

Tutorials. No. 1: Ideal and real gas (Correction)

Exercise 01 :

Let's solve each part of the exercise based on the given function $f(x, y) = x^2y - y^3$.

1) Calculation of $f(\alpha x, \alpha y)$

To calculate $f(\alpha x, \alpha y)$, we substitute αx for x and αy for y into the function:

$$\begin{aligned} f(\alpha x, \alpha y) &= (\alpha x)^2(\alpha y) - (\alpha y)^3 \\ &= \alpha^2 x^2 \alpha y - \alpha^3 y^3 \\ &= \alpha^3 (x^2 y) - \alpha^3 (y^3) \\ &= \alpha^3 (x^2 y - y^3) \\ &= \alpha^3 f(x, y) \end{aligned}$$

This shows that $f(x, y)$ is a homogeneous function of degree 3.

2) First Order Partial Derivatives of f

The partial derivatives of $f(x, y) = x^2y - y^3$ are calculated as follows:

Partial derivative with respect to x ($\frac{\partial f}{\partial x}$):

$$\begin{aligned} \frac{\partial}{\partial x}(x^2y - y^3) &= \frac{\partial}{\partial x}(x^2y) - \frac{\partial}{\partial x}(y^3) \\ &= 2xy - 0 \\ &= 2xy \end{aligned}$$

Partial derivative with respect to y ($\frac{\partial f}{\partial y}$):

$$\begin{aligned} \frac{\partial}{\partial y}(x^2y - y^3) &= \frac{\partial}{\partial y}(x^2y) - \frac{\partial}{\partial y}(y^3) \\ &= x^2 - 3y^2 \end{aligned}$$

3) Calculate the expression: $x \left(\frac{\partial f}{\partial x} \right)_y + y \left(\frac{\partial f}{\partial y} \right)_x$

Using the partial derivatives calculated:

$$\begin{aligned} x \left(\frac{\partial f}{\partial x} \right)_y + y \left(\frac{\partial f}{\partial y} \right)_x &= x(2xy) + y(x^2 - 3y^2) \\ &= 2x^2y + x^2y - 3y^3 \\ &= 3x^2y - 3y^3 \end{aligned}$$

$$= 3(x^2y - y^3)$$
$$= 3f(x, y)$$

4) Deduce the general statement of Euler's theorem relating to a homogeneous function of degrees n .

From the calculation above in part 3, we deduced that for our function $f(x, y)$, which is homogeneous of degree 3, the expression $x \left(\frac{\partial f}{\partial x} \right)_y + y \left(\frac{\partial f}{\partial y} \right)_x = 3f(x, y)$.

Euler's Theorem for Homogeneous Functions states that for a homogeneous function $f(x, y, \dots, z)$ of degree n :

$$x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + \dots + z \frac{\partial f}{\partial z} = n f(x, y, \dots, z)$$

This theorem is demonstrated by our calculation, which shows that if a function is homogeneous of degree n , then the sum of all variables each multiplied by their respective partial derivatives results in n times the function. In our specific example, $n = 3$ was confirmed.

Exercise 02 :

To show that the differential form $\delta w = y \sin(x) dx - \cos(x) dy$ is completely exact, we need to determine if there exists a function $F(x, y)$ such that:

$$\frac{\partial F}{\partial x} = y \sin(x)$$
$$\frac{\partial F}{\partial y} = -\cos(x)$$

Step 1: Check if δw is exact

For a differential form $M dx + N dy$ to be exact, it must satisfy the condition that:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

where $M = y \sin(x)$ and $N = -\cos(x)$.

Calculate $\frac{\partial M}{\partial y}$:

$$\frac{\partial M}{\partial y} = \frac{\partial}{\partial y} (y \sin(x)) = \sin(x)$$

Calculate $\frac{\partial N}{\partial x}$:

$$\frac{\partial N}{\partial x} = \frac{\partial}{\partial x} (-\cos(x)) = \sin(x)$$

Since $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$, the differential form δw is exact.

Step 2: Determine the primitive function $F(x, y)$

Given $\frac{\partial F}{\partial x} = y \sin(x)$, integrate this expression with respect to x to find F :

$$F(x, y) = \int y \sin(x) dx = -y \cos(x) + g(y)$$

Here, $g(y)$ is a function of y alone, as the integration constant can depend on y when integrating with respect to x .

Now, consider the partial derivative with respect to y :

$$\frac{\partial F}{\partial y} = \frac{\partial}{\partial y} (-y \cos(x) + g(y)) = -\cos(x) + g'(y)$$

Since we know from the problem statement that:

$$\frac{\partial F}{\partial y} = -\cos(x)$$

it implies that:

$$-\cos(x) + g'(y) = -\cos(x)$$

Thus, $g'(y) = 0$, indicating that $g(y)$ is a constant.

Since $g'(y) = 0$, we can conclude $g(y) = C$ (a constant).

Final primitive function

Hence, the primitive function $F(x, y)$ of the differential form $\delta w = y \sin(x) dx - \cos(x) dy$ is:

$$F(x, y) = -y \cos(x) + C$$

This is the potential function whose derivatives with respect to x and y give back the components of the original differential form, confirming that δw is not only exact but also integrable to a specific scalar potential.

Exercice 03 :

To determine whether $S(T, P)$ is a state function and derive its expression, we start by examining the given partial derivatives:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{7}{2} \frac{R}{T}$$
$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{R}{P}$$

A function is a state function if its mixed partial derivatives are equal, according to Schwarz's theorem, i.e., the second derivatives of the function are continuous and mixed partials are equal:

$$\frac{\partial^2 S}{\partial T \partial P} = \frac{\partial^2 S}{\partial P \partial T}$$

Step 1: Mixed partial derivatives

First, take the derivative of $\left(\frac{\partial S}{\partial T}\right)_P$ with respect to P :

$$\frac{\partial}{\partial P} \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial P} \left(\frac{7}{2} \frac{R}{T}\right) = 0$$

since $\frac{7}{2} \frac{R}{T}$ does not depend on P .

Next, take the derivative of $\left(\frac{\partial S}{\partial P}\right)_T$ with respect to T :

$$\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_T = \frac{\partial}{\partial T} \left(-\frac{R}{P}\right) = 0$$

since $-\frac{R}{P}$ does not depend on T .

Both mixed partial derivatives are zero, hence equal:

$$\frac{\partial^2 S}{\partial T \partial P} = \frac{\partial^2 S}{\partial P \partial T} = 0$$

Step 2: Expression for $S(T, P)$

To find $S(T, P)$, integrate the given partial derivatives with respect to their respective variables:

1. Integrate $\left(\frac{\partial S}{\partial T}\right)_P = \frac{7}{2} \frac{R}{T}$ with respect to T at constant P :

$$S(T, P) = \int \frac{7}{2} \frac{R}{T} dT = \frac{7}{2} R \ln T + f(P)$$

Here, $f(P)$ is an integration function depending solely on P .

2. Integrate $\left(\frac{\partial S}{\partial P}\right)_T = -\frac{R}{P}$ with respect to P at constant T :

$$S(T, P) = \int -\frac{R}{P} dP = -R \ln P + g(T)$$

Here, $g(T)$ is another integration function depending solely on T .

Since S must satisfy both conditions simultaneously, combining and aligning the integrated forms gives:

$$S(T, P) = \frac{7}{2} R \ln T - R \ln P + C$$

where C is a constant of integration.

Conclusion

The function $S(T, P) = \frac{7}{2} R \ln T - R \ln P + C$ shows that S is indeed a state function, as its mixed partial derivatives are consistent and equal. This expression fulfills the conditions given by the partial derivatives and confirms the continuity and dependability of S as a function of state variables T and P .

Exercise 04 :

Part I - Ideal Gas

1. Proof of Identity

We start with the ideal gas law:

$$PV = nRT$$

where P is pressure, V is volume, T is temperature, n is the number of moles, and R is the ideal gas constant.

We need to prove the identity:

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

Step-by-step derivatives:

- **First term** $\left(\frac{\partial P}{\partial V}\right)_T$:

$$P = \frac{nRT}{V} \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2}$$
- **Second term** $\left(\frac{\partial V}{\partial T}\right)_P$:

$$V = \frac{nRT}{P} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$
- **Third term** $\left(\frac{\partial T}{\partial P}\right)_V$:

$$T = \frac{PV}{nR} \Rightarrow \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{nR}$$

Multiplying them together:

$$\left(-\frac{nRT}{V^2}\right) \left(\frac{nR}{P}\right) \left(\frac{V}{nR}\right) = -\frac{T}{V} \frac{V}{P} = -\frac{T}{P}$$

Given $T = \frac{PV}{nR}$, substituting back we get:

$$-\frac{T}{P} = -1$$

Thus proving the identity.

2. Relationship Between Thermoelastic Coefficients

From the calculated partial derivatives, we can express the coefficients:

- **Thermal Expansion Coefficient** α :

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \frac{nR}{P} = \frac{R}{P}$$

- **Isothermal Compressibility** χ_T :

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(-\frac{nRT}{P^2}\right) = \frac{RT}{P^2}$$

- **Pressure Coefficient** β :

$$\beta = \frac{1}{P} \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{P} \frac{nR}{V} = \frac{R}{V}$$

Units:

- α and χ_T both have units of $\frac{1}{K}$ (inverse Kelvin).
- β has units of $\frac{1}{K}$.

Relations Derived:

$$\alpha = \frac{R}{P}, \chi_T = \frac{RT}{P^2}, \beta = \frac{R}{V}$$

Part II - Real Gas

Van der Waals Gas Constants Units

- The units of a are derived from $\frac{a}{V^2}$ being in pressure units (Pa, Pascal), so a has units of $\text{Pa m}^6/\text{mol}^2$.
- The unit of b is m^3/mol from the equation directly as a volume correction term.

Van der Waals Equation for n moles

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For n moles, V becomes nV_m where V_m is the molar volume:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Coefficient β for Van der Waals Gas

$$\beta = \frac{1}{P} \left(\frac{\partial P}{\partial T}\right)_V$$

To compute this, differentiate the Van der Waals equation with respect to T while keeping V constant. This requires implicit differentiation and careful consideration of V terms.

Comparison to Ideal Gas:

For an ideal gas, $\beta = \frac{R}{P}$. The coefficient β for a Van der Waals gas generally involves more complex dependency on P and V and differs due to the non-ideal interactions captured by a and b .

Exercise. 05 :

Part 1: Diagram (P, V)

1.1. Line AM ($V = \text{const.}$)

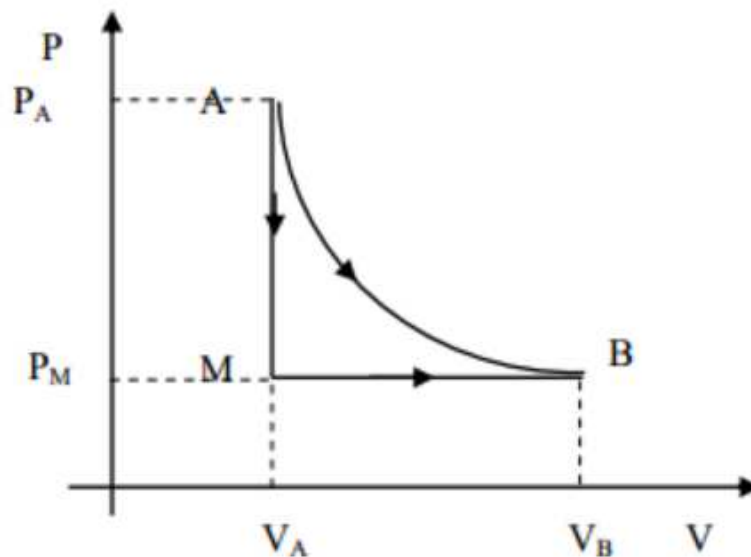
This represents an isochoric process (constant volume). In a P-V diagram, this is a vertical line because volume doesn't change, but pressure varies. If $P_A > P_M$, the line goes downward.

1.2. Line MB ($P = \text{const.}$)

This represents an isobaric process (constant pressure). In the P-V diagram, this is a horizontal line because pressure is constant while the volume changes. Given $V_B > V_M$, the line extends to the right.

1.3. Curve AB ($PV = \text{const.}$)

This represents an isothermal process for an ideal gas (Boyle's law). In a P-V diagram, this is a hyperbolic curve. The curve descends and moves rightward as volume increases and pressure decreases while the product PV remains constant.



Part 2: Work Calculations

The work done during a reversible process is given by:

$$\delta W = -P dV$$

2.1. Passing through M, following AM then MB

- **AM (V = const.):** Since the volume is constant, $dV = 0$ along AM, hence:

$$W_{AM} = 0 \text{ J (no work is done during isochoric processes)}$$

- **MB (P = const.):** The work done along this path can be calculated by integrating $P dV$ from V_M to V_B :

$$W_{MB} = -P \int_{V_M}^{V_B} dV = -P_M(V_B - V_M)$$

2.2. Following the curve AB (PV = const.)

The work done along an isothermal process (Boyle's Law) for an ideal gas from state A to B can be calculated using the integral of $P dV$, knowing that $P = \frac{C}{V}$ where $C = P_A V_A = P_B V_B$ (constant for the process):

$$W_{AB} = - \int_{V_A}^{V_B} \frac{C}{V} dV = -C \ln \frac{V_B}{V_A} = -P_A V_A \ln \frac{V_B}{V_A}$$

Part 3: Comparison and Geometric Interpretation

2.3. Comparison

- **Through M (AM + MB):** The work is simply the area under the horizontal line MB in the P-V diagram.
- **Direct AB (PV = const.):** The work corresponds to the area under the hyperbolic curve from A to B.

3. Geometric Interpretation of Work

In the P-V diagram:

- Work is represented by the area under the curve on this diagram between two volumes.
- For **AM + MB**, the work is the rectangular area under MB.
- For the **isothermal process AB**, the work is the area under the hyperbolic curve.

Conclusion

- The work done in an isothermal process AB (following $PV = \text{const.}$) will generally be greater in magnitude than the combined work along AM and MB , due to the nature of logarithmic integration providing a larger area under the curve.
- Geometrically, this can be visualized as the difference between the area under a rectangle (simpler but less area) and a curve (more complex and typically more area).
- The geometric representation in the P-V diagram effectively demonstrates that different processes between the same two states can result in different amounts of work being done, highlighting the path-dependent nature of work in thermodynamics.

B –Concepts and Definitions

Exercise 01 :

The categorization of physical quantities into extensive and intensive properties is essential in thermodynamics and various fields of physics. Here's a simple explanation followed by a table:

- **Extensive Quantities:** These quantities depend on the amount of substance or system size. Doubling the system size (while keeping its nature the same) doubles these quantities.
- **Intensive Quantities:** These quantities do not depend on the system size or the amount of substance. They are properties that characterize the system's conditions regardless of its size.

Here is the requested table categorizing the given physical quantities into extensive and intensive:

Extensive Quantities	Intensive Quantities
Volume	Pressure
Energy	Temperature
Momentum	Density
Electric Charge	

Explanation:

- **Volume** is extensive because it depends directly on the amount of substance or system size.
- **Pressure** is intensive; it remains the same regardless of system size but changes with the system's state.
- **Temperature** is intensive as it is a measure of the average kinetic energy per particle in a system, independent of the amount of substance.
- **Density** is intensive because it is defined as mass per unit volume, which does not change if the system size is increased proportionally.
- **Energy** (including forms like thermal energy, kinetic energy, etc.) is extensive because it depends on the system size or amount of substance.
- **Momentum** is extensive as it depends on the mass and velocity of the system, both of which scale with the size of the system.
- **Electric Charge** is extensive as it scales with the quantity of charged particles in the system.

This distinction helps in understanding and applying fundamental concepts in various areas of physics, chemistry, and engineering, particularly in the study of thermodynamics and materials science.

Exercise 02 :

To determine whether the described systems are in thermodynamic equilibrium, we should evaluate each system's energy exchange and potential phase changes, considering the temperature and phase balance criteria. Here's the analysis:

System 1: Two Identical Copper Blocks at Different Temperatures

- **Thermodynamic Equilibrium:** No, this system is not in thermodynamic equilibrium initially.
- **Reason:** The two copper blocks have different temperatures, which means there is a temperature gradient causing heat flow from the hotter block to the cooler block.
- **Evolution:** Heat will transfer from the higher temperature block to the lower temperature block until both reach the same temperature, at which point no net heat transfer occurs, and the system reaches thermal equilibrium.

System 2: Mixture of Liquid Water and Ice at 0°C and Under Atmospheric Pressure

Scenario 1: Ambient Air at 0°C

- **Thermodynamic Equilibrium:** Yes, this system is in thermodynamic equilibrium.
- **Reason:** The mixture of ice and water at 0°C represents a phase equilibrium between the liquid and solid phases of water. The ambient temperature being the same as the system's temperature (0°C) means there is no net heat exchange with the surroundings, and both phases coexist stably.
- **Evolution:** None required; the system is stable as long as the external conditions remain unchanged.

Scenario 2: Ambient Air at 25°C

- **Thermodynamic Equilibrium:** No, this system is not in thermodynamic equilibrium.
- **Reason:** Although the mixture of ice and water is initially at a phase equilibrium, the ambient air temperature being higher than the system's temperature will cause heat transfer from the air to the ice-water system.
- **Evolution:** The ice in the mixture will absorb heat from the warmer ambient air, leading to melting of the ice. The system will continue to absorb heat, and ice will melt until possibly all the ice turns into liquid water, or the ambient temperature changes. If all ice melts and the water's temperature starts rising above 0°C, it would no longer be in the initial phase equilibrium state.

Summary

In these cases, whether a system is in thermodynamic equilibrium depends on both the internal state of the system and its interactions with the environment. For systems not in equilibrium, their evolution towards equilibrium involves processes that minimize energy disparities (like temperature differences) and maximize entropy, moving towards a balance of energy and phase state consistent with external conditions.

Exercise 03 :

To determine whether the transformations described in each scenario are reversible, it's crucial to understand the definition of a reversible process in thermodynamics. A reversible process is an idealized or theoretical process that happens so slowly and with infinitesimal gradients in temperature, pressure, and chemical potential that the system remains in thermodynamic equilibrium throughout the process. A reversible process can be exactly reversed by an infinitesimal change in a variable.

1. Spring Slowly Undergoing Slight Elongations

- **Reversibility:** Yes, this transformation is likely reversible.
- **Justification:** When a spring undergoes slight elongations, especially slowly, it

obeys Hooke's Law ($F = kx$, where k is the spring constant and x is the displacement), remaining within its elastic limits. Because the process is slow, the spring doesn't heat up significantly due to internal friction or external forces, meaning it can return to its original state without any residual deformation or heat generation, hence preserving its energy.

2. Spring Slowly Undergoing Very Large Elongations

- **Reversibility:** No, this transformation is not reversible.
- **Justification:** Very large elongations, even if done slowly, can exceed the elastic limit (yield point) of the spring. Beyond this point, the deformation can become

plastic, meaning the spring will not return to its original shape after the force is removed. This introduces hysteresis in the stress-strain curve, and the energy is dissipated as heat, making the process irreversible.

3. Two Copper Blocks, One Hot and the Other Cold

- **Reversibility:** No, this transformation is not reversible.
- **Justification:** When two copper blocks at different temperatures are brought into contact, heat flows spontaneously from the hotter to the colder block until thermal equilibrium is achieved. This process involves an increase in entropy and is typically irreversible due to the significant and non-infinitesimal gradient in

temperature between the two blocks. Heat flows without any external work or control, making it impossible to reverse the process without additional work or energy input.

4. A Box Divided into Two Compartments Separated by a Partition: One Contains a Gas, the Other is Empty

- **Reversibility:** No, this transformation is not reversible.
- **Justification:** When the partition between a gas-filled compartment and a vacuum is removed, the gas expands spontaneously to fill the entire volume. This free expansion of the gas occurs without doing external work and without any heat

transfer (an adiabatic process). While the energy of the gas remains constant (since there is no heat exchange and no work is done), the entropy of the gas increases as it occupies a greater volume (more microstates become available), making the process irreversible. The process cannot be reversed without doing work or changing the environment's conditions.

In summary, of the processes described, only the slight elongation of a spring done slowly can potentially be reversible if it remains within the elastic limit. Other scenarios inherently involve changes that cannot spontaneously revert to their original state without external intervention or additional energy, hence are irreversible.

Exercise 04 :

Part 1: Domain of Validity of the Ideal Gas Equation $PV = nRT$

The ideal gas law, $PV = nRT$, has a specific domain of validity, primarily depending on the nature of the gas and the conditions under which it operates. Here are key factors influencing its validity:

- **Temperature and Pressure Conditions:** The ideal gas law tends to hold accurately at high temperatures and low pressures. At high temperatures, the kinetic energy of the gas molecules is high enough that the volume occupied by the molecules themselves is negligible compared to the total volume of the gas. At low pressures, the gas molecules are far enough apart that intermolecular forces are insignificant.
- **Gas Type:** The law is a good approximation for monatomic gases like helium and argon under normal conditions, but deviations can be more significant for complex molecules due to interactions and size effects.
- **Equilibrium State:** The ideal gas law assumes the gas is in a thermodynamic equilibrium state. This means that the temperature, pressure, and volume are uniformly distributed throughout the gas and do not change with time unless the external conditions change. It is **not valid when the gas is out of equilibrium**, such as during non-uniform or rapid changes where gradients of temperature, pressure, or chemical potential exist.

Part 2: Representation in the Clapeyron (P-V) Diagram

For the given cycle, let's describe the steps in the cycle and then represent them on a P-V diagram:

- **A to B: Isobaric Expansion**
 - **Isobaric** means that the pressure remains constant.
 - As the gas expands, the volume increases and the temperature increases (since $PV = nRT$ and P is constant, V increasing means T must increase).
- **B to C: Isochoric (Isovolumetric) Expansion**
 - **Isochoric** means the volume remains constant.
 - Since the volume does not change and if we call this an expansion, the pressure must increase as the temperature increases (since V is constant, T increasing implies P must increase from $PV = nRT$).
- **C to A: Isothermal Compression**
 - **Isothermal** means the temperature remains constant.
 - The gas is compressed, reducing its volume and increasing the pressure while maintaining constant temperature.

Diagram Representation:

In the Clapeyron (P-V) diagram:

- **A to B (Isobaric Expansion):** A horizontal line moving right as the volume increases.
- **B to C (Isochoric Expansion):** A vertical line moving upward as the pressure increases.
- **C to A (Isothermal Compression):** A hyperbolic curve moving left and downward as the volume decreases and pressure increases back to the initial state.

This creates a cycle on the diagram with distinct shapes characteristic of each process type:

- Horizontal for isobaric (constant P)
- Vertical for isochoric (constant V)
- Curved for isothermal (constant T, $PV = \text{constant}$)

This cycle would typically exhibit work being done by the system during the isobaric expansion and work being done on the system during the isothermal compression, with energy exchanges with the surroundings during the isochoric processes in the form of heat.

