VI. Thermodynamic Potentials and Maxwell Relations

Consequences of → central equation $TdS = dU + pdV\ (-\mu dN)$

→ 2nd law $dS \geq \frac{dQ}{T_0}$ ("=" holds for reversible process & then $T_0 = T$ ← system)

A. Connecting Point of Thermodynamics and Statistical Mechanics

- Included for completeness

$$dS = \frac{1}{T}dU + \frac{p}{T}dV\ \left(-\frac{\mu}{T}dN\right)$$

(U, V, N: extensive variables; called "natural variables" as observed in dS)

$\Rightarrow$ if $S(U,V)$ OR $S(U,V,N)$ is known

then $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$; $\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$; $\frac{-\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V}$

Statistical Mechanics

"U" in thermodynamics

Boltzmann $S(E, V, N) = k \ln W(E, V, N)$

thermodynamics [macroscopic]

microstates for a system of N particles in a volume V having a total energy E

[microscopic] (Statistical Mechanics)

Using this connection is the method of Microcanonical Ensemble

(More on this later)

Now, we go back to U, H, F, G

B. Internal Energy U

$$dU = TdS - pdV$$

c.f. $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

dU: state function

"$U(S,V)$ is a surface"

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V, \quad p = -\left(\frac{\partial U}{\partial V}\right)_S} \quad (1)$$

If $U(S,V)$ is known, can obtain T and p.

Cross 2nd derivatives equal $\Rightarrow$ $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V} \quad (2)$$ Maxwell relation

Saw $\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$ (3), isochoric (constant V) and reversible $dQ_V = TdS$, $\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V}$ (4)

C. Enthalpy H

$$dU = TdS - pdV \quad \Rightarrow \text{Try to know } U(S,V), \text{ then other quantities follow.}$$

Don't like "V", prefer "p" (e.g. preparing for processes at constant pressure)

$$\boxed{H = U + pV} \quad (5)$$ (Legendre Transform, see picture discussed previously)

$$\boxed{dH = TdS + Vdp} \quad (6) \quad \Rightarrow \text{know } H(S,p), \text{ other quantities follow}$$

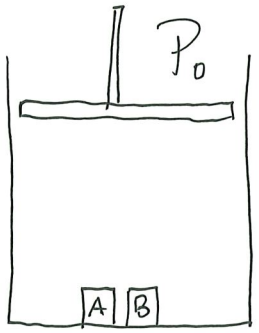
$$\boxed{\left(\frac{\partial H}{\partial S}\right)_p = T \text{ and } \left(\frac{\partial H}{\partial p}\right)_S = V} \quad (7)$$ (exact differential)

Cross 2nd derivatives equal $\Rightarrow$ $\boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$ (8) another Maxwell relation

Law $\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p}$ (9), isobaric (constant p) and reversible $dQ_p = TdS$, $\boxed{C_p = T\left(\frac{\partial S}{\partial T}\right)_p}$ (10)

Remarks on using ΔH

- Many processes in chemistry (chemical reactions) are carried out at a constant pressure



"Picture"

A and B reacts slowly, some gas produced

$P_{inside} \approx P_0$

(very close to equilibrium) despite reaction is irreversible

W = Work done by system

$$= P_0 \int_{V_1}^{V_2} dV = P_0 (V_2 - V_1)$$

then $\Delta H = Q_p$

Related Topics

- exothermic/endothermic reactions ($\Delta_r H < 0$, $\Delta_r H > 0$) ($\Delta_r H$: r ↑ reaction)
- Heat of reaction, thermochemistry
- $H(T)$ from $C_p(T)$ data
- Enthalpy of formation (tables)

} see Physical Chemistry books

D. Helmholtz Function F or Helmholtz Free Energy

Def: $\boxed{F = U - TS}$ (11) (another Legendre Transform, $U(S,V)$ → transform to T : $F(T,V)$)

$$dF = dU - TdS - SdT$$

$$= \cancel{TdS} - pdV - \cancel{TdS} - SdT$$

$$\boxed{dF = -SdT - pdV} \quad (12)$$

$dF = -SdT - pdV \; (+\mu dN)$

↳ This is an identity, relating quantities in an infinitesimal change.

From (12) : $F(T,V)$ or $F(T,V,N)$

c.f. $dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$

$$\boxed{\left(\frac{\partial F}{\partial T}\right)_V = -S; \quad \left(\frac{\partial F}{\partial N}\right)_T = -p} \quad (13)$$

also $\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$

↑ getting S and p from $F(T,V)$

Cross 2nd derivatives equal $\Rightarrow$ $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V$

or $\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$ (14) Another Maxwell Relation

Remarks on F

(a) ΔF is related to Work done by system in contact with a Heat Bath

Practical/Engineering viewpoint: Take "W" be Work Done by a system

- Newtonian Mechanics $W = -\Delta U$
- Thermodynamics (1st law) $\Delta U = Q - W$ → now by system for $W > 0$

$W = -\Delta U + Q$

$$W = -\Delta U + Q$$

so W can be larger or smaller than $-\Delta U$ depending on Q.

- A common situation is system in contact with Huge Heat Bath

"a process taking system from initial state A to final state B"

at temperature T_0 (of Bath)
(even some Q into (or out) system, bath is too big that its T_0 is unchanged)

We know $$\int_A^B \frac{dQ}{T_0} \leq S_B - S_A = \Delta S$$ (Clausius Theorem)

dQ = Heat into system in a segment of process (needs not reversible)

T_0 = source's (heat bath's) temperature

$$\therefore \quad \frac{1}{T_0}\int_A^B dQ \leq \Delta S \Rightarrow \underbrace{Q}_{\text{in process from A to B}} \leq T_0 \Delta S$$

[Meaning: Under the given situation, system takes in some Q, with value BOUNDED by $T_0 \Delta S$.
Only when process is reversible, system takes in $T_0 \Delta S = T \Delta S$]

There is $\Delta U = U_B - U_A$ as well

$$\therefore \underbrace{W}_{\text{by system when in contact with heat bath at } T_0} \leq \underbrace{U_A - U_B}_{-\Delta U} + T_0 \Delta S$$

Practical stuff emerging: W is bounded, best ("=") when process is reversible

State A (B) is equilibrium state [states in between? NOT sure! Don't care!]

system in contact with T_0 bath

Equilibrium $\Rightarrow$ state A and state B with temperature $T = T_0$ (System → T, Bath → T_0)

We do care about the two end points (with temp. equals to T_0 of bath)

$$W \leq U_A - U_B + T_0(S_B - S_A) = U_A - U_B + TS_B - TS_A$$

$$= -[(U_B - TS_B) - (U_A - TS_A)]$$

$$= -(F_B - F_A)$$ [Helmholtz functions]

$$\therefore \boxed{W \leq -\Delta F} \quad (15)$$ (contact with bath that controls the temperature)

not necessarily reversible → isothermal ← not implying $T = T_0$ every step in process

In words, Eq. (15) says...

(16) In a process in which the END POINT temperatures are the same as the heat bath (surroundings), the MAXIMUM WORK OBTAINABLE is equal to the DECREASE in the Helmholtz function.

$$\underbrace{F_A - F_B}_{\text{"drop in } F\text{"}} = \overbrace{-\Delta F}^{(F_B - F_A)} \quad \text{controls} \quad W_{max}$$

"hope that" it is positive (so W can be positive)

i.e. "Free" some Helmholtz function as useful Work

$F(T,V)$: Helmholtz Free Energy

Remark: $W = -\Delta F$ only when the (isothermal) process is reversible. Usually worse!

(b) Equilibrium Condition for system held at fixed V and in thermal contact with Heat Bath

T controlled by bath, V = constant ($dV = 0$)

heat transfer between system and bath

can't "exchange volume" with surroundings $\Rightarrow W = 0$

Eq. (15) with $W = 0$ is

$$0 \leq -\Delta F = \underbrace{F_A}_{\text{from A (higher)}} - \underbrace{F_B}_{\text{to B (lower)}} \quad \text{OR} \quad F_B \leq F_A \qquad (17)$$

$\leftarrow$ F dropping, OR at best the same

Helmholtz Free energy of system CANNOT increase in processes (fixed V, contact with heat bath). [Ban those with increasing F!]

[A consequence of 2nd law, where an inequality was introduced]

Given V (and N particles) fixed, system in contact with heat bath, if system starts from a state out-of-equilibrium†, the system will evolve in the "direction" of decreasing F (these are the naturally observed irreversible phenomena because the other way would increase F). When equilibrium is achieved, F attains a minimum.

Summary:

The condition for thermodynamic equilibrium in a system in thermal contact with a heat bath and held at a constant volume is that the Helmholtz Free Energy is a MINIMUM. (18)

Key to understand Canonical Ensemble Theory in Statistical Mechanics

† See Ch. I Sec. I on how to start a discussion from a non-equilibrium state

(c) $F = -kT \ln Z$ (Another connecting point)

Thermodynamics [Macroscopic] $\longleftrightarrow$ Statistical Mechanics [Microscopic]

For Systems with V, N, T ← fixed by Bath

$F(T, V, N)$ is the key function.

$Z(T, V, N)$ is the Partition Function (later...)

$F(T, V, N) \overset{\text{the bridge}}{=} -kT \ln Z(T, V, N)$

then S, p, μ, equation of state follow from doing partial derivatives!

E. Gibbs Function G_T or Gibbs Free Energy+

Def: $$\boxed{G_T = U + pV - TS = H - TS = F + pV} \quad (19)$$ (Legendre Transforms)

$$dG_T = dU + p\,dV + V\,dp - T\,dS - S\,dT$$

$$= (T\,dS - p\,dV) + p\,dV + V\,dp - T\,dS - S\,dT$$

$$\boxed{dG_T = V\,dp - S\,dT} \quad (20) \quad \text{or} \quad dG_T = V\,dp - S\,dT + \mu\,dN$$

$G_T(p,T)$ — p: intensive, T: intensive [c.f. $S(U,V)$, U, V: extensive]

$$\boxed{\left(\frac{\partial G_T}{\partial p}\right)_T = V \;;\; \left(\frac{\partial G_T}{\partial T}\right)_p = -S} \quad (21) \qquad \left(\frac{\partial G_T}{\partial N}\right)_{p,T} = \mu$$

+ Many discussions are analogous to those of F. We will skip some steps.

Cross 2nd derivatives equal: $\boxed{\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T}$ (22) Maxwell Relation[+]

(a) What $G_T(p,T)$ does?

In discussing F, we used a heat bath to fixed the temperature T_0 of heat in/out, then $-\Delta F$ sets $W_{max.}$

Here, we use (i) a heat bath to fix the temperature T_0 of heat in/out between system & heat bath AND (ii) a pressure bath (pressure reservior) that is at a pressure P_0 for work to be done on/by system by/on reservior.

[+] At this point, you have seen the four Maxwell's relations. Nothing fancy! Cross 2nd derivatives are equal.

In a process in which system starts at state A (T_0, p_0) and ends at state B (T_0, p_0) [no need to constraint what happens in between]

$$Q \leq T_0 \Delta S \qquad \text{(Clausius Theorem)}$$

$$\Delta U = Q - p_0 \Delta V \Rightarrow Q = \Delta U + p_0 \Delta V \qquad (1^{st}\ \text{Law})$$

(p_0: bath)

$\therefore$ $\Delta U + p_0 \Delta V \leq T_0 \Delta S$ or $\Delta U + p_0 \Delta V - T_0 \Delta S \leq 0$

End points have system and baths in equilibrium $T = T_0$, $p = p_0$

(T: system, T_0: bath, p: system, p_0: bath)

$\therefore$ $\Delta U + \Delta(PV) - \Delta(TS) \leq 0 \Rightarrow \underline{\Delta G \leq 0}$ (23) (dropping or at best not dropping)

for naturally allowed processes in system in thermal contact with heat bath and mechanical contact with pressure bath [end points that of baths]

It also follows (c.f. discussion on F) that the equilibrium condition is that the Gibbs function is A MINIMUM.

Summary

The condition for thermodynamic in a process in thermal and mechanical contact with a heat and pressure bath is that the Gibbs function is a minimum. (24)

"Connection" to Statistical Mechanics?

T-p ensemble theory (not often used)

Key idea in understanding phase transitions

(e.g. $G_{\text{liquid}}^{(\text{a mole})}$ vs $G_{\text{vapour}}^{(\text{a mole})}$)

which is lower for given T, p.

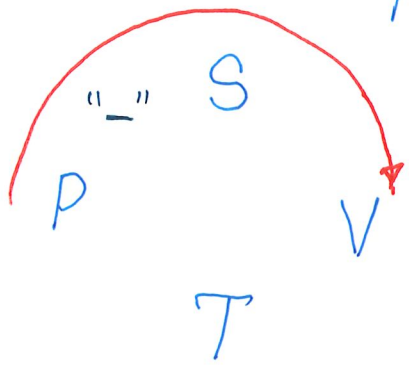
There is an analogous argument that $-\Delta G$ gives a bound on useful work when the system is constrained appropriately. (Skipped here.)

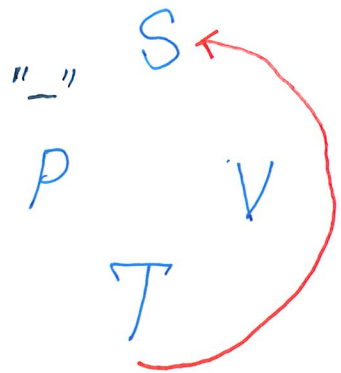
F. Maxwell Relations

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}_{\text{from } U} \quad ; \quad \underbrace{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}_{\text{from } H} \quad ; \quad \underbrace{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}_{\text{from } F} \quad ; \quad \underbrace{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}_{\text{from } G_T}$$

- Identities! (from central equation + partial differentiation)
- Be careful with $(\ )_{\square}$ ← condition
- Useful in expressing "strange" derivative $\left[\overbrace{-\left(\frac{\partial S}{\partial P}\right)_T}^{\text{e.g.}}\right]$ to meaningful one $\left[\overbrace{\left(\frac{\partial V}{\partial T}\right)_P}^{\text{expansion at constant pressure}}\right]$
- Derive them vs Memorize them (?)

This is NOT physics! A Pattern...

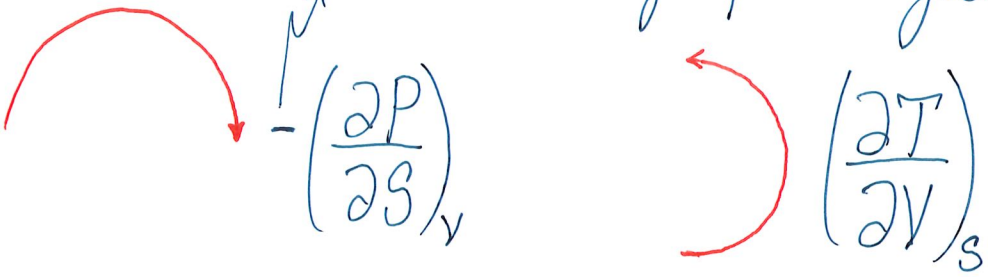




"−" means when S and P appear together in a derivative, there is a "−" sign

* start anywhere, left pattern goes clockwise
  right pattern goes anti-clockwise

this is the "−"



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

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

(the one from U)

But you need to memorize the pattern!

References

The discussions followed

- Finn, "Thermal Physics" and Adkins, "Equilibrium Thermodynamics"
- Fermi, "Thermodynamics" has a concise and masterful discussion on the thermodynamic potentials
- McQuarrie and Simon, "Physical Chemistry: A molecular approach" gives examples of chemistry applications