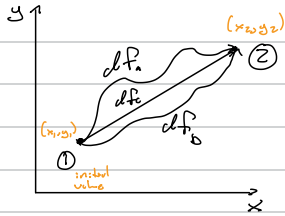




# Math Review

- ① **Differential**  $\equiv$  an infinitesimal change in a function or variable For constants / functions  $P, Q$   
 ex: If  $f = f(x, y)$ , then the **total differential** of  $f$  is  $df = P(x, y)dx + Q(x, y)dy$   
 and is exact and independent of integration paths



$df_a = df_b = df_c = \dots$  is guaranteed as it is defined as independent of integration paths

- ② **Partial Derivatives**  $\equiv$  the differential change in one variable with respect to a differential change in another variable, while holding other variables fixed/constant

ex: Let  $f(x, y) = x^2y + x \sin y + \sin x \sin y$ .

Differential change in  $f$  ( $df$ ) @ constant  $y = \left( \frac{\partial f}{\partial x} \right)_y$   
 Differential change in  $x$  ( $dx$ )

Here  $\left( \frac{\partial f}{\partial x} \right)_y = 2xy + \sin y + \cos x \sin y \leftarrow P$

Similarly  $\left( \frac{\partial f}{\partial y} \right)_x = x^2 + x \cos y + \sin x \cos y \leftarrow Q$

Now note that for our total differential,  $df = P(x, y)dx + Q(x, y)dy$   
 $\rightarrow$  If  $y$  is held constant and hence  $dy = 0$ ,  $df = P(x, y)dx \Rightarrow \left( \frac{\partial f}{\partial x} \right)_y = P(x, y)$   
 $\rightarrow$  Similarly for constant  $x$ , then  $\left( \frac{\partial f}{\partial y} \right)_x = Q(x, y)$

- ③ **Integration**  $\equiv$  continuous sum over differential changes

$\int f(x) dx$   
 Integral  $\leftarrow$  differential

1. **Indefinite Integral**: No upper/lower bounds

ex:  $\int (A + BT + CT^2 + \frac{D}{T} + \frac{E}{T^2}) dT$  where  $A, B, C, D, E$  are constants, &  $T$  is temperature  
 $= AT + \frac{1}{2}BT^2 + \frac{1}{3}CT^3 + D \ln T - \frac{E}{T} + (\text{constant})$

2. **Definite Integral**: Specified lower & upper bounds (no constant of integration)

$$\int_{T_0}^{T_1} (A + BT) dT = \left[ AT + \frac{B}{2}T^2 \right]_{T_0}^{T_1} = A(T_1 - T_0) + \frac{B}{2}(T_1^2 - T_0^2)$$

**Summary** - common points of confusion!

① **Differential**: infinitesimal changes denoted ' $df$ '

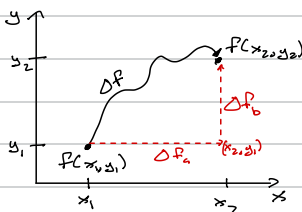
② **Derivative**: change in one variable with respect to another ( $\approx$  differential / another differential)

ex:  $\frac{df}{dx}, \frac{df}{dt}, \left( \frac{\partial f}{\partial x} \right)_y$

③ **Integral**: Continuous sum over differential changes

ex:  $f = P(x); P(x_b) - P(x_a) = \int_{x_a}^{x_b} df$  prohibited! Need to differentiate to make variable in our bounds of integration  $= \int_{x_a}^{x_b} \left( \frac{df}{dx} \right) dx$  derivative!

ex:  $f = P(x, y);$



$$f(x_2, y_2) - f(x_1, y_1) = \Delta f = \Delta f_a + \Delta f_b$$

$$= \int_{x_1}^{x_2} \left( \frac{\partial f}{\partial x} \right)_{y=y_1} dx + \int_{y_1}^{y_2} \left( \frac{\partial f}{\partial y} \right)_{x=x_2} dy$$

We can do this bc the differential is independent of path

**\* Math no-no!**

$\times \Rightarrow \int \frac{df}{dx}$  cannot be evaluated! Missing the differential!

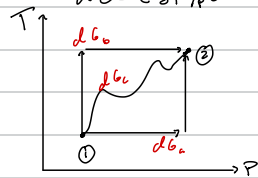
$\checkmark \Rightarrow \int \left( \frac{df}{dx} \right) dx$  is allowed! Must integrate over differential changes

# Chapter 1 - Thermodynamic Properties

Thermodynamic Properties are state functions that do not depend on path and have exact differentials.

ex:  $G = G(T, P)$  Gibbs Free Energy

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$



$$dG_a = dG_b = dG_c = dG$$

Since all equilibria choose exact path

Inexact Differentials are path functions (i.e., they do depend on path)

ex: work (W) and heat (Q)

→  $dW$  and  $dQ$  do depend on path

→ use notation  $\delta Q$  and  $\delta W$  to denote an inexact differential

What is thermodynamics?

↳ A self-contained, logically consistent theory that can be expressed in two laws:

• First Law: Conservation of energy

$$\Delta E_{\text{universe}} = 0 \text{ for any process}$$

• Second Law: Entropy increases

$$\Delta S_{\text{universe}} \geq 0 \text{ for any process}$$

• Two benefits of the 2nd Law

(i) Is our process consistent with 2nd Law?

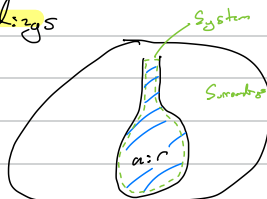
(ii) Entropy of system + surroundings should reach a maximum over time.

① System and Surroundings

ex:



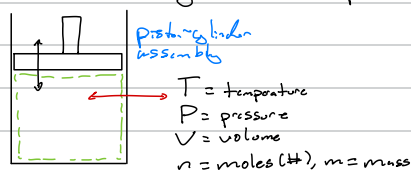
Typically



• Three Types of Systems

	"closed" "R plug" System energy	"open" mass System energy	"isolated" "R plug" perfect insulation System
energy transfer	yes	yes	no
mass transfer	no	yes	no

## ② Thermodynamic Properties of Fluids (mostly gases & liquids, only some solids)



### Types of Properties

- (i) extensive  $\equiv$  varies w/ size of system
- (ii) intensive  $\equiv$  independent of system size

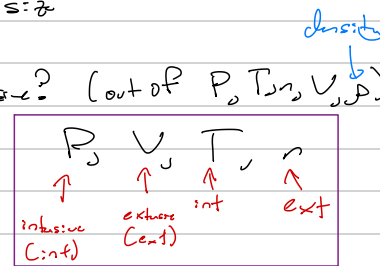
Q: Which of the following thermodynamic properties are intensive? (out of  $P, T, n, V, \rho$ )

①  $P, T, n$

③  $V, n$

②  $P, T, \rho$  Here, of these depend on how large the system is, or how much stuff is in it!

④  $\rho, n$



We can count ext quantities to int ones:

extensive property = "specific property"  $\leftarrow$  intensive quantity normalized by mass  $\leftarrow$  lowercase with a hat

ex:  $\frac{\text{Volume}}{\text{mass}} = \hat{v} = \frac{1}{\rho}$  (specific volume)

extensive = "molar property"  $\leftarrow$  (also intensive) lowercase w/ subscript m

ex:  $\frac{\text{Volume}}{\text{moles}} = v_m$  (molar volume for each multiplicity & standard is distinct from textbook)

## ③ "State" of a System

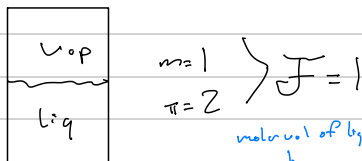
- The "state" of a system depends on its thermodynamic properties
- $\rightarrow$  can be described by the Gibbs phase rule:

$$F = m - \pi + 2 \quad \text{for non-reactive systems}$$

↑ degrees of freedom    ↑ # of chemical species    ↑ # of phases

- Degrees of Freedom  $\Rightarrow$  # of intensive properties that must be specified to constrain properties of a system
- To fully specify a state, also need to know amount of material

Example: Vapor-liquid mixture of  $H_2O$



We could, for example, specify  $v_m$  for each phase

$\rightarrow$  constrains all other intensive properties

Also need to specify total amount in each phase

$\rightarrow V_{tot} = V_{liq} + V_{vap}$

$V_{tot} = V = V_{m,liq} n_L + V_{m,vap} n_V \rightarrow \text{divide by } n_{tot} = n_L + n_V$

$\Rightarrow \frac{V}{n} = v_m = (1-x) v_{m,liq} + x v_{m,vap}$

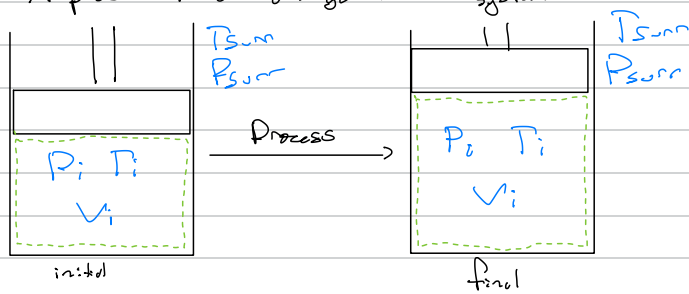
↑ average molar volume    ↑ "quality"

Quality = mole or mass fraction of vapor for saturated (vapor-liquid) mixture

Also:  $v = (1-x) v_L + x v_V$

## ④ Processes

- A process is a change in the system



## 4 speed Types of Processes

- (i) **Isothermal**  $\rightarrow$  const  $T$
- (ii) **Isobaric**  $\rightarrow$  const  $P$
- (iii) **Isochoric**  $\rightarrow$  const  $V$
- (iv) **Adiabatic**  $\rightarrow$  No heat transfer to/surroundings  
 $\rightarrow$  can also be describes well-insulated

## ⑤ Equilibrium

- A system does not change @ equilibrium and there is no driving force for change

$\rightarrow$  Examples:

- (i) Thermal Equilibrium  $\rightarrow T_{sys} = T_{sur}$  (also btwn phases)
- (ii) Force/mechanical  $\rightarrow P_{sys} = P_{sur}$
- (iii) Phase Equilibrium  $\rightarrow$  Composition of phases is constant
- (iv) Chemical Equilibrium  $\rightarrow$  No mass transfer into/out of a phase, or no net chemical reaction

## Thermodynamic Property Sources

- (i) Experiment  $\rightarrow P, T, V, \dots$
- (ii) Graphical representation: PVT diagrams

