perfect Gas

- If C_V is constant, $\Delta U = q + w$ becomes

$$C_V\left(T_2 - T_1\right) = w$$

rev. adiabatic process,
perfect gas, C_V constant

Exercise

- A cylinder fitted with a frictionless piston contains 3.00 mol of He gas at P = 1.00 atm and is in a large constant-temperature bath at 400 K. The pressure is reversibly increased to 5.00 atm. Find w, q and Δ U for the process.

Solution

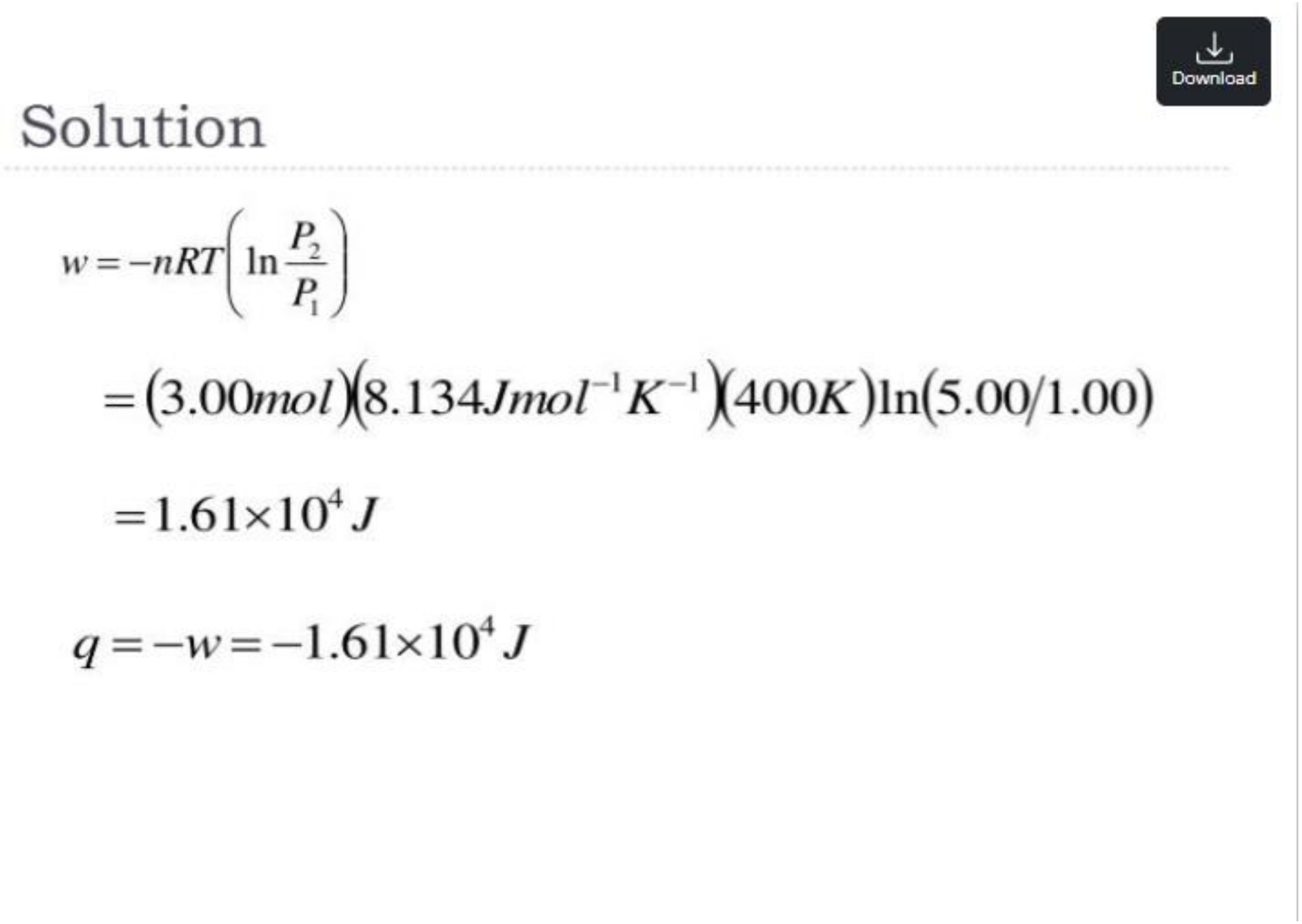
- A cylinder fitted with a frictionless piston contains 3.00 mol of He gas at P = 1.00 atm and is in a large constant-temperature bath at 400 K. The pressure is reversibly increased to 5.00 atm. Find w, q and Δ U for the process.

Assumption: He as a perfect gas.

ΔU =0 since T is constant (U depends only on T)

$$\Delta U = q + w = 0$$

$$w = -\int_1^2 P dV = -\int_1^2 \frac{nRT}{V} dV = nRT - \int_1^2 \frac{1}{V} dV = -nRT\left(\ln \frac{V_1}{V_2}\right) = -nRT\left(\ln \frac{P_2}{P_1}\right)$$



Solution

$$w = -nRT\left(\ln\frac{P_2}{P_1}\right)$$

$$= (3.00mol)(8.134Jmol^{-1}K^{-1})(400K)\ln(5.00/1.00)$$

$$= 1.61\times10^4 J$$

$$q = -w = -1.61\times10^4 J$$


Thank
you