EQUATIONS OF STATE

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Equations of State

- **Equation of state or EOS**
- **Thermodynamic relationships between three properties of a pure (or one-component) substance.**
- **The term EOS most commonly refers to the relationship of the properties p, V, and T of a gas.**
- **Solids and liquids are also described by p-V-T equations of state, but are very different in forms.**

Equations of State

- **The EOS relating V, p, and T provides no information about the other thermodynamic properties, in particular about the internal energy U and the entropy S.**

- **Knowledge of the function U(T,V) requires information about the substance beyond that contained in its p-V-T relationship. Functional relationships such as U(T,V) are sometimes called thermal equations of state.**

The Joule experiment

Thermometer

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

High pressure gas

Vacuum
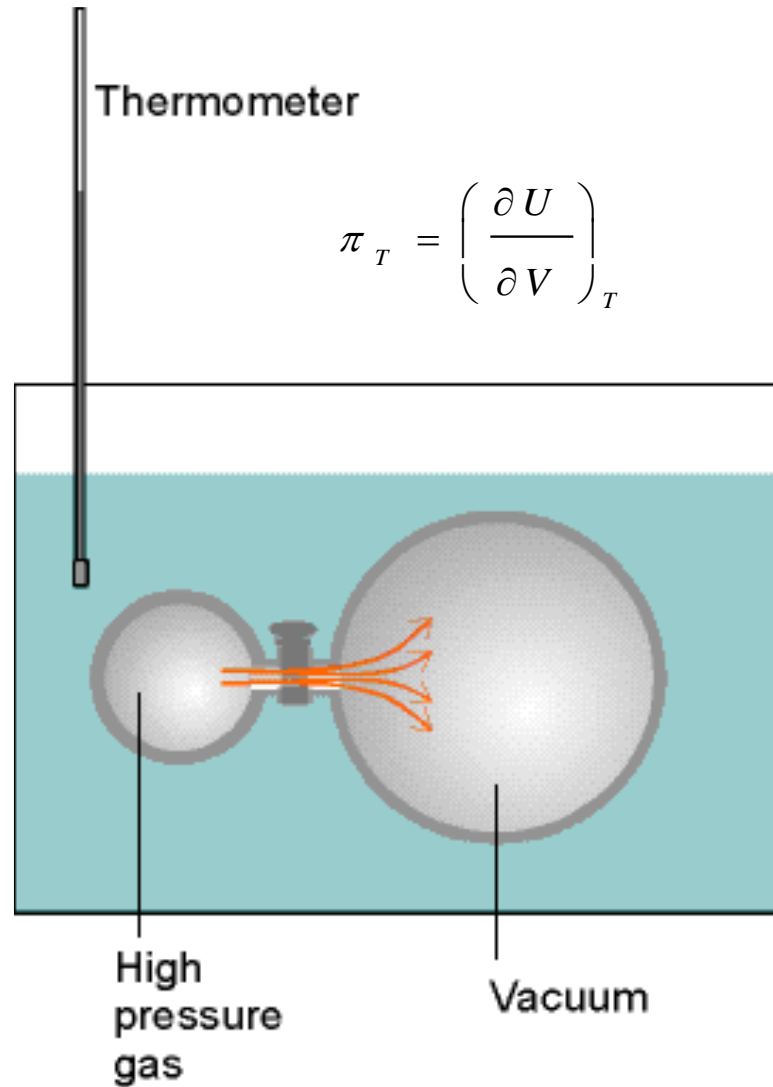
The Joule experiment

- **Joule detected no temperature change,**
  - i.e. $q = 0$.
- **Any work done? Since the gas was expanding against zero pressure no work was done,**
  - so $w = 0$.
  - $\Delta U = q + w = 0$ (1st law).
- **The process is at constant internal energy.**

The Joule experiment

- **Heat capacity is defined as (more rigorous will be given later)   C = q/ΔT = $\Delta Q/\Delta T$**

- **Recall the First Law**

$$dU = dQ + dW$$

- **where dW is work including many forms**

- **If constant volume or no work done**

$$dU = dQ \qquad \textbf{Cv} = \Delta U/\Delta T$$

- **If constant pressure**

- $dU = dQ + dW = (dQ + dPV) + dW'$ **Cp = $\Delta H/\Delta T$**

The Joule experiment

- **For a mole of ideal gas**
- $\Delta u = c_v \Delta T$ *or more generally*

$$\Delta u = \int_{T_1}^{T_2} c_v \Delta T$$

- **By definition, one mole of gas, h = u+pv**
- **For change from state 1 to state 2**
- $\Delta h = \Delta u + \Delta (pv) = \Delta u + \Delta (RT) = c_v \Delta T + R\Delta T = c_p \Delta T$

The Joule experiment

- **For one mole of ideal gas**
    - $\Delta u = c_v \Delta T$
    - $\Delta h = c_p \Delta T$
    - $c_p = c_v + R$
- **Independent of p, V**
- **If c_v and c_p vary with temperature,**

$$\Delta u = \int_{T_1}^{T_2} c_v \Delta T \qquad \Delta h = \int_{T_1}^{T_2} c_p \Delta T$$

The Joule experiment

- **In Joule's experiment, clearly, ΔV ≠ 0 because the gas expanded to fill both bulbs. The question was, did *T* change? Δ*T* was measured to be zero, no temperature change.**

- **In effect, Joule was trying to measure the derivative** $\left(\dfrac{\partial T}{\partial V} \right)_U$

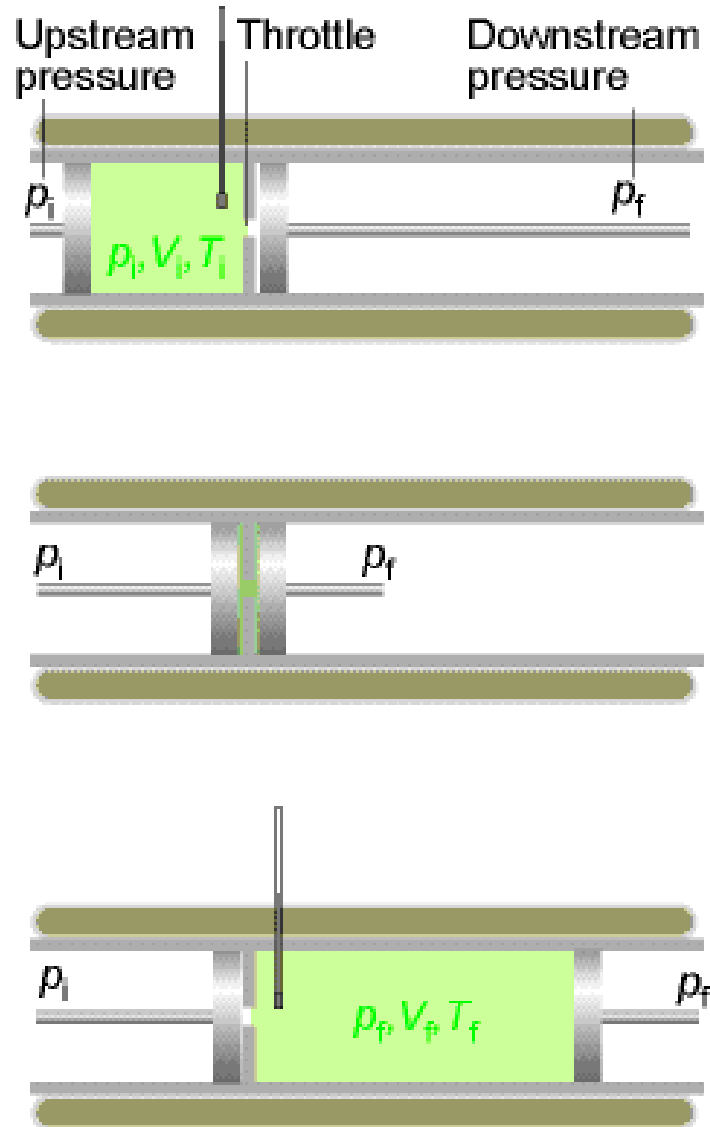- **And found** $\left(\dfrac{\partial T}{\partial V} \right)_U = 0$

The Joule experiment

- **Joule found ΔT = 0, even though p and V do change**

- **That means u ≠ f(p,V), but that u = f(T) (batch)**

- **From the *Euler's chain relation*,**

$$\left(\frac{\partial T}{\partial V} \right)_U = - \frac{\left(\frac{\partial U}{\partial V} \right)_T}{\left(\frac{\partial U}{\partial T} \right)_V} = \frac{\left(\frac{\partial U}{\partial V} \right)_T}{C_V} = 0$$

- **Therefore, for ideal gas,** $\left(\frac{\partial U}{\partial V} \right)_T = 0$

The Joule-Thompson experiment

Upstream pressure | Throttle | Downstream pressure

p_i

p_i, V_i, T_i

p_f

p_i

p_f

p_i

p_f, V_f, T_f

p_f

- It soon became apparent that the result of the Joule expansion experiment was not valid for real gases.

- A more accurate experiment, slightly different, was carried out by Joule and J. J. Thompson to further elucidate the properties on real gases under expansion.

The Joule-Thompson experiment

- **The total work is**

$$w = -p_1(0 - V_1) - p_2(V_2 - 0)$$

$$= p_1V_1 - p_2V_2$$

- **Since $q = 0$, the change in internal energy of the gas is,**

$$\Delta U = q + w$$

$$= 0 + p_1V_1 - p_2V_2$$

$$\neq 0$$

The Joule-Thompson experiment

- **This process, unlike the Joule expansion, is not at constant internal energy.**

- **The enthalpy is given by,**

$$\Delta H = \Delta U + \Delta(pV)$$

$$= p_1 V_1 - p_2 V_2 + p_2 V - p_1 V_1$$

$$= 0$$

- **So the Joule Thompson experiment is a process at constant enthalpy.**

The Joule-Thompson experiment

- **In the experiment a value for Δ*p* was selected and Δ*T* was measured. The ratio of these two quantities is an approximation to a derivative,**

$$\frac{\Delta T}{\Delta p} \approx \left(\frac{\partial T}{\partial P} \right)_H = - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_p} = - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{C_p}$$

- **is zero for an ideal gas, but not necessarily zero for a real gas. We realize there are "real" gases!**

Euler's chain relation

- **In the previous slides, we been using *Euler's chain relation***

$$\left(\frac{\partial v}{\partial x} \right)_y = -\left(\frac{\partial v}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_v$$

$$\left(\frac{\partial x}{\partial y} \right)_v \left(\frac{\partial y}{\partial v} \right)_x \left(\frac{\partial v}{\partial x} \right)_y = -1$$

Ideal gas Equation of State

$$pV = nRT$$

- **No real gas obeys the ideal gas equation of state for all temperatures and pressures. However, all gases obey the ideal gas equation of state in the limit as pressure goes to zero (except possibly at very low temperatures). Another way to say this is to say that all gases become ideal in the limit of zero pressure.**

Ideal gas

- **Boyles law was first published in 1662. It states: The pressure times the volume of a gas is equal to some constant k. *PV= k*.**
- **Charles/Gay-Lussac Law states that: At constant pressure, the volume of a given mass of an ideal gas increases or decreases by the same factor as its temperature (in kelvin) increases or decreases.**

Ideal gas

- **Avogadro's Law, states that the volume *V* is related to the number of moles of gas, *n* by**

  V/n = k

- **Therefore, in more familiar form, the**

  PV= nRT

The van der Waals Equation of State

$$\left(p + a \, \frac{n^2}{V^2} \right)\left(V - nb \right) = nRT$$

- **the van der Waals equation of state differs from the ideal gas by the addition of two adjustable parameters, *a*, and *b* (among other things).**
  - *b* corrects for the finite size of the molecules
  - *a* corrects for the attractive forces between the molecules.
  - Omission in the ideal gas equation of state.

The van der Waals Equation of State

- **Assume that an Avogadro's number of molecules (one mole of the molecules) takes up a volume of space - just by their physical size - of *b* units.**

- **Then any individual molecule doesn't have the whole (measured) volume, *V*, available to move around in. The space available to any one molecule is just the measured volume less the volume taken up by the molecules themselves, *nb*. So the "effective" volume,**

- $V_{eff} = V - nb.$

The van der Waals Equation of State

- The molecules at the edge of the gas (near the container wall) are attracted to the interior molecules.

- The number of "edge" molecules is proportional to n/V and the number of interior molecules is proportional to n/V also.

- The number of pairs of interacting molecules is thus proportional to n^2/V^2

- so that the forces attracting the edge molecules to the interior are proportional to n^2/V^2. These forces give an additional contribution to the pressure on the gas proportional to n^2/V^2.

- the proportionality constant is a, $\quad p_{eff} = p + a \dfrac{n^2}{V^2}$

Redlich–Kwong equation of state

- **Relatively simple in form, while superior to the van der Waals equation of state**

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}\, V_m\, (V_m + b)}$$

$$a = \frac{0.42748\ R^2 T_c^{2.5}}{p_c}$$

$$b = \frac{0.08662\ RT_c}{p_c}$$

Soave modification of Redlich-Kwong

$$p = \frac{RT}{V_m - b} - \frac{\alpha a}{V_m(V_m + b)}$$

$$a = \frac{0.42748 \, R^2 T_c^2}{p_c}$$

$$b = \frac{0.08662 \, RT_c}{p_c}$$

$$\alpha = \left(1 + \left(0.48508 + 1.55171 \, \omega - 0.17613 \, \omega^2\right)\left(1 - T_r^{0.5}\right)\right)^2$$

$$T_r = \frac{T}{T_c}$$

where, ω is the acentric factor of the species

Peng-Robinson equation of state

$$p = \frac{RT}{V_m - b} - \frac{\alpha a}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45274 \; R^2 T_c^2}{p_c}$$

$$b = \frac{0.07780 \; RT_c}{p_c}$$

$$\alpha = \left(1 + \left(0.37464 + 1.54226\, \omega - 0.26992\, \omega^2\right)\left(1 - T_r^{0.5}\right)\right)^2$$

$$T_r = \frac{T}{T_c}$$

where, ω is the acentric factor of the species

The Virial equation of state

- **The virial expansion is a power series in powers of the variable, *n/V*, and has the form,**

$$\frac{pV}{nRT} = Z = 1 + B(T)\frac{n}{V} + C(T)\frac{n^2}{V^2} + \cdots$$

- **The coefficient, *B*(*T*), is a function of temperature and is called the "second virial coefficient. *C*(*T*) is called the third virial coefficient, and so on.**

The Virial equation of state

- **Notice that the quantity pV/nRT equal to Z. This quantity (Z) is called the "compression factor." It is a useful measure of the deviation of a real gas from an ideal gas. For an ideal gas the compression factor is equal to 1.**

Critical Phenomena

- **All real gases can be liquefied. Depending on the gas this might require compression and/or cooling. However, there exists for each gas a temperature above which the gas cannot be liquefied. This temperature, above which the gas cannot be liquefied, is called the critical temperature and it is usually symbolized by, T_C. In order to liquefy a real gas the temperature must be at, or below, its critical temperature.**

Critical Phenomena
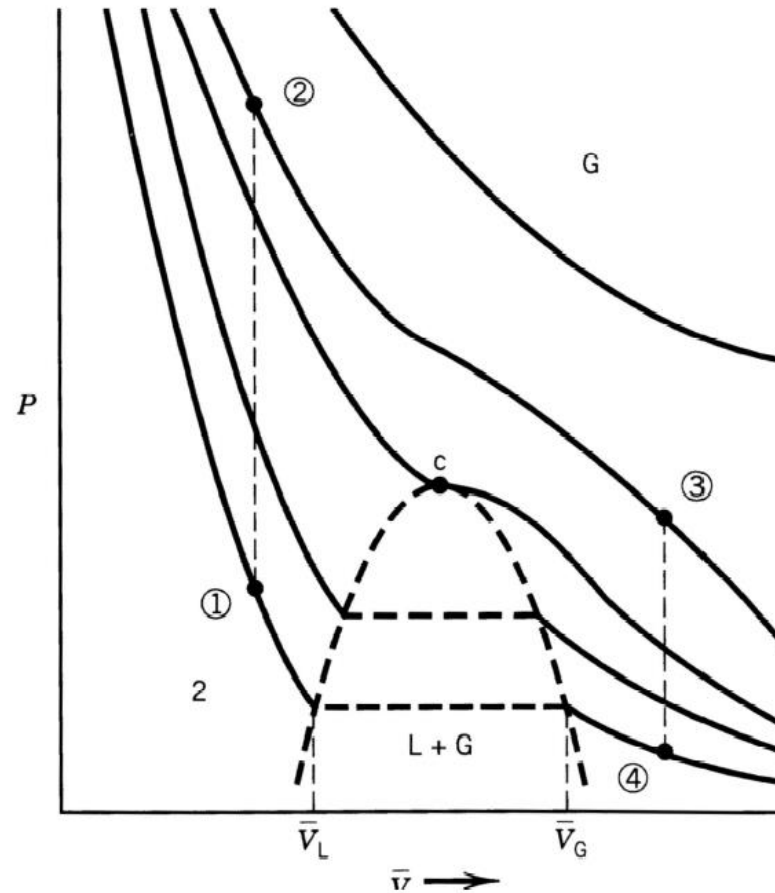
From vapor to gas

Liquid-Vapor P-V phase diagram isotherms near the critical point.

Critical Phenomena

- **when a substance is liquefied the isotherm becomes "flat," that is, the slope becomes zero.**

- **On the critical isotherm the slope "just barely" becomes flat at one point on the graph.**

- **The mathematical characteristic of this point is** $\left(\dfrac{\partial p}{\partial V} \right)_T = 0$ and $\left(\dfrac{\partial^2 p}{\partial V^2} \right)_T = 0$

Critical Phenomena

- **ideal gas:**

$$p = \frac{nRT}{V}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{V^2} = 0 \qquad ?$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2\,nRT}{V^3} = 0 \qquad ?$$

- **These can only be satisfied when $T = 0$, or $V = \infty$.**

- **Neither of these solutions is physically reasonable**

- **So it can be concluded that the ideal gas does not have a critical point.**

Critical Phenomena

- **The van der Waals equation of state**

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

$$V = V_c = 3\,nb$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{(V - nb)^2} + 2\,a\frac{n^2}{V^3} = 0$$

$$T = T_c = \frac{8\,a}{27\,b}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2\,nRT}{(V - nb)^3} - 6\,a\frac{n^2}{V^4} = 0$$

$$p = p_c = \frac{a}{27\,b^2}$$

- **Therefore, the van der Waals equation of state does give a critical point**

Critical Phenomena

- **However, the van der Waals equation of state is still an approximate equation of state and does not represent any real gas exactly.**

- **It has some of the features of a real gas and is therefore useful as the next best approximation to a real gas.**

Partial Derivatives

- **For a <u>closed system of constant composition</u>**
- $U = f (V, T)$, **extensive**

Constant *T*, change *V* to *V+dV*, then *U* changes to:

$$U ' = U + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Constant *V*, change *T* to *T+dT*, then *U* changes to:

$$U ' = U + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Change *V* to *V+dV* and *T* to *T+dT*, then *U* changes to:

$$U ' = U + \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Because *dU = U'-U*, then:

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

Partial Derivatives

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

A small (infinitesimal) change in internal energy is proportional to small changes in volume and temperature.

Recall: $\quad C_V = \left(\dfrac{\partial U}{\partial T} \right)_V$

We introduce a new term, π_T, the **<u>internal pressure</u>**. $\quad \pi_T = \left(\dfrac{\partial U}{\partial V} \right)_T$

$$dU = \pi_T dV + C_V dT$$

Partial Derivatives

- **The Joule expansion (valid for ideal gases) demonstrated experimentally that for an ideal gas,**

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

- **It would be nice to be able to calculate this quantity from an equation of state or other *pVT* data.**

- **The "thermodynamic equation of state", which will allow us to do this.**

The "Thermodynamic Equation of State"

- **Thermodynamic equation of state**

$$dU = TdS - pdV$$

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

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

- **From Maxwell's Relation**

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

- **For an ideal gas,**

$$p = \frac{nRT}{V}$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{nR}{V}$$

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

$$= T\left(\frac{nR}{V} \right) - p$$

$$= p - p$$

$$= 0$$

The "Thermodynamic Equation of State"

- **What about the van der Waals gas?**

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V - p = a\frac{n^2}{V^2} \geq 0$$

- **Therefore, the internal energy of van der Waals gas always increases when it expands isothermally.**

The "Thermodynamic Equation of State"

- **Thermodynamic equation of state (the other version)**

$$dH = TdS + Vdp$$

$$\left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + V$$

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p + V$$

- **From Maxwell's Relation**

$$\left(\frac{\partial S}{\partial p} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_p$$

- **For an ideal gas,**

$$V = \frac{nRT}{p}$$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}$$

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p + V$$

$$= -T \left(\frac{nR}{p} \right) + V$$

$$= -V + V$$

$$= 0$$

Joule–Thomson (Kelvin) Coefficient

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

$$\left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial V}{\partial T} \right)_p - V \qquad \text{Previous Slides}$$

$$\left(\frac{\partial V}{\partial T} \right)_p = V \alpha$$

Introduce : $\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1)$

Partial Derivatives

- **The volume of a sample of an isotropic material is known experimentally to be a function of temperature and pressure.**

- $V = V(T, p)$

$$dV = \left(\frac{\partial V}{\partial p} \right)_T dp + \left(\frac{\partial V}{\partial T} \right)_p dT$$

$$\frac{dV}{V} = \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T dp + \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p dT$$

- Introduce $\quad \kappa_T = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad$ and $\quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

Partial Derivatives

- **For ideal gas:**

$$V = \frac{nRT}{p}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{nR}{p}\right) = \frac{nR}{pV} = \frac{1}{T}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{V}\left(\frac{nRT}{p^2}\right) = \frac{p}{nRT}\frac{nRT}{p^2} = \frac{1}{p}$$

Recap

Internal Pressure	$\pi_T = \left(\dfrac{\partial U}{\partial V} \right)_T$	$\pi_T = 0$	**Strength/nature of interactions between molecules**
Joule-Thomson Coefficient	$\mu = \left(\dfrac{\partial T}{\partial p} \right)_H$	$\mu = 0$	**Another indication of molecular interactions.**
Expansion Coefficient	$\alpha = \dfrac{1}{V} \left(\dfrac{\partial V}{\partial T} \right)_p$	$\alpha = 1 / T$	**The higher *T*, the less responsive is its volume to a change in temperature**
Isothermal Compressibility	$\kappa_T = -\dfrac{1}{V} \left(\dfrac{\partial V}{\partial p} \right)_T$	$\kappa_T = 1 / p$	**The higher the *p*, the lower its compressibility**

Quiz

- **Find out the**

$$\left(\frac{\partial p}{\partial T} \right)_V$$

- **Given :**

- **Hg, α = 1.82$\times$10-4 K-1 and κ_T = 3.87 $\times$ 10^{-5} atm^{-1}**

- **Calculate pressure rise per degree of temperature increase**

- **What will happen when mercury has reached the top of the thermometer, but temperature continue to rise.**

Answer

$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = - \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T} \right)_p}{\frac{1}{V}\left(\frac{\partial V}{\partial p} \right)_T} = \frac{\alpha}{\kappa_T}$$

$$\left(\frac{dp}{dT} \right)_V = \frac{\alpha}{\kappa_T} = \frac{1.82 \times 10^{-4} \, K^{-1}}{3.87 \times 10^{-5} \, atm^{-1}} = 4.70 \; atm \; / \, K$$