

### §. Thermo. D. in "Materials"

- Component ( $\bar{n}$ ): element, compound
1. One component / Multi-component  
Unary / Binary, Ternary, Quaternary
  2. Homogeneous / Heterogeneous
  3. Closed / Open
  4. Non-reacting / Reacting
  5. Simple / Complex  
Q.W.D. / E.M. Op. etc.

### § Thermodynamics Variables

T, P, V,  $n_i$ , U, Q, W, H, S, A, G

U: internal E.

Q: Heat

W: work

H: enthalpy (焓)

S: entropy (熵)

Free E. (A, G)



$$\Delta Z$$

$$dZ$$

$$\delta Z$$

state 1  $\rightarrow$  state 2  $\Delta Z$   
18°C 100°C

Math.

State Function: T, P, V,  $n_i$ ,  
Indep. of path U, H, S, A, G  
 $\Delta Z = \int_1^2 dZ$

Process variables: Q, W  
dep. on path  $\Delta Z \neq \int_{\text{path}} \delta Z$

任意Z同

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Q.W.L. / E.M. Opt.

$$\Delta U = \int_1^2 dU$$

$$\Delta Q = \int_{\text{path}} \delta Q$$

State 1  $\rightarrow$  state 2

$$dz \rightarrow \Delta z = (z_2 - z_1) = \int_1^2 dz$$

$$\oint dz = 0$$

$$\delta Q \rightarrow \Delta Q = \int_{\text{path}} \delta Q$$

$$\oint \delta Q \neq 0$$

$$\delta W_{\text{rev}} = (\vec{F} \cdot d\vec{x}) = P \cdot dV$$

reversible

System

★ 任意の2個

Intensive Variables: T, P.

Idep. of mass  
size  
moles

★ 外変

Extensive variables:  $n_i, U, S$

dep. on mass,  
size

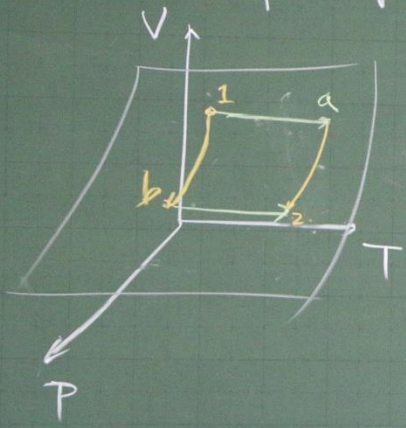
state 2  
 $u) = \int_1^2 dz$   
 $dz = 0$   
 $\delta \theta$   
 $\neq 0$   
 $p \cdot dV$

System.  
 ☆ 任意の2個  
Intensive Variables: T, P,  $\rho$ ,  $X_i$   
 Indep. of mass size moles  
 $\rho$  ↑ density  $\frac{g}{cm^3}$   
 $X_i$  ↑ mole fraction  
 ☆ 外延  
Extensive variables:  $n_i, U, S, H, A, G, Q, W$   
 dep. on mass size

State  
 one mole  
Unary System: ⇒ Two Indep Variables  
 Any  
 e.g.  $V = V(T, P, X_i, U, S, \dots)$   
 mole fraction  
 equation of state  
 most convenient variables: T, P, V  
 state 1 → state 2  
 e.g.  $V_1 \rightarrow V_2, \Delta V = \int_{V_1}^{V_2} dV, V = V(T, P) = ?$   
 $G, Q, W$

e.g.  $V_1$   
 $(P_1, T_1) \rightarrow (P_2, T_2) \rightarrow \Delta V = ?$

consider a pure gas



Two paths

- 1  $\xrightarrow{\text{constant } P}$  a  $\xrightarrow{\text{constant } T}$  2
- 1  $\xrightarrow{\text{constant } T}$  b  $\xrightarrow{\text{constant } P}$  2

path 1:

$$\Delta V_{\text{path 1}} = \int_{T_1}^{T_a} \left( \frac{\partial V}{\partial T} \right)_P \cdot dT + \int_{P_a}^{P_2} \left( \frac{\partial V}{\partial P} \right)_T \cdot dP$$

If  $\Delta V_{\text{path 1}} = \Delta V_{\text{path 2}}$

$V \Rightarrow$  state function

$dV$  exact differential

$V = V(T, P)$

$$dV = \underbrace{\left( \frac{\partial V}{\partial T} \right)_P}_M \cdot dT + \underbrace{\left( \frac{\partial V}{\partial P} \right)_T}_N \cdot dP$$

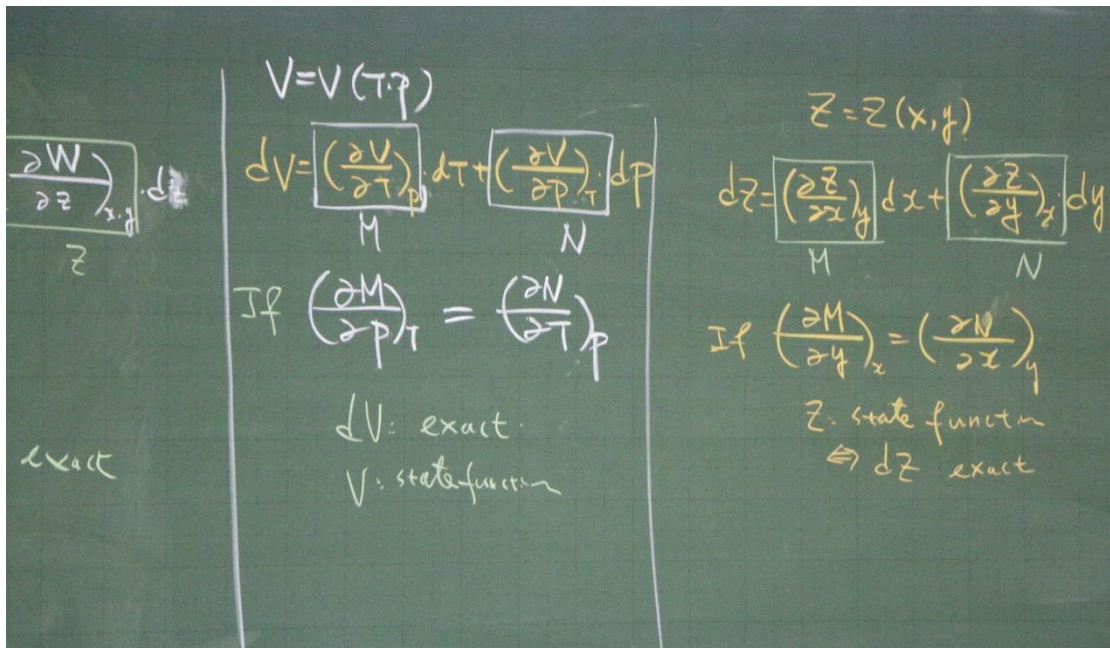
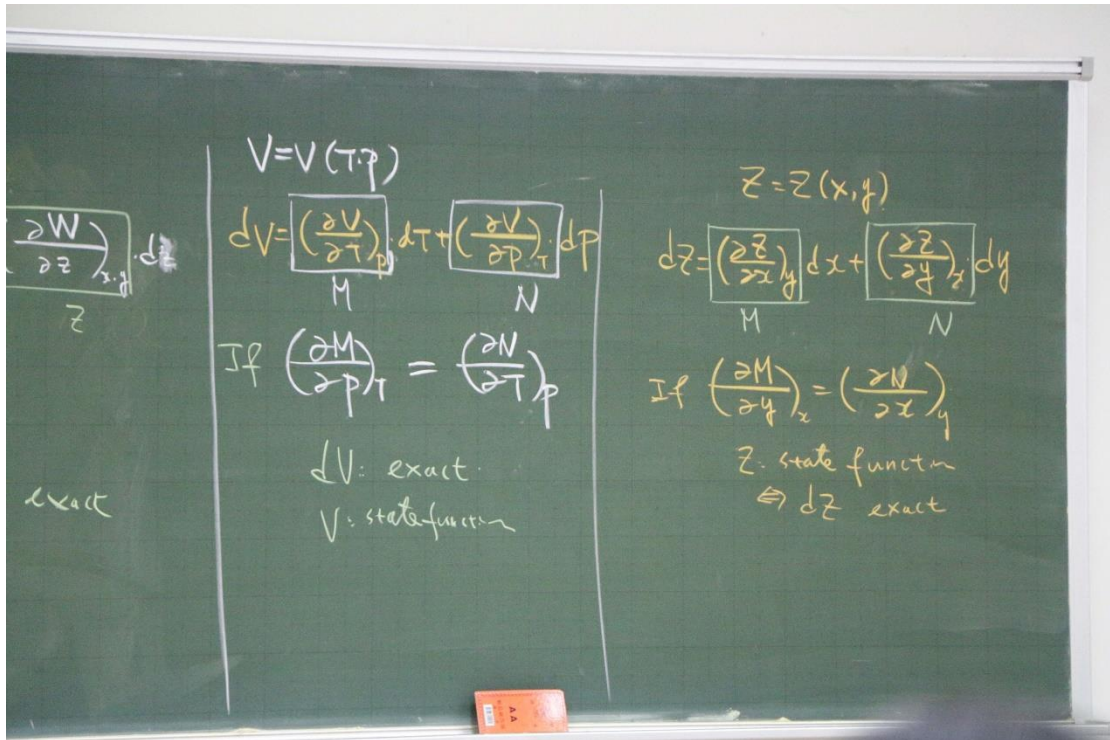
If  $\left( \frac{\partial M}{\partial P} \right)_T = \left( \frac{\partial N}{\partial T} \right)_P$

$dV$ : exact  
 $V$ : state function

$\frac{2}{dT}$   
 $\frac{2}{dP}$   
 $dT$   
 $dP$

path 2

$$\left. \begin{aligned} V_b - V_1 &= \int_{P_1}^{P_b} \left( \frac{\partial V}{\partial P} \right)_T \cdot dP \\ V_2 - V_b &= \int_{T_b}^{T_2} \left( \frac{\partial V}{\partial T} \right)_P \cdot dT \end{aligned} \right\} \Delta V_{\text{path 2}}$$



B

$W = W(x, y, z)$

$$dW = \left( \frac{\partial W}{\partial x} \right)_{y,z} dx + \left( \frac{\partial W}{\partial y} \right)_{x,z} dy + \left( \frac{\partial W}{\partial z} \right)_{x,y} dz$$

$X$                        $Y$                        $Z$

If

$$\begin{cases} \left( \frac{\partial X}{\partial y} \right) = \left( \frac{\partial Y}{\partial x} \right) \\ \left( \frac{\partial Y}{\partial z} \right) = \left( \frac{\partial Z}{\partial y} \right) \\ \left( \frac{\partial X}{\partial z} \right) = \left( \frac{\partial Z}{\partial x} \right) \end{cases} \quad \therefore dW \text{ exact}$$

$y^3 + x \cdot z$

$$\left( \frac{\partial X}{\partial y} \right) = 3xy^2$$

$$\left( \frac{\partial Y}{\partial x} \right) = 6xy^2$$

$$\left( \frac{\partial Y}{\partial z} \right) = 0$$

$$\left( \frac{\partial Z}{\partial y} \right) = 0$$

$$\left( \frac{\partial X}{\partial z} \right) = 1 = \left( \frac{\partial Z}{\partial x} \right) = 1$$

Appendix B

Ex 1: If  $W = x^2 y^3 + x \cdot z$

$$\begin{cases} X = \left( \frac{\partial W}{\partial x} \right) = 2xy^3 + z & \left( \frac{\partial X}{\partial y} \right) = 6xy^2 \\ Y = \left( \frac{\partial W}{\partial y} \right) = 3x^2 y^2 & \left( \frac{\partial Y}{\partial x} \right) = 6xy^2 \\ Z = \left( \frac{\partial W}{\partial z} \right) = x & \left( \frac{\partial Y}{\partial z} \right) = 0 \\ & \left( \frac{\partial Z}{\partial y} \right) = 0 \end{cases}$$

$\therefore dW \text{ exact}$

$W =$

$$dW = \left( \frac{\partial W}{\partial x} \right)_{y,z} dx$$

$X$

If

$$\begin{cases} \left( \frac{\partial X}{\partial y} \right) \\ \left( \frac{\partial Y}{\partial z} \right) \\ \left( \frac{\partial X}{\partial z} \right) \end{cases}$$

$$\boxed{x^2} dy + \boxed{x^2} dz$$

$$\left(\frac{\partial Y}{\partial x}\right) = 2x$$

$$\left(\frac{\partial Z}{\partial y}\right) = 0$$

$$\left(\frac{\partial Z}{\partial x}\right) = 2x$$

exact.

$$V_1 \rightarrow V_2 \cdot \Delta V = \int dV$$

$$V = V(T, p) = ?$$

equation of state?

Ideal gas:  $pV = nRT$

## Ch 1. Introduction

Definitions of Terms

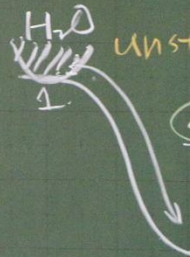
Heat  $\rightarrow$  Me

1. Why do we learn "Thermodynamics"?

What determines  
how matter behaves?

material  
subject

e.g. Energy



e.g. 2

Heat  $\rightarrow$  Mechanical Work

in "Thermodynamics"?

Energy

unstable

$\Delta E < 0$   $E_1$

(Equilibrium!!)  
stable

$E_{min}$

e.g. 2

$\rightarrow$  Mechanical Work

Thermodynamics"?

unstable

$\Delta E < 0$   $E_1$

(Equilibrium!!)  
stable

$E_{min}$

H<sub>2</sub>O  
T = 30°C P = 1 atm

Ice  $\rightarrow$  Water  
(-5°C)  $\Delta E < 0$

state 1  $\rightarrow$  state 2

$\Delta E = (E_2 - E_1) = ?$



→ Mechanical Work

nam:fs" ?

unstable

$\Delta E < 0$   $E \downarrow$

(Equilibrium)

stable

$E_{min}$

e.g. 2

$H_2O$

$T = 30^\circ C$   $P = 1 \text{ atm}$

Ice  $\rightarrow$  water

(-5C)  $\Delta E < 0$

state 1  $\rightarrow$  state 2

$\Delta E = (E_2 - E_1) = ?$

3 ✓ Macroscopic  $\rightarrow$  Classical.

Microscopic  $\rightarrow$  Statistical  $\rightarrow$  S. U.

atoms  
molecules  
electrons  
particles

distribution  
probability

← max. probability