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DRAGONS

EQUATIONS!

What is Physical Chemistry?

- Physics of Chemistry

What is Thermodynamics?

- **THERMO** - heat, energy
- **DYNAMICS** - changes
- Consider

$$PV = nRT$$

  - Rewrite as:

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

- What can cause P to change?
  - V - volume

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = -\frac{nRT}{V^2}$$

  - n - number of moles of gas

$$\left(\frac{\partial P}{\partial n}\right)_{V,T} = \frac{RT}{V}$$

  - T - temperature

$$\left(\frac{\partial P}{\partial T}\right)_{n,V} = \frac{nR}{V}$$

- How do we describe the change if all three are changing at once?

$$dP = \left(\frac{\partial P}{\partial V}\right)_{n,T} dV + \left(\frac{\partial P}{\partial n}\right)_{V,T} dn + \left(\frac{\partial P}{\partial T}\right)_{n,V} dT$$

- Note carefully the difference between ∂ and d
  - ∂ describes the partial change due to the change in a particular variable
  - d describes the total change

- Some other ways of describing changes (useful for numerical applications)
  - Δ - a finite change
  - δ - an infinitesimal change

UNITS

- Even when represented by a symbol, physical quantities have units.
  - Verification of units can help detect mistakes in a derivation.

- P - force per unit area. The SI unit is the Pascal (Pa).
  - 1 Pa = 1 N m^{-2} = 1 kg m s^{-2} m^{-2}
  - 1 Pa = 1 kg m^{-1} s^{-2} (fundamental units)
- V - volume
  - m^3 (fundamental units)
- n -number of moles
  - mol (fundamental units)
- R - Gas Constant
  - 8.314 J K^{-1} mol^{-1} = 8.314 kg m^2 s^{-2} K^{-1} mol^{-1}
  - (1 J = 1 kg m^2 s^{-2} (fundamental units))
  - (1 J = 1 Pa m^3 or 1 Pa = 1 J m^{-3})
- T K (fundamental units)
  - temperature is on absolute Kelvin scale. See page 3 of Winn.

UNITS ARE YOUR FRIENDS

EQUATIONS OF STATE

Definition (Winn p. 5.)

"An equation of state is the mathematical relationship among the relevant thermodynamic variables of an equilibrium system."

- Examples (from gas behaviour):
  - Ideal Gas Equation of State

$$PV = nRT$$

  - van der Waals Equation of State

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

  - Virial Equation of State

$$\frac{P\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \ldots$$

THERMODYNAMIC VARIABLES

- Intensive
- Extensive
- Relation to Equation of State

- Description of Equilibrium
- **RECOMMENDED READING:**

  Chapter 1 Winn

COMPRESSIBILITY

$$Z \equiv \frac{\overline{V}(\text{real})}{\overline{V}(\text{ideal})} = \frac{P\overline{V}}{RT}$$

- Ideal gas

$$Z \equiv \frac{P\overline{V}}{RT} = 1$$

- van der Waals

$$Z \equiv \frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$$

- Virial equation

$$Z \equiv \frac{P\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \ldots$$

- **THEREFORE:**

  Deviation from one of the value of Z, the compressibility factor, is a measure of the nonideal behaviour of a gas.

A closer look at the virial equation:

  - $B(T)$ has units of volume
  - $C(T)$ has units of volume^2.

- What would we expect temperature dependence of $B(T)$ to be?
  - High T - repulsions important
  - Low T - attraction important

The Boyle temperature and the van der Waals equation:

- Consider the van der Waals equation of state written in virial form:

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^{\,2}} + \ldots$$

  or:

$$Z \equiv \frac{P\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^{\,2}} + \ldots$$

  where:

$$B(T) = b - \frac{a}{RT} \;\; ; \;\; C(T) \;=\; b^2$$

What is the temperature dependence of $B(T)$ for a van der Waals gas?

- If T is large, $B(T) \to b$, which is positive.

  - Repulsion accounts for most of the deviation from ideal behaviour.
- If T is small, $B(T)$ becomes negative.

$$B(T) \rightarrow -\frac{a}{RT}$$

  - Attraction accounts for most of the deviation from ideal behaviour.
- When $B(T) = 0$, the corresponding temperature is the Boyle temperature, T_B.

$$B(T) = 0 = b - \frac{a}{RT_B}$$

$$T_B = \frac{a}{Rb}$$

  - A physical interpretation of the Boyle temperature is that temperature at which the average attractive and repulsive forces are balanced.

Dimensionless Scales

- For a van der Waals gas, the Boyle temperature, T_B, allows us to define a dimensionless temperature scale in terms of multiples of the Boyle temperature.

$$B(T) = 0 = b - \frac{a}{RT_B}$$

- Dividing both sides of the equation by b gives:

$$\frac{B(T)}{b} = 1 - \frac{a}{RbT} = 1 - \frac{T_B}{T}$$

  which means:

  - that any temperature can be expressed as a multiple of of the Boyle temperature, T_B;
  - and that the second virial coefficient, $B(T)$, can be expressed as a multiple of the second van der Waal's parameter b.
- Dimensionless scales allow the convenient comparison of a number of different gases described by the van der Waals equation.

- In Figure 1.6 of your text, $B(T)/b$ is plotted against T/T_B for the noble gases
- From this plot we can see:
  - how nonideal these gases are
  - how well van der Waals works for these gases.

More Dimensionless Variables

- Consider a van der Waals gas. If we can scale volume and pressure in a way similar to that used for temperature, then we can use one equation or graph to represent the properties of many different van der Waals gases.
- We already have way to scale temperature T with the Boyle temperature, T_B
  - Recall that $T_B = a/Rb$, i.e. a combination of parameters that have the same dimensions as temperature
  - Our scaled temperature is:

$$\tilde{T} = \frac{T}{T_B}$$

- To set up scales for V and P, we will look for combinations of parameters that have the "right" dimensions.
- Consider first molar volume, $\overline{V}$:
  - The van der Waals parameter, b, also has units of molar volume.
  - Therefore our scaled dimensionless variable is:

$$\tilde{V} = \frac{\overline{V}}{b}$$

- Now consider pressure, P.
  - We note that the quantity $a/\overline{V}^2$ has the same dimensions as pressure.
  - We need to replace $\overline{V}$ with something that has the same units, in this case, b.
  - Therefore our scaled dimensionless variable is:

$$\tilde{P} = \frac{Pb^2}{a}$$

- With

$$\tilde{T} = \frac{T}{T_B} = \frac{TRb}{a}$$

  we can now rewrite the van der Waals equation in scale dimensionless variables:

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V} - 1} - \frac{1}{\tilde{V}^2}$$

- Thus we can represent all van der Waals gases with this dimensionless equation.
  - To obtain information for a specific gas, we just need to undo the scaling with using the values of a and b specific to that gas.
- Consider the van der Waal's isotherms (Figure 1.7 page 22 Winn). Note:
  - That the isotherms for the lower temperatures have a minimum and a maximum while the isotherms for higher temperatures have no minimum or maximum.
  - That as temperature increases the maximum and minimum move closer together until they meet at a point (called the critical point) above which the maximum and minimum have disappeared.
  - The critical point is characterized by the critical temperature (T_C), the critical pressure (P_C) , and the critical molar volume ($\overline{V}_C$) .
  - Below the critical temperature, the van der Waals curve has a region of positive slope, $\left(\partial\tilde{P}/\partial\tilde{V}\right)_T$, joining the maximum and the minimum.

What is the physical significance of this?

- Note that the bulk isothermal compressibility is defined as:

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

  - κ is positive for all real substances.

  - Therefore we have a region below T_C where the van der Waals equation breaks down because it gives a negative value for κ.
- Consider first the van der Waals equation at T_C
  - The critical point is mathematically an inflection point.

- Mathematical properties of an inflection point:
  - First derivative is zero.
  - Second derivative is zero.
- This means that we can write three equations in three unknowns $(\tilde{P}_C, \tilde{V}_C, \tilde{T}_C)$ and solve for each of the unknowns.

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V}-1} - \frac{1}{\tilde{V}^2}$$

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{V}}\right)_{\tilde{T}=\tilde{T}_C} = 0 = \frac{-\tilde{T}}{(\tilde{V}-1)^2} + \frac{2}{\tilde{V}^3}$$

$$\left(\frac{\partial^2 \tilde{P}}{\partial \tilde{V}^2}\right)_{\tilde{T}=\tilde{T}_C} = 0 = \frac{2\tilde{T}}{(\tilde{V}-1)^2} + \frac{-6}{\tilde{V}^4}$$

- To solve for $(\tilde{P}_C, \tilde{V}_C, \tilde{T}_C)$.
  - Isolate $\tilde{T}_C$ in the first and second derivatives.
  - Combine the resulting two equations and isolate $\tilde{V}_C$.
  - Substitute $\tilde{V}_C$ into one of the equations and evaluate $\tilde{T}_C$.
  - Substitute $\tilde{V}_C$ and $\tilde{T}_C$ in the van der Waals equation and get $\tilde{P}_C$.
- In scaled variables, this gives:

$$\tilde{V}_C = 3; \quad \tilde{T}_C = \frac{8}{27}; \quad \tilde{P}_C = \frac{1}{27}$$

- Undoing the scaling gives:

$$\overline{V}_c = 3b; \quad T_C = \frac{8a}{27Rb}; \quad P_C = \frac{a}{27b^2}$$

- The critical point variables, (P_C ,$\overline{V}_C, T_C$), provide us another way to scale $(P, \overline{V}, T)$.
  - The resulting set of scaled variables are known as *the reduced variables*, $(p, \overline{v}, t)$.
  - Different gases described by the same set of reduced variables are in *corresponding states.*

- Figure 1.10 compares isotherms of compressibility in terms of reduced pressure.

- Something to try on your own (between now and the first term test):
  - Write the van der Waals equation in terms of reduced variables.

HINT: Recall how we determined the van der Waals equation in scaled variables (i.e. substitutions and cancellations).

Some useful properties of partial derivatives

(that we will be using)

- Consider some function $z(x,y)$.

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y^{-1}$$

  if z is a continuous function of x.

  - Most thermodynamic functions are continuous functions.

- An application of this would be the evaluation for a van der Waals gas of:

$$\left(\frac{\partial \overline{V}}{\partial P}\right)_T$$

The Cyclic Rule

- Another useful property of partial derivatives.
- Again consider the function $z(x,y)$. The cyclic rule is:

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

- This in combination with the previous property allows us to find one of the derivatives given the other two.
- An application of this would be the evaluation for a van der Waals gas of:

$$\left(\frac{\partial \overline{V}}{\partial T}\right)_P$$

The Chain Rule

- Consider function $f(x_1,x_2)$ such that
  - $x_1 = x_1(y_1,y_2)$
  - $x_2 = x_2(y_1,y_2)$
- Then the chain rule is:

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} =$$

$$\left(\frac{\partial f}{\partial y_1}\right)_{y_2} \left(\frac{\partial y_1}{\partial x_1}\right)_{x_2} + \left(\frac{\partial f}{\partial y_2}\right)_{y_1} \left(\frac{\partial y_2}{\partial x_1}\right)_{x_2}$$

- Consider the case where

$$x_1 = T,\ x_2 = P,\ y_1 = T,\ y_2 = V$$

  - Then the chain rule becomes:

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

  - If $f = P$ then this becomes:

$$0 = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

  - From this the cyclic rule may be derived:

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

  or

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

State Functions and Path Functions

- Consider a system initially at equilibrium in state 1.
- The system undergoes a change and comes to a new equilibrium at state 2.
- The value of a **state function** at state 2 is **independent of the path** taken from state 1 to state 2.
- The value of a **path function** at state 2 is **dependent on the path** taken from state 1 to state 2.

Exact and Inexact Differentials

- An infinitesimal change on a path for a state function between state 1 and state 2 is described by an exact differential.
- An infinitesimal change on a path for a path function between state 1 and state 2 is described by an inexact differential.
- Consider some function z such that:

$$dz = f_x(x,y)dx + f_y(x,y)dy$$

  where chosen arbitrarily are functional forms for f_x and f_y. For example:

$$f_x(x,y) = xy \text{ and } f_y(x,y) = x^2y^2$$

- Does there exist some function $z(x,y)$ such that dz is the total derivative?
  - If there does, then z is a state function.
  - If there does not, then z is a path function.

How to Test for State Functions

- If z is a state function, it must pass the cross derivative equality test.
- If the state function $z(x,y)$ exists then:

$$\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

- Applied to $dz = f_x(x, y)dx + f_y(x, y)dy$, the test becomes whether:

  $$\frac{\partial f_y(x,y)}{\partial x} = \frac{\partial f_x(x,y)}{\partial y}$$

- Applied to $dz = xydx + x^2y^2dy$, we see that the cross derivative equality test is failed because:

  $$\frac{\partial xy}{\partial y} = x$$

  and

  $$\frac{\partial (x^2y^2)}{\partial x} = 2xy^2$$

  Therefore in this case z is a path function.