Summary Notes on

CH 1201

Chemical Thermodynamics



Spring 2023

by

Susnata Chattopadhyay

[22MS077]

Course Instructor:

Shri Debansu Chaudhuri

Indian Institute of Science Education and Research, Kolkata,
Mohanpur, West Bengal, 741246, India.

THERMODYNAMICS

Energy · 8.314 · Molar Mass · Macroscopic

Temp. · Enthalpy · Gas const · Nature · Entropy $\frac{dq}{T}$

0. INTRODUCTION

System ⇒ Open — Mass + Energy ⇌

Closed — Energy ⇌

Isolated — None.

- System ∪ Surrounding = Universe
- ↳ boundary.
- state variables. ≠ f(T).
- system should be in Eqlbm for THM.

Note: • Any single-phase- 1 component system can be completely defined by only two state ϕ. variables.

0.1 Variables

Intensive - C_p, C_v, ρ, T.

Extensive - V, m, C (Heat cap), U

1. 0th Law - A-B in thermal Eqlbm, B-C " " " ⇒ A-C must also " " . } $T_A = T_B = T_C$

Temp. is direct measure of average KE of molecules. $T \propto \langle \bar{\varepsilon} \rangle$

DOMS

$(W_{rev})_{exp} > (W_{irrev})_{exp}$

1.1 Work



$W = \vec{F_x} \cdot d\vec{x}$

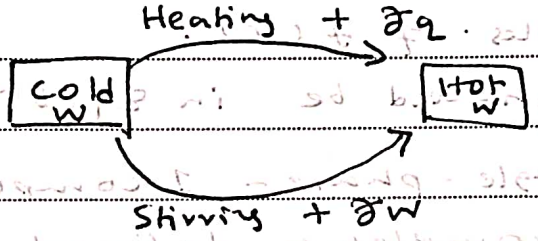
Comp. ⊕ → Surr works on system

Exp. ⊖ → Syst. work on Surr.

1.2 E, W, Q

Energy – State variable → dE

Heat / Work – Path variable – $\eth W$, $\eth q$



Work – Directional Motion

Heat – Random Motion

→ Same energy change thro' diff paths.

A process is REVERSIBLE if it can be reversed by an infinitesimal modification in some variable.

- System is in eqlbm with surrounding at each stage of the process.

2. Laws of Thermodynamics.

1st Law: $dU = dq + dW$

where $dW = \eth W_{exp} + \eth W_{add}$

$\eth W_{exp} = -pdV$

2nd Law $\Delta S_{univ} \geq 0$ for any spontaneous process

Fundamental Eqn (1+2) $dU = TdS - PdV$

* HEAT CAPACITIES

$dV = 0 \rightarrow dU = dq_V$

$\therefore C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$dP = 0 \rightarrow dH = dq_P$

$\therefore C_P = \left(\frac{\partial H}{\partial T}\right)_P$

For an ideal gas, for any process

$\Delta U = n C_{V,m} \Delta T$

$\Delta H = n C_{P,m} \Delta T$

□ $C_P - C_V = nR$

$\pi_T = \left[\frac{\partial U}{\partial V}\right]_T$

Internal pressure.

use:- $U = f(T,V)$, $PV = nRT$

const. pres. condition.

* JOULES' WORKS :-

1) Joule's Experiment → Free exp. of ideal gas, $dU = 0$

$U = f(T,V)$ $\left(\frac{\partial U}{\partial V}\right)_T = -C_V \frac{\Delta T}{\Delta V}$

DOMS

2) Joule Thomson Expt. Isenthalpic Process ($\Delta H_{JT} = 0$)

Achieved slow-throttling of gas.

$H = f(T, P)$

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P \cdot \mu_{JT}$$

where, $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$

Joule-Thomson Coefficient.

3) μ_{JT} → See Lennard Jones Potential graphs, Theory from Notes

$\mu_{JT} > 0$ $T \uparrow$ $P \uparrow$

$\mu_{JT} < 0$ $T \uparrow$ $P \downarrow$

$= 0$ (Ideal gas)

For Real gas, $(a = 0, b \neq 0)$

$$\mu_{JT} = -\frac{b}{C_P} < 0$$

⇒ Real gas expand → cool.

* ADIABATIC PROCESSES (isolated container)

$dq = 0$

$dU = dW$

$W = \frac{nR}{\gamma - 1}(T_2 - T_1)$

$PV^\gamma = C$

$TV^{\gamma-1} = C$

$= \frac{1}{\gamma - 1}(P_2V_2 - P_1V_1)$

DOMS

3. ENTROPY

$$dq_{rev} = TdS$$

$\Delta S_{sys} \Rightarrow \Delta S_{rev} = \Delta S_{irrev} = \dfrac{q_{rev}}{T}$

Spontaneous process $\Rightarrow$ Irreversible.

$$\Delta S_{surr} = \frac{q_{irrev}}{T} \quad (\because C_{v,surr} = \infty)$$

$W = 0$, $\Delta V \sim 0$.

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$

For spontaneity.

- Isothermal Exp. of Ideal gas.

$$\Delta S_{irrev} = nR \ln \frac{V_f}{V_i}$$

- Adiabatic Exp. of Ideal gas.

if Reversible $\rightarrow \Delta S = 0$.

$$\Delta S_{sys} = nR \ln \frac{V_f}{V_i} + n C_v \ln \frac{T_2}{T_1}$$

A reversible path can be constructed by

① Isochoric cooling

② ~~Isothermal~~ Isothermal Expansion.

$\Delta S_{irrev} > 0$

$\therefore (T_f)_{rev} < (T_f)_{irrev}$.

For any Reversible Process

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

MUST!!

DOMS

$dq_{irrev} = -P_{ex}\,dV$ ✍
(if $dV = 0$)

__/__/____

3.1) CRITERIONS FOR SPONTANEITY

$$dS - \frac{dq}{T} \geq 0$$

at $\delta w_{exp.} = 0$, $\delta w_{add} = 0$

3.1.1 $dV = 0$

$$(dU - TdS)_V \leq 0$$

$$\downarrow \qquad \downarrow$$

$$dS_{U,V} \geq 0 \quad \& \quad dU_{S,V} \leq 0$$

3.1.2 $dP = 0$

$$(dH - TdS)_P \leq 0$$

$$\downarrow$$

$$dS_{H,P} \geq 0 \quad \& \quad dH_{S,P} \leq 0$$

At eqlbm condition only!!

From both these eqns we obtain →

$$dA_{T,V} \leq 0 \quad \& \quad dG_{T,P} \leq 0$$

$$\rightarrow \quad \Delta S_{univ} \geq 0$$

- $(-dW)_{max} = (-dA_T)$ (RW process)
- $dW_{add,max} = dG_{T,P}$

DOMS

* 4.

Clausius Inequality: $dS \geq \frac{dq_{irrev}}{T}$

- Carnot's Theorem. $\oint_{cycle} dS = \oint \frac{dq_{rev}}{T} = 0$

For any arbitrary cyclic process.

$$\eta = \frac{W}{q_H} = 1 - \frac{q_L}{q_H} = 1 - \frac{T_L}{T_H}$$

- No Heat engine can be more efficient than a reversible Heat Engine.

$$\eta_{real} < \eta_{rev} < 1$$

- Gibbs Helmholtz Eqn: $\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_P = -\frac{H}{T^2}$

- Van't Hoff Eqn $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Important State Functions :-

- Enthalpy: $H = U + PV$
- Helmholtz Energy: $A = U - TS$
- Gibbs Energy: $G = H - TS$

DOMS

__/__/____

* 4

Important Exact Differentials

- $dU = \delta q + \delta W$
- $\delta W_{rev} = \delta W_{add} - pdV$
- $dH = dU + pdV + Vdp$
- $dG = dH - TdS - SdT$
- $dA = dU - TdS - SdT$

In rev. process,

$$\delta q = TdS$$

1) $dU = TdS - pdV$ $\quad U = f(S, V)$
2) $dH = TdS + Vdp$ $\quad H = f(S, P)$
3) $dA = -pdV - SdT$ $\quad A = f(V, T)$
4) $dG = Vdp - SdT$ $\quad G = f(P, T)$

Maxwell's Relations

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

2) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

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

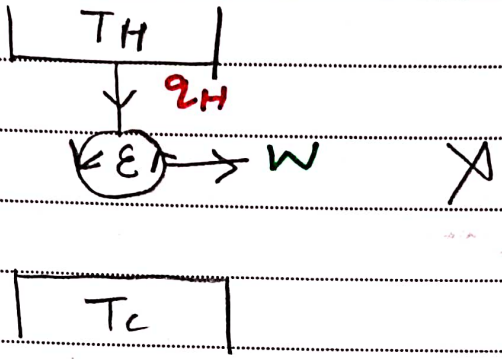
4) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

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

5. HEAT ENGINES & HEAT PUMPS.

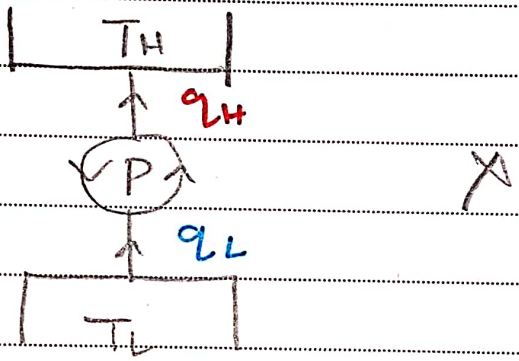
5.1 Kelvin-Planck Statement →

No Heat Engine (cyclic process) exists, such that $q_H = W$



5.2 Claussius statement

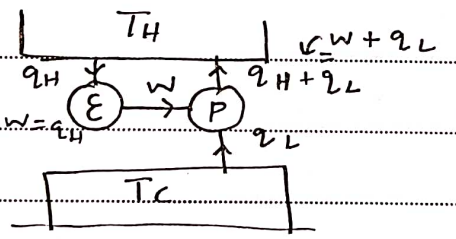
No Heat Pump / Refrig. (cyclic process) exists, such that $q_H = q_L$



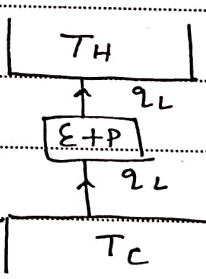
L=C

Equivalence

P + (5.1✗)

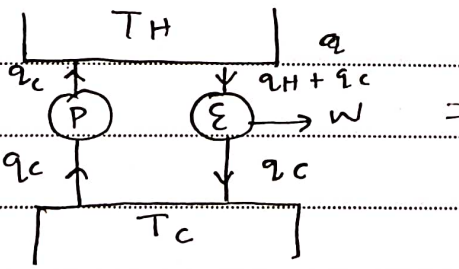


=

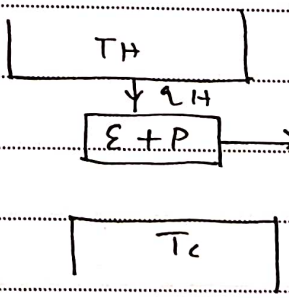


(5.2✗)

E + (5.2✗)



=



(5.1✗)