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Investigation of the enthalpy of Vaporization for carbon dioxide gas with fixed Temperature condition

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Abstract. Enthalpy of vaporization, which asserts that when heat or enthalpy is applied to any liquid substance at a specific pressure and temperature, the liquid turns into a gaseous form, is a crucial characteristic of any liquid. Thus, a change from one state to another takes place. In this work, the Enthalpy of vaporization study is carried out on CO_2 gas to understand the variation in it with a change in pressure at a fixed constant temperature. The work is further extended to multiple temperatures, to understand the effect of pressure and temperature change simultaneously on enthalpy. It was found that the enthalpy is directly proportional to pressure and temperature.

Keywords: CO_2 gas, Thermodynamic Equilibrium, Enthalpy

1. Introduction

Pressurized pipes are regarded as the most practical and effective method for transporting the substantial amounts of CO2 captured from fossil fuel power plants for eventual sequestration as part of the carbon capture and sequestration (CCS) cycle. The safety of CO2 pipes is commonly regarded as being of the utmost significance and in fact crucial to the public acceptance of CCS as an effective method of minimizing the effects of global warming because CO2 gas is an asphyxiant at concentrations higher than 7%. Predictions of the transient discharge rate and air dispersion of the fleeing inventory in the case of pipeline collapse utilizing trustworthy validated mathematical models are essential to the risk assessment of such pipelines. This information controls all pipeline failure-related repercussions, such as the minimum safe distances to populated regions and emergency response preparation.

The adoption of a suitable equation of state (EoS) for the precise estimation of the thermo-physical and phase equilibrium properties of the escaping CO2 is a critical factor determining the effectiveness of the pipeline outflow and dispersion models. The computational efficiency of the EoS used is a necessary and crucial additional criterion given that a reliable pipeline outflow model generally necessitates time-consuming (up to a few hours on a current PC) iterative numerical solution of the conservation equations. Most of the EoS that have been created so far can handle two-phase liquid-vapor combinations. Although this is appropriate for the majority of hydrocarbon combinations, the particularly high Joule-Thomas expansion coefficient of CO2 might lead to pipeline release temperatures as low as -70 oC. Solid CO2, commonly referred to as dry ice, is anticipated to form during pipeline discharge given that the triple point for CO2 is -56.6 oC at 0.518 MPa.

Enthalpy is a property or state function that resembles energy; it has the same dimensions as energy and is therefore measured in joules or ergs. The enthalpy value solely depends on the system's temperature, pressure, and composition, not on its history.[1] The change in internal energy is equal to the heat transmitted to, less the work done by, the system, according to the law of energy conservation. The enthalpy change is precisely equal to the heat transmitted to the system if the sole work performed is a change in volume at constant pressure. The amount of energy required to convert a substance from a liquid to a gas is known as the enthalpy (or latent heat) of vaporization and is measured in joules per mole.[2] Similar enthalpy shifts are also present during other phase transitions, such as the fusion enthalpy (or latent heat) that occurs when a solid transforms into a liquid. Similar to other energy functions, figuring out enthalpy's absolute values is neither convenient nor required. The zero-enthalpy state for each material can serve as a useful benchmark.[3]

Because of the internal energy's unknown, difficult-to-access, or irrelevant to [4], the total enthalpy of a system cannot be directly determined. Since it makes the description of energy transfer simpler, a change in enthalpy is typically the favoured formulation for measurements at constant pressure. At constant pressure, the enthalpy change equals the energy that is exchanged with the environment through heat when the transfer of materials into or out of the system is likewise prevented. The standard enthalpy of reaction in chemistry is the change in enthalpy that occurs when reactants transform into products in their standard states (p = 1 bar; often, T = 298 K).[5,6] This quantity is the standard heat of reaction at constant pressure and temperature, but it may still be measured using calorimetric techniques even if the temperature changes while it is being done, so long as the initial and final pressure and temperature are consistent with the standard state. Enthalpy is a state function; hence the value is independent of the transition from the beginning to the final state.

In practical applications, particularly for the burning of liquid fuels, an accurate assessment of enthalpy of vaporization (or latent heat of vaporization) and its fluctuation with temperature is of major interest. The fitting formulas that exist for different fluids are currently system-dependent and lack a theoretically sound formulation for latent heat. While chemical reactions really take place in the gas phase, most thermal engineering facilities use liquid fuels. [7] Therefore, during its combustion, liquid fuel vaporization is essential [8–10]. The amount of energy that equilibrium vaporization consumes at constant temperature and pressure, which helps the liquid molecules escape the attractive potential caused by molecular interactions, is known as the enthalpy of vaporization.

The latent heat has a significant impact on the vaporization rate; the lower the latent heat, the higher the vaporization rate. Enthalpy of vaporization was frequently taken for granted as a constant in theoretical discussion in the literature on multi-phase combustion.[11] The combustion process, which involves a large rise in temperature and pressure, may cause this assumption to be loosely true.[12,13] For instance, ignition often takes place when the system is initially at room temperature and atmospheric pressure and the combustible reactants are given the required ignition energy. Due to the exothermic reaction, ambient temperature rises dramatically as combustion approaches the steady state, and combustion in a closed chamber may also cause a significant rise in pressure. Because of this, it is often physically improbable to assume that latent enthalpy is constant.

Chemical compounds' enthalpies are typically given for a normal condition of 1 bar (100 kPa) pressure. Tables often list the standard temperatures of the production of compounds at 25 °C even though enthalpies and enthalpy changes for reactions vary as a function of temperature (298 K). The change H is a positive value for endothermic (heat-absorbing) processes and a negative value for exothermic (heat-releasing) processes.

The enthalpy of an ideal gas depends only on its temperature, which is correlated to its thermal energy and is independent of its pressure or volume. This behaviour frequently closely resembles that of real gases at normal pressures and temperatures, which makes it easier to do practical thermodynamic design and analysis.The residual solution cools as a result of vaporization, which happens as a result of a phase shift and heat transfer. The amount of heat needed to evaporate any liquid from its pure or solution form at a fixed temperature, pressure, and concentration is known as the enthalpy of vaporization (Hvap) in this process. The amount of vaporized liquid must not considerably alter the solution's concentration in order to quantify this parameter, but it must be enough to keep the equilibrium vapor pressure constant at the same temperature. Here, it is assumed that the solute is entirely involatile, like common salt.

In addition to being crucial for many sectors, including desalination and evaporative air conditioning, the Hvap values of salt solutions are a fundamental thermodynamic fact that is frequently covered in introductory chemistry and physics courses.

The amount of energy (enthalpy) that must be added to a liquid substance in order to convert a portion of that substance into a gas is referred to as the enthalpy of vaporization (symbol Hvap), also known as the (latent) heat of vaporization or heat of evaporation. The pressure at which the transformation occurs affects the enthalpy of vaporization. The enthalpy of vaporization is frequently stated for the substance's typical boiling point. Despite the fact that tabulated values are typically corrected to 298 K, the error in the measured value is frequently smaller.

The enthalpy of vaporization can be written as

$$\Delta H_{Vap} = \Delta U_{Vap} + p\Delta V$$

According to research, undergraduate students frequently struggle to comprehend chemical thermodynamics, particularly the precise definition of words like enthalpy. A quick laboratory experiment might help students gain a deeper understanding of key ideas by having them utilize enthalpy and enthalpy change to explain an easily apparent occurrence. Enthalpy of vaporization is typically taught using the Clausius–Clapeyron equation and observed vapor pressures, primarily for pure organic liquids and solutions. In order to measure the Hvap values of salt solutions by monitoring simple, steady-state temperatures, which was directly related to evaporative cooling, a unique and straightforward laboratory experiment was given in this study.

In addition to the work put in against atmospheric pressure, it is equal to the vapour phase's higher internal energy than the liquid phase. It is possible to interpret the rise in internal energy as the energy needed to overcome intermolecular interactions in the liquid (or solid, in the case of sublimation). Since the van der Waals interactions between helium atoms are so weak, helium has a notably low enthalpy of vaporization of 0.0845 kJ/mol. The enthalpy of vaporization of liquid water, however, which is 40.65 kJ/mol, is more than five times greater than the energy needed to heat the same amount of water from 0 °C to 100 °C (cp = 75.3 J/Kmol). This is because the molecules in liquid water are held together by relatively strong hydrogen bonds.

However, caution must be used when utilizing enthalpies of vaporization to gauge the strength of intermolecular forces, as these forces may continue to operate to some extent in the gas phase (as is the case with hydrogen fluoride), resulting in an underestimation of the bond strength. This is especially true for metals, which frequently form covalently bound molecules in the gas phase. In these circumstances, the enthalpy of atomization must be utilized to determine the bond energy's actual value.[14]

2. Methodology

Due to the significance of carbon dioxide, it would seem desirable to precisely explore its thermodynamic properties. It presents an unusually good opportunity to compare the entropy derived from the third law of thermodynamics with that derived with the aid of the spectroscopic data because its band spectrum has been observed and very successfully interpreted by a number of researchers. It is known that the molecule is linearly symmetrical. The occurrence of false equilibrium of the end-for-end random orientation kind, as seen in solid carbon monoxide, nitric oxide, and nitrous oxide, should therefore be quite unlikely.

Since CO2's physical qualities differ greatly from those of natural gas and are greatly impacted by temperature, pressure, and pollutants, transporting it requires a phase transition. In order to avoid the development of the hydrate, special attention should be paid to the temperature and pressure during the transit of natural gas. It's also important to consider the CO2 contamination limit.

The fluid management interface must be used to set up the sample fluid under consideration. The sample fluid in this study is the CO2 gas for which the enthalpy is being calculated. As a result, the defined gas mol per cent is chosen, and the fluid management system of the PVTsim's sample fluid function is activated. As the selected gas sample is pure gas, this mole per cent will be 100. After the concentration has been established, the system is normalized to make sure the gas system is being simulated as a whole system.

The property generator function is then selected after opening the simulations tab. The property generator toolbox is then prompted and the look of it is displayed in Figure 1. It can be observed that using this many properties for various conditions of a chosen gas or liquid can be found. So, in this study, the property that needs to be evaluated is selected as enthalpy, and the PT specs are chosen to be single-point calculations as the simulation will be easier to calculate one point at a time. The output format is selected as the constant temperature as the pressure is varied in this work and the temperature is maintained constant. The water properties are considered to be in line with SRK – EOS. Then, the pressure details are entered, and the simulations are carried out.

In this work, based on the critical pressure, a range of pressure is chosen with an interval of 5 bar. The temperature setting considered for each set of simulation runs was considered as 0,1,2,3 °C.
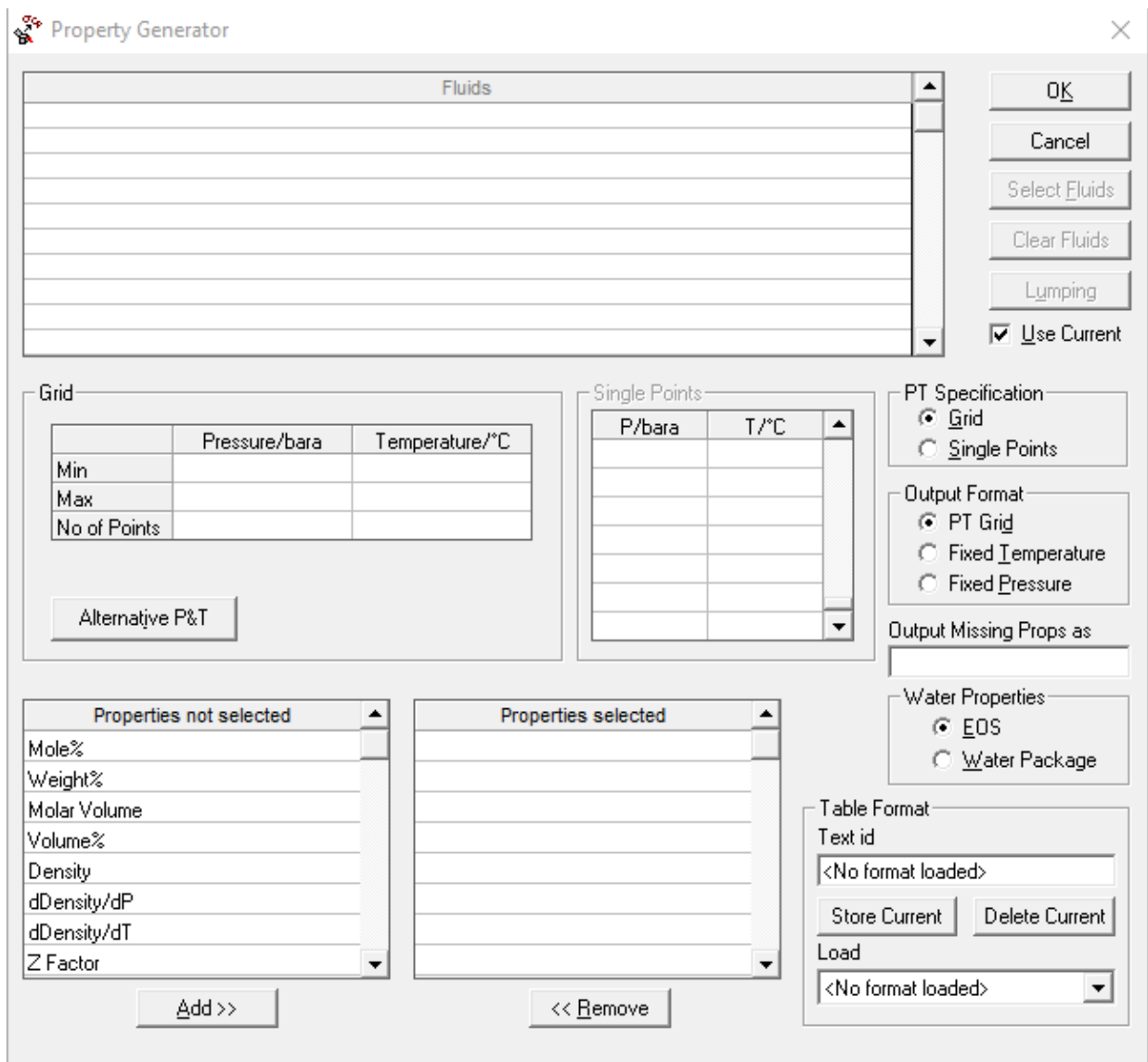

Figure 1: Simulation command window for defining enthalpy

3. Results & Discussion

The results of the enthalpy of vaporization are presented in Table – 1. Representation of the variation of the enthalpy with respect to change in pressure at a fixed temperature (0°C) is shown in Figure – 2. From these results it can be observed that the increase in pressure is causing the increase in enthalpy as well. Enthalpy strongly depends on both pressure and temperature. Because of the rotational, translational, and vibrational motion of the molecules, the system has internal energy. The temperature has a significant impact on internal energy. The relationship between pressure and gas temperature is straightforward. During a phase change, both dependent on the region of the vapour-liquid mixture. Intermolecular forces will be higher in materials that have been squeezed more. The intermolecular force of solids is greater than that of liquids, which in turn is greater than that of gas.

Similarly, the results at Temperatures 1,2,3°C. Results were found to be the same at any given constant temperature condition. For studying the effect on enthalpy with variance in pressure & temperature, a graph is plotted with Enthalpy of Vaporization for various temperature and pressure conditions. From that, it can be found that both temperature and pressure are directly proportional to enthalpy.
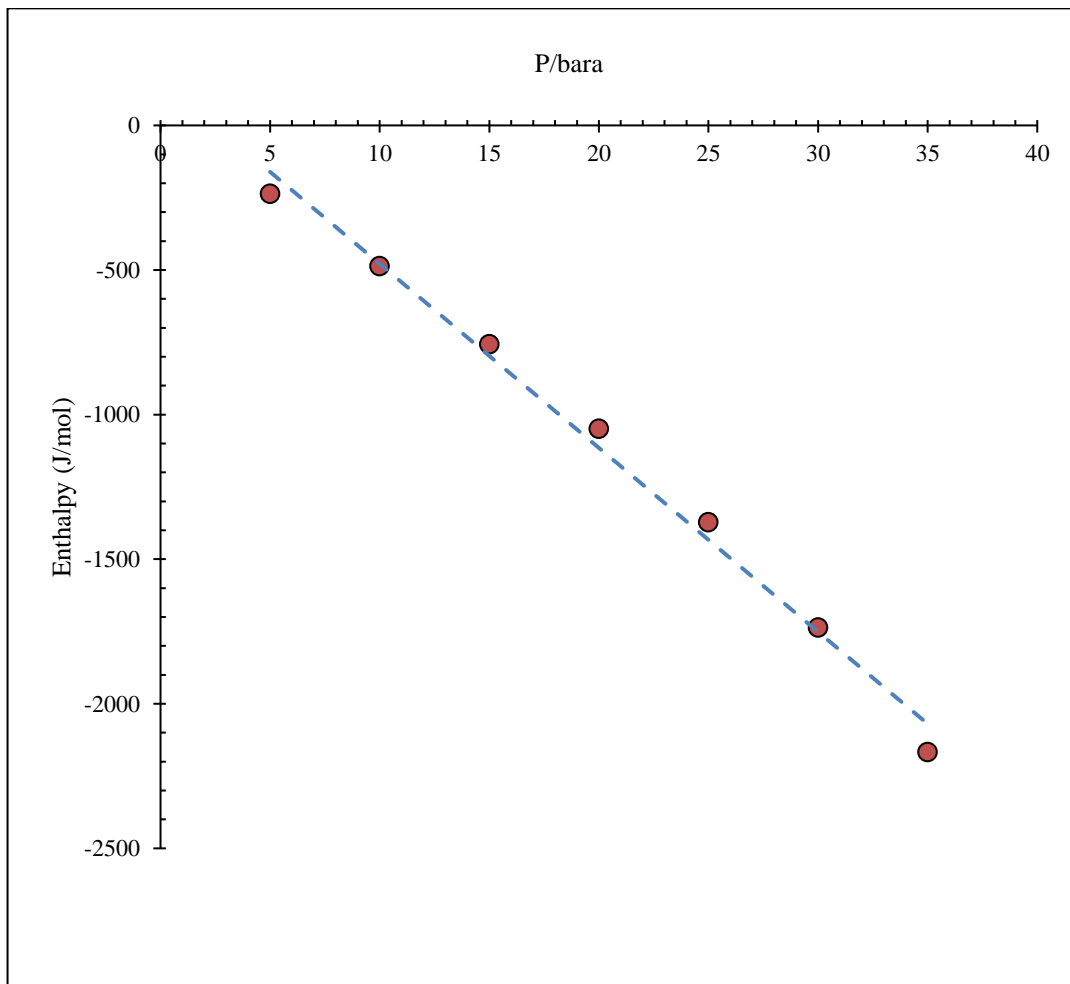

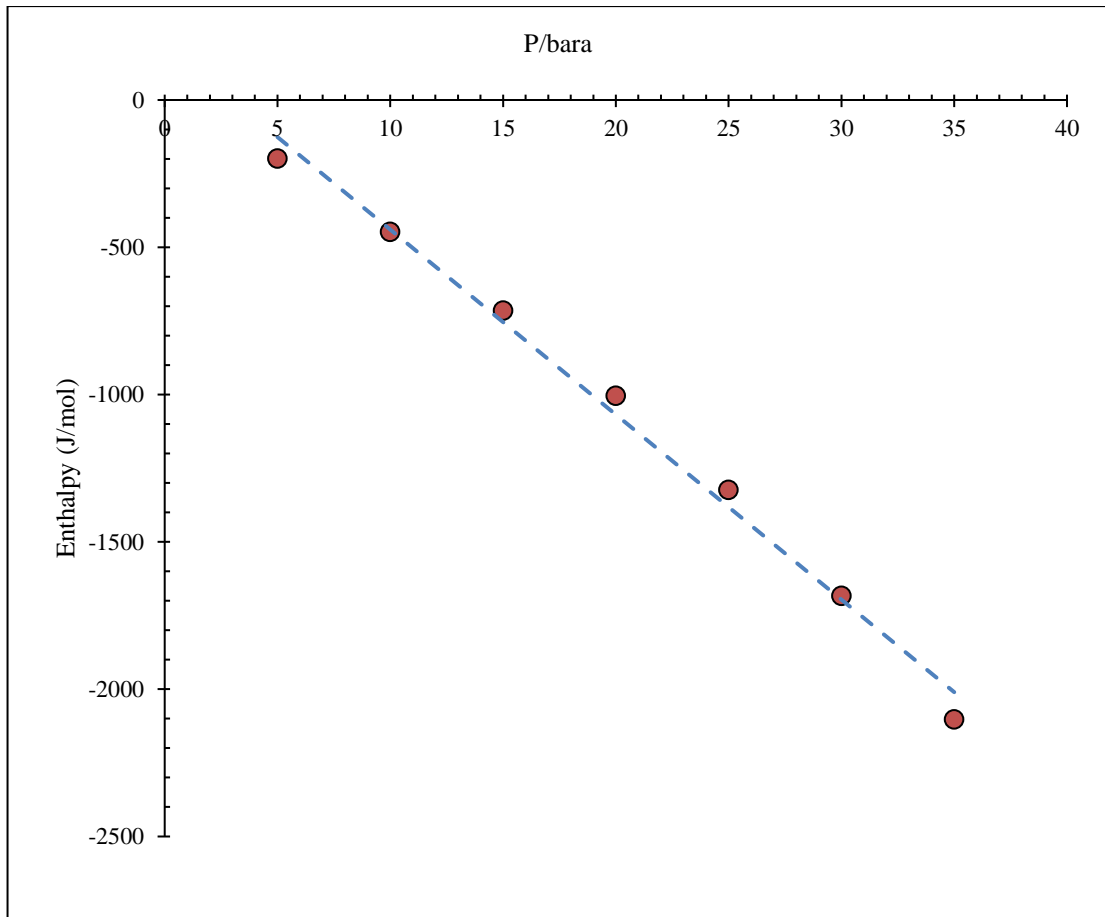Figure 2: Pressure vs Enthalpy at 0°C

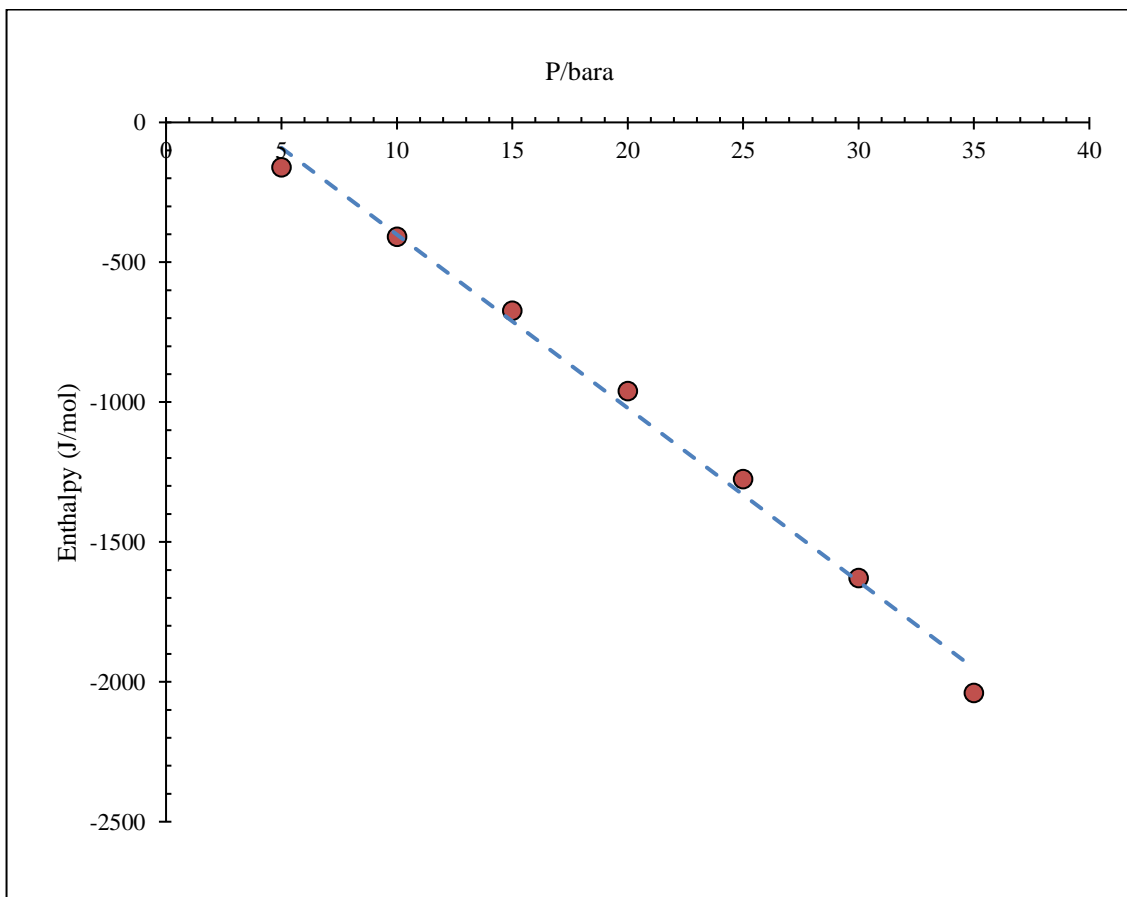Figure 3: Pressure vs Enthalpy at 1°C

Figure 4: Pressure vs Enthalpy at 2°C

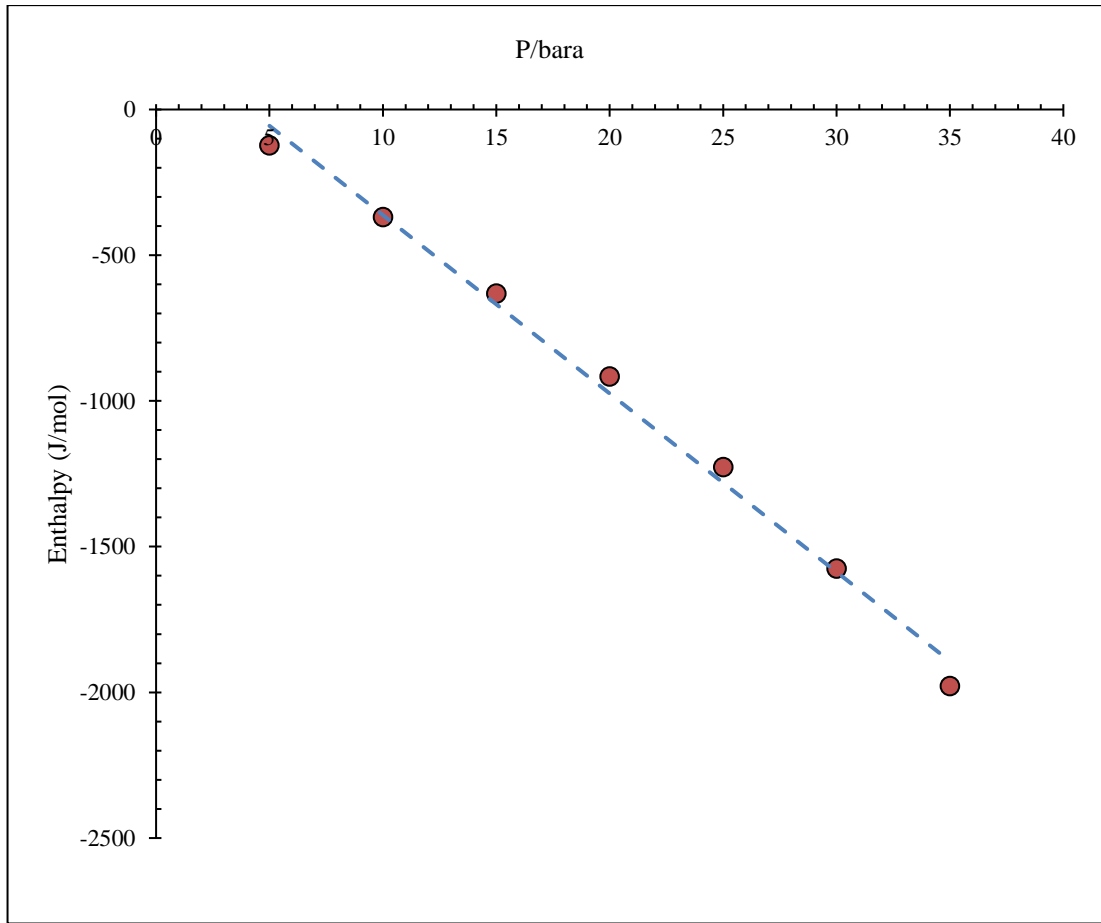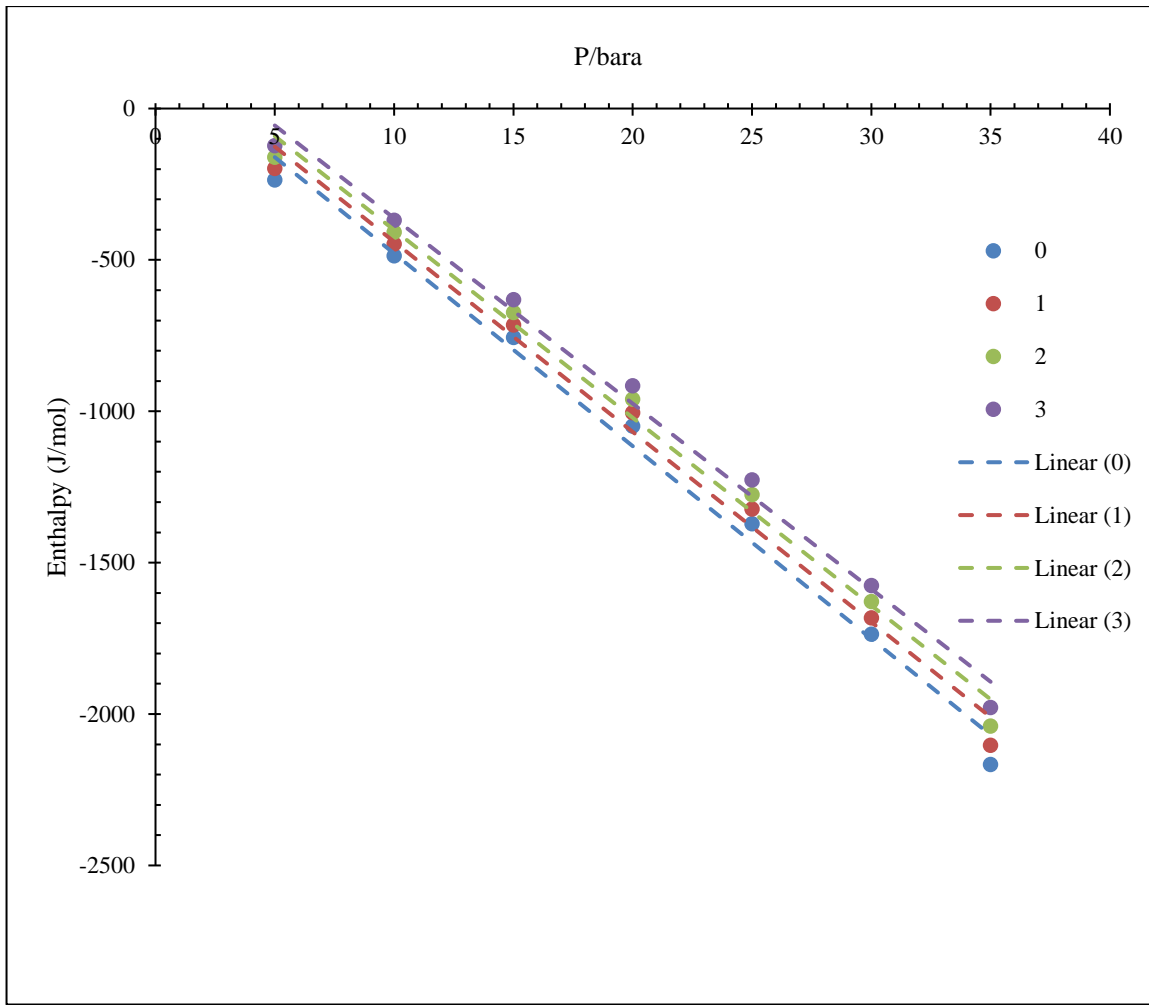Figure 5: Pressure vs Enthalpy at 3°C

Figure 6: Enthalpy of Vaporization Comparison for various conditions

Table 1. Enthalpy of vaporization at 0°C

Gas Sample	S.No	P (bara)	T (°C)	Enthalpy (J/mol)
	1	5	0	-236.1
	2	10	0	-487.2
	3	15	0	-756.6
CO_2	4	20	0	-1049.2
	5	25	0	-1372.1
	6	30	0	-1737.1
	7	35	0	-2166.78

Table 2. Enthalpy of vaporization at 1°C

Gas Sample	S.No	P (bara)	T (°C)	Enthalpy (J/mol)
	1	5	1	-198.54
	2	10	1	-447.85
	3	15	1	-715.08
CO$_2$	4	20	1	-1004.76
	5	25	1	-1323.67
	6	30	1	-1682.94
	7	35	1	-2103.14

Table 3. Enthalpy of vaporization at 2°C

Gas Sample	S.No	P (bara)	T (°C)	Enthalpy (J/mol)
	1	5	2	-236.1
	2	10	2	-487.2
	3	15	2	-756.6
CO$_2$	4	20	2	-1049.2
	5	25	2	-1372.1
	6	30	2	-1737.1
	7	35	2	-2166.78

Table 4. Enthalpy of vaporization at 3°C

Gas Sample	S.No	P (bara)	T (°C)	Enthalpy (J/mol)
	1	5	3	-198.54
	2	10	3	-447.85
	3	15	3	-715.08
CO$_2$	4	20	3	-1004.76
	5	25	3	-1323.67
	6	30	3	-1682.94
	7	35	3	-2103.14

4. Conclusion

Enthalpy of vaporization, which asserts that when heat or enthalpy is applied to any liquid substance at a specific pressure and temperature, the liquid turns into a gaseous form, is a crucial characteristic of any liquid. Thus, a change from one state to another takes place. In this work, the Enthalpy of vaporization study is carried out on CO2 gas to understand the variation in it with a change in pressure at a fixed constant temperature. The work is further extended to multiple temperatures, to understand the effect of pressure and temperature change simultaneously on enthalpy. It was found that the enthalpy is directly proportional to pressure and temperature.

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