CL 326 - Course Project

Temperature-Dependent Vapor Pressure Measurements and Interpretation of Antoine's Constants

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Introduction

Purpose of the Experiment

- The experiment investigates how the vapor pressure of volatile liquids (acetone, ethanol, methanol, and benzene) changes with temperature.
- Vapor pressure is a key thermodynamic property that helps us understand phase changes (liquid to vapor) and equilibrium conditions.

Objective

- **Measure vapor pressures** of acetone, ethanol, methanol, and benzene across a range of temperatures (313.15 K to 363.15 K).
- **Compare experimental data** with theoretical values calculated using the **Antoine equation**.
- **Calculate the enthalpy of vaporization** using the **Clausius-Clapeyron equation** for pure acetone, and analyze results for a binary mixture (acetone-benzene).

Real-World Relevance

- **Industrial Applications**:
  - **Distillation and Separation**: Vapor pressure data is crucial for designing distillation columns and understanding liquid-vapor equilibrium.
  - **Refrigeration**: Accurate vapor pressure data helps in the design of refrigeration systems.
  - **Evaporation**: Essential in understanding processes in chemical engineering, food science, and material processing.
- **Environmental Impact**: Vapor pressure data also helps in estimating the volatility of chemicals, which is crucial for assessing air quality and chemical behavior in the environment.

Importance of the Study

- Understanding vapor pressure at different temperatures aids in optimizing various industrial processes.
- Helps in the design and operation of equipment such as heat exchangers, condensers, and evaporators.

Literature Review

Vapor Pressure Modeling

- **Antoine Equation**: $log_{10}(p) = A - \frac{B}{C+T}$
    - Empirical relationship used to predict vapor pressures of liquids over a specific temperature range.

Clausius-Clapeyron Equation

- Relates **vapor pressure** to **enthalpy of vaporization**: $lnp = -\frac{\Delta H_{vap}}{RT} + C$
- Used to calculate **enthalpy of vaporization** from vapor pressure data.

Previous Studies

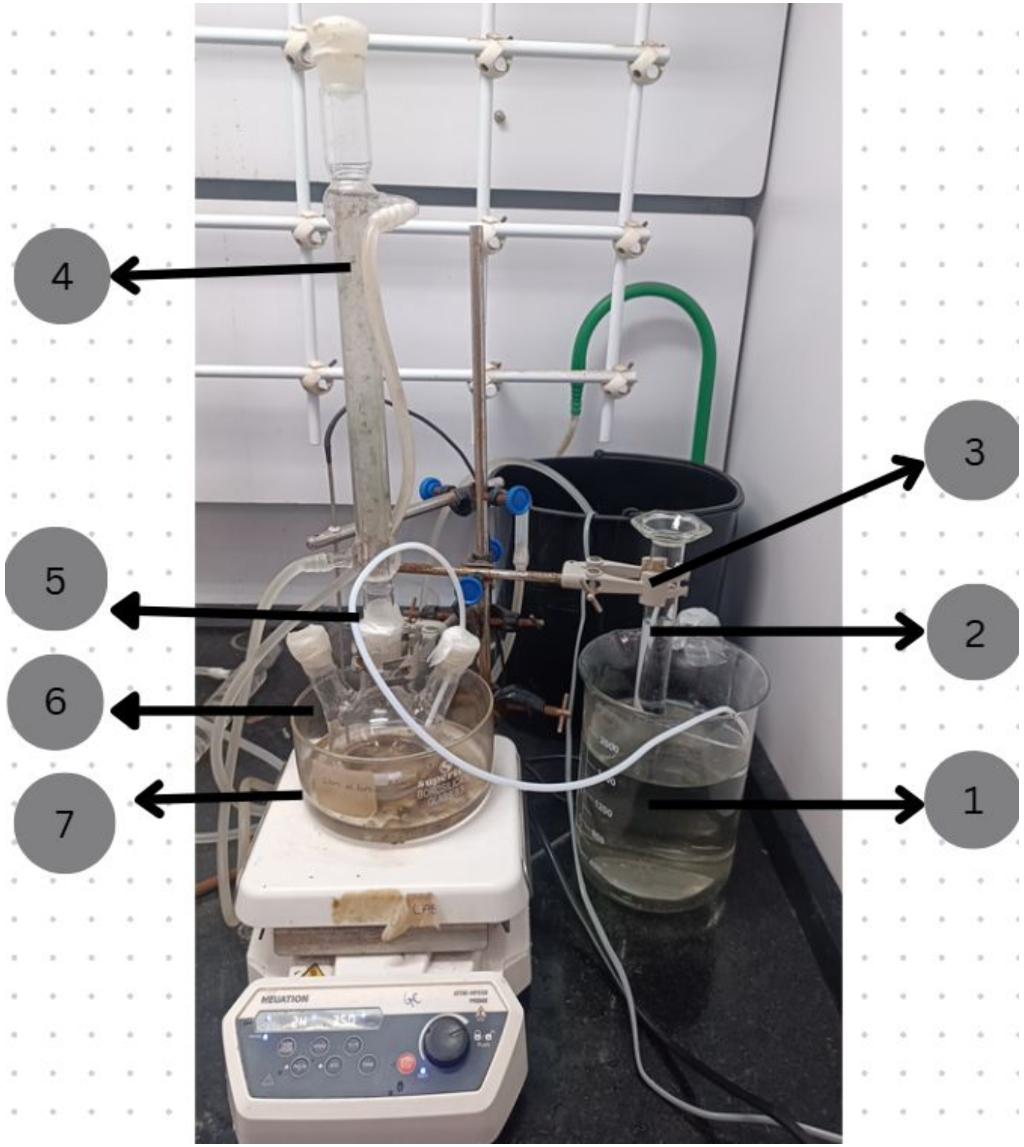
- Validated **Antoine constants** for various chemicals and mixtures.
- Demonstrated **enthalpy calculations** for liquids like acetone and ethanol using experimental data.

Modeling Approaches

- **Analytical Models**: Used for estimating vapor pressure at a temperature using the displacement method based on empirical formulas.
- **Numerical Models**: Regression techniques and **finite difference** methods for data fitting and error minimization for calculations of antoine's constants.

Experimental System Setup

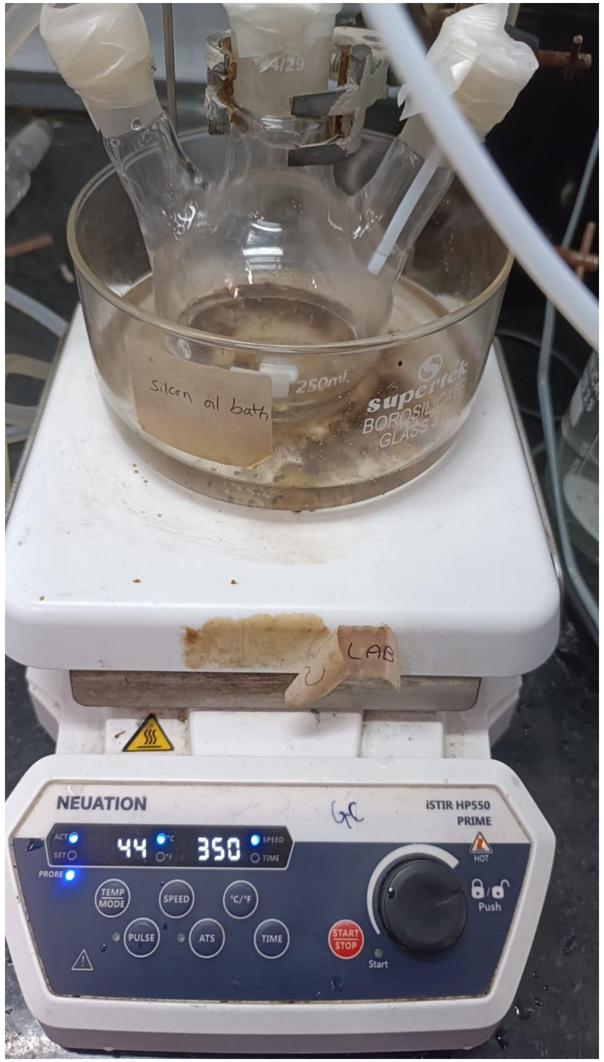
Setup:
1. 2l beaker filled with acidified water
2. Inverted measuring cylinder (100 ml)
3. Ring Clamp Stand
4. Condenser
5. Rubber bung
6. Round Bottom flask (250 ml)
7. Magnetic stirrer with silicon oil hot plate apparatus



Method:

- Heat the liquid in an oil bath.
- Measure displaced volume in the inverted cylinder.
- Calculate vapor pressure using displaced volume and ideal gas law.

Experimental System Setup



Calculations (Modelling approach) - Analytical

- **Ideal Gas Law:** PV = nRT
- **Calculation of Number of Moles:** $n = \frac{\rho V}{M}$

  where:

  ρ is the density of the solution in kg/m^3,

  M is the molar mass of solution in kg/kmol.

- **Calculation of Experimental Vapor Pressure:** $P = \frac{nRT}{V}$

  where P will be in Pascals (Pa).

  R is the universal gas constant, 8.314 J/mol.K

  T is the temperature in Kelvin (K).

- **Calculation of Theoretical Vapor Pressure using Antoine Equation:** $lnP = A - \frac{B}{C+T}$

  where:

  P is the vapor pressure in Pascals (Pa),

  A, B, and C are substance-specific constants,

  T is the temperature in Celsius (°C).

- **Clausius Clapeyron Equation:** $$lnP = -\frac{\Delta H_{vap}}{RT} + C$$

Plotting lnP vs. 1/T : y = mx+c

$$\Delta H_{vap} = -(\text{Slope} \times R)$$

ΔH_{vap}: Latent heat of vaporization (J/mol)

Calculations (Modelling approach) - Analytical

- **For Binary Solution (Acetone + Benzene)**

No. of moles:

- Acetone:

$$n_{Acetone} = \frac{\rho_{Acetone} . V_{Acetone}}{M_{Acetone}}$$

- Benzene:

$$n_{benzene} = \frac{\rho_{Benzene} . V_{Benzene}}{M_{Benzene}}$$

$$n_{Total} = n_{Acetone} + n_{benzene}$$

Mole fraction:

- $x_{Acetone} = \frac{n_{Acetone}}{n_{Total}}$
- $x_{Benzene} = 1 - x_{Acetone}$

Calculation of Partial Pressures using Raoult's Law:

- $P_{Acetone} = x_{Acetone} . P^0_{Acetone}$
- $P_{Benzene} = x_{Benzene} . P^0_{Benzene}$

Comparison of Experimental and Theoretical Vapor Pressure:

$$\% \text{ Error} = \frac{\left|P_{Exp} - P_{Theo}\right|}{P_{Theo}} \times 100$$

Results and Analysis

Acetone				
T (K)	Volume displaced (ml)	P_Exp (Pa)	P_theo (Pa)	%Error
313.15	10.21	11,598.26	13,807.45	16.00
323.15	12.76	12,319.02	16,209.23	24.00
333.15	28.57	15,511.27	18,824.57	17.60
343.15	33.41	17,136.83	21,650.04	20.85
353.15	43.84	20,913.19	24,681.03	15.27
363.15	49.46	23,894.23	27,911.94	14.39

Benzene				
T (K)	Volume displaced (ml)	P_Exp (Pa)	P_theo (Pa)	%Error
313.15	21.08	7,674.02	9,601.33	20.07
323.15	24.78	8,152.95	11,397.44	28.47
333.15	51.31	10,665.51	13,365.30	20.20
343.15	54.46	11,347.62	15,502.16	26.80
353.15	70.54	14,041.99	17,804.22	21.13
363.15	79.06	16,172.87	20,266.75	20.20

Methanol				
T (K)	Volume displaced (ml)	P_Exp (Pa)	P_theo (Pa)	%Error
313.15	4.20	8,068.55	11,296.34	28.57
323.15	27.05	10,899.53	13,731.66	20.62
333.15	30.95	11,861.58	16,475.92	28.01
343.15	33.17	12,617.52	19,537.34	35.42
353.15	45.85	15,972.28	22,921.87	30.32

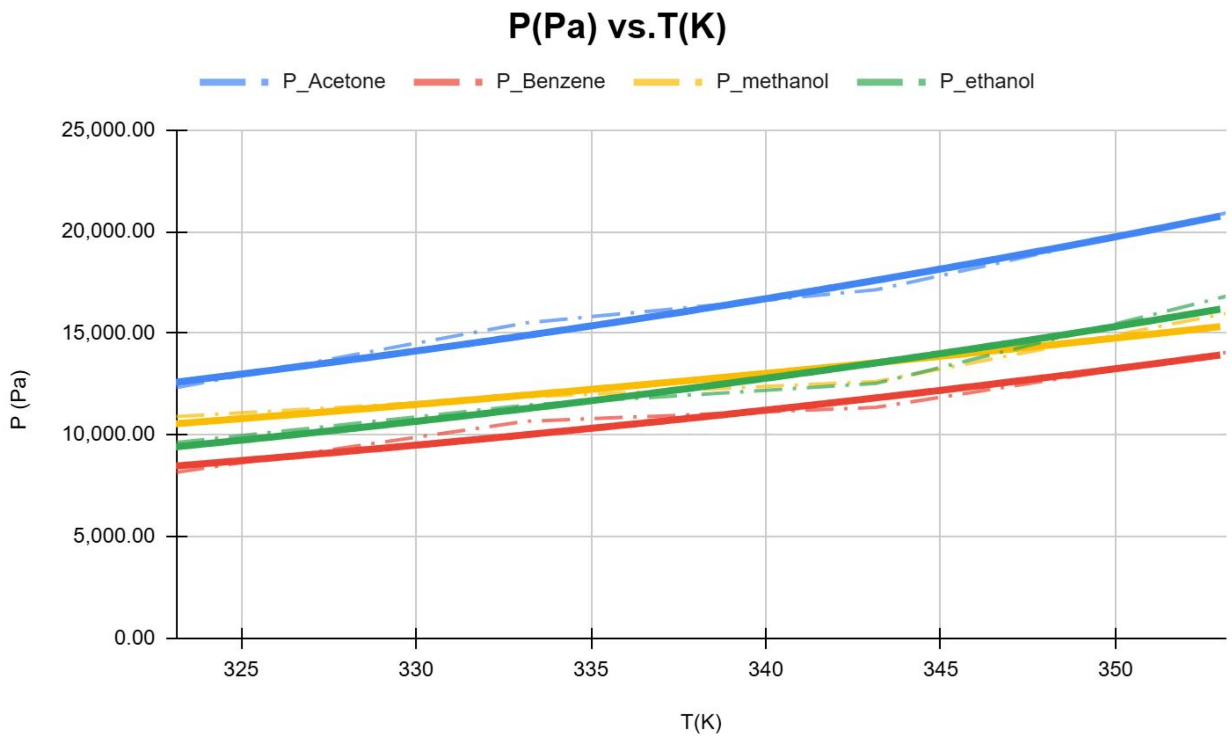
Ethanol				
T (K)	Volume displaced (ml)	P_Exp (Pa)	P_theo (Pa)	%Error
323.15	8.24	9,615.80	11,320.89	15.06
333.15	23.31	11,458.42	13,772.14	16.80
343.15	28.90	12,526.01	16,534.22	24.24
353.15	50.15	16,812.81	19,615.01	14.29
363.15	50.97	17,495.24	23,020.06	24.00

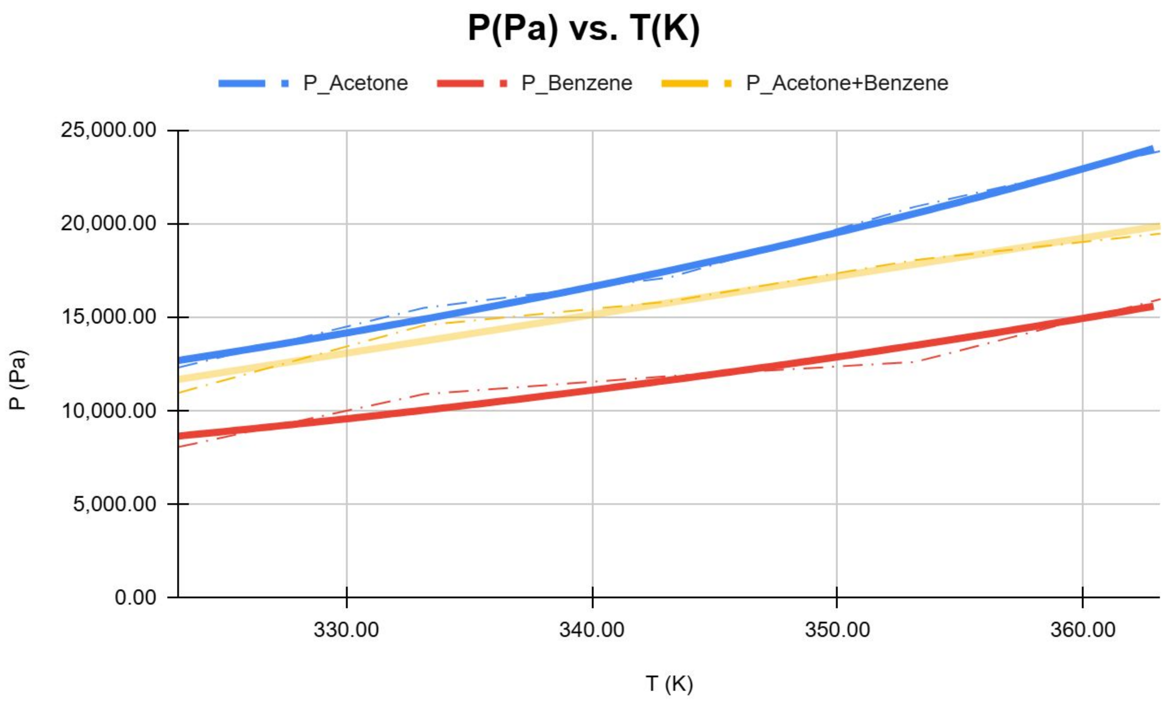
Binary solution (acetone + Benzene)				
T (K)	Volume displaced (ml)	P_Exp (Pa)	P_theo (Pa)	%Error
323.15	2.00	10,966.00	14797.01519	25.89
333.15	24.00	14,577.94	17222.31937	15.35
343.15	28.00	15,849.72	19845.68908	20.14
353.15	35.00	18,068.24	22662.74577	20.27
363.15	38.00	19,478.90	25668.13946	24.11

Result and Analysis

Liquid	Enthalpy of vaporization		
	EXP (J/mol)	THEO (J/mol)	%Error
Acetone	26,039.45	32,000.00	18.626725
Benzene	20,710.17	26,347.07	21.39476175
Ethanol	32540.996	37770.502	13.84547656
Methanol	23,121.23	29115.628	20.58823529

Enthalpy of Vaporization calculated using the slope of lnP vs 1/T plot





Modeling Approach - Numerical

Determine Antoine constants (A, B, C) for substances (Acetone, Benzene, Methanol, Ethanol) by minimizing the error between observed and predicted vapor pressures using a numerical optimization method.

Mathematical Formulation of the Objective Function:

The optimization method used is the **Nelder-Mead method**, a direct search algorithm for finding the minimum of an objective function without requiring gradient information.

$$f(A,B,C) = \sum_{i=1}^{n} \left(\ln(P_i) - \left(A - \frac{T_i}{B} + C \right) \right)^2$$

- P_i is the vapor pressure at temperature T_i for the i-th data point,
- $ln(P_i)$ is the natural logarithm of the observed vapor pressure,
- T_i is the temperature at the i-th point (in Kelvin),
- n is the total number of data points used for fitting,

Results and Analysis

	Optimized Values			True Values		
	A	B	C	A	B	C
Acetone	17.8899	4470.78	203.522	7.2316	1277.03	237.23
Benzene	15.9489	2866.362	93.689	6.9056	1211.03	220.79
Methanol	15.6309	2708.051	99.404	8.07919	1581.34	239.65
Ethanol	15.0803	1976.621	11.037	8.04494	1554.3	226.65

Constant A (Intercept)

- **Role**: Adjusts baseline vapor pressure.
- **Interpretation**: Reflects vapor pressure at reference temperature.
- **Significance**: Higher A indicates higher volatility.

Constant B (Slope)

- **Role**: Controls vapor pressure change with temperature.
- **Interpretation**: Related to latent heat of vaporization.
- **Significance**: Higher B means stronger intermolecular forces.

Constant C (Offset)

- **Role**: Adjusts temperature scale.
- **Interpretation**: Shifts curve for broader temperature range.
- **Significance**: Aligns vapor pressure with experimental data.

Sensitivity Analysis

(Impact on Antoine Equation Parameters)

Key Parameters and Their Impact

- **Intercept Term (A)**
  - **Role**: Influences vapor pressure magnitude.
  - **Impact**: Higher A increases predicted pressures.
  - **Sensitivity**: High.
- **Slope Term (B)**
  - **Role**: Controls vapor pressure increase with temperature.
  - **Impact**: Higher B steepens the pressure curve.
  - **Sensitivity**: High.
- **Offset Term (C)**
  - **Role**: Temperature at which vapor pressure tends to zero.
  - **Impact**: Shifts pressure curve along temperature axis.
  - **Sensitivity**: Moderate.

Parameter Sensitivity

- **Initial Guesses**
  - **Effect**: Influence optimization process.
  - **Sensitivity**: High.
- **Temperature Range**
  - **Effect**: Affects parameter fitting.
  - **Sensitivity**: High.
- **Measurement Errors/Noise**
  - **Effect**: Lead to parameter deviations.
  - **Sensitivity**: High.
- **Discrepancies in Units**
  - **Effect**: Distort parameter values.
  - **Sensitivity**: High.
- **Model Assumptions**
  - **Effect**: May not capture non-ideal behavior.
  - **Sensitivity**: Moderate to High.

Sources of Error

Human Errors:

- Data recording, experiment setup, calculations.
- **Mitigation**: Double-check all steps and data.

Vapor Leakage:

- Non-airtight seals.
- **Mitigation**: Use airtight seals.

Temperature Gradients:

- Uneven heating in the oil bath.
- **Mitigation**: Regularly stir the oil bath.

Inefficient Condensation:

- Vapor loss affecting pressure measurements.
- **Mitigation**: Ensure proper condenser function and temperature.

Parallax Error:

- Incorrect cylinder reading due to viewing angle.
- **Mitigation**: Read at eye level.

Initial Guess for A, B, C:

- Non-optimal guesses lead to local minima.
- **Mitigation**: Use better initial guesses and consider alternative algorithms.

Limited Temperature Range:

- Incomplete data spectrum affecting Antoine constants.
- **Mitigation**: Extend temperature range.

Impurities:

- Affects vapor pressure measurements.
- **Mitigation**: Use high-purity reagents and clean equipment.

Future Work: Suggestions for Improvements and Extensions

Refining Experimental Setup:

- **Increase Precision**: Integrate pressure transducers for more accurate pressure measurements.
- **Control Temperature**: Use a more stable temperature control system (e.g., automated oil bath) to minimize fluctuations.

Explore Non-Ideal Systems:

- Investigate systems with intermolecular forces and non-ideal gas behavior using activity coefficients or real gas models, especially for complex mixtures.

Binary and Ternary Mixtures:

- Expand analysis to other mixtures to explore vapor pressure interactions and deviations from Raoult's law.

Use of Computational Models:

- Implement molecular dynamics simulations to study intermolecular interactions and improve predictions for vapor pressures.

Longer-Term Studies:

- Conduct experiments over extended periods with continuous data collection to observe equilibrium stability and the effects of environmental fluctuations. This will offer deeper insights into the system’s behavior and improve model accuracy.

Discussion and Conclusions

Experimental Insights:

- Vapor pressures of acetone, benzene, methanol, and ethanol measured successfully.
- Results align with theoretical predictions (Antoine equation) with minor deviations at higher temperatures.

Binary Mixture Behavior:

- Acetone-benzene mixture followed Raoult's Law.
- Vapor pressure dominated by acetone due to its higher mole fraction.

Thermodynamic Analysis:

- Clausius-Clapeyron equation used to calculate latent heat of vaporization.
- Constants A, B, and C from the Antoine equation require refined optimization.

Applications:

- Key for distillation, refrigeration, and chemical separations.
- Relevant for large-scale processes in petrochemicals and pharmaceuticals.

Future Scope:

- Extend to non-ideal systems and more complex mixtures.
- Scale up for industrial application and explore molecular-level modeling.

References

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5. Johnson, Mark. *Vapor Pressure Data Analysis*. Report no. 1234, National Research Council, 2018.

Appendices

Excel Sheet:

https://docs.google.com/spreadsheets/d/1MjJGTnFN9dmhcPmg_imZlbZvM0SXR3ZoctFdWlji26k/edit?usp=sharing

Google Colab:

https://colab.research.google.com/drive/1fPbP0hPO1XjPQCSoo7XQR682glX37KBI#scrollTo=1kBKLv9kHht8&uniqifier=1

Thank You