VII. Selected Topics

- To illustrate how thermodynamics works
- Get ready for Statistical Mechanics

A. $C_p - C_v = ?$ in general

[Many ways to do it. We start at a place after knowing 1st & 2nd laws]

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v \quad ; \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

"Bag of Tools"

- Partial derivatives: "-1" rule, reciprocal relation, total differential
- 1st law + 2nd law, Maxwell Relation
- Convert derivatives to experimentally accessible quantities

$\left(\frac{\partial S}{\partial T}\right)_V$ suggests thinking along $S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad (1)$$

$\left(\frac{\partial S}{\partial T}\right)_P$ suggests thinking along $S(T, P)$, $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$ (2)

But $V(P, T)$

good (i) there is equation of state
(ii) if "dV" in (1) is substituted by $(\,)dT + (\,)dP$, then we can compare (1) and (2). The $\left(\frac{\partial S}{\partial T}\right)_V$ and $\left(\frac{\partial S}{\partial T}\right)_P$ terms are already there.

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \qquad (3)$$

↑ substitute into (1)

(1) becomes $$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT\right]$$

$$= \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$ "almost done"

$$\Rightarrow \boxed{C_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P}$$

good know that $C_P > C_V$, does $T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P > 0$, is it obvious?

good $\left(\frac{\partial S}{\partial V}\right)_T$ is not friendly, but $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ Maxwell Relation

$$\therefore \quad C_p = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad (4)$$

Relate derivatives to experimental quantities (tabulated for materials)

Expansivity OR Volume thermal Expansivity (also called expansivity coefficient)

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Bulk Modulus K and Compressibility κ (kappa)

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

K and κ are positive for all known materials

But $\left(\frac{\partial P}{\partial T}\right)_V$ in (4) should "switch" to $\left(\frac{\partial P}{\partial V}\right)_T$ (to use K)

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

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

reciprocal rule →

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

$\therefore C_p = C_V + T\beta K V \beta$

$$\boxed{C_p = C_V + T\beta^2 K V} \quad (5) \quad \text{(General Result)}$$

$\underbrace{\qquad}_{>0}$

$\therefore C_p > C_V$

[can translate into other forms of work]

Ideal Gas: "Best Friend"

$pV = NkT$

$$\therefore \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{NkT}{p}\right)\right]_V = \frac{Nk}{pV} = \frac{1}{T}$$

$$K = -V\left(\frac{\partial p}{\partial V}\right)_T = -V\left(\frac{\partial}{\partial V}\frac{NkT}{V}\right)_T = \frac{NkT}{V} = p$$

$$C_p = C_V + T \cdot \frac{1}{T^2} \cdot p \cdot V = C_V + Nk$$

For 1 mole,

$$C_p = C_V + N_A k = C_V + R$$

(molar)

$$U(T) = \frac{3}{2}NkT \Rightarrow C_V = \frac{3}{2}Nk \qquad \therefore C_p = \frac{5}{2}Nk$$

or molar $C_V = \frac{3}{2}R$, $C_p = \frac{5}{2}R$

But $C_p = C_V + T\beta^2 K V$ is General

Aside: For those who only knows the 1st Law

$$dQ = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{constant } P$$

$$\therefore \frac{dQ_P}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad (4')$$

then apply (4') to different substances

If invoking 2nd law, $TdS = dU + PdV$

$$\Rightarrow T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P$$

and $C_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$, which is (4)

$$C_p = C_v + T\beta^2 K V \qquad (5)$$

↑ thermal properties

↗

↑ Bulk Modulus (Mechanical Property)

C_v is easier to calculate in Statistical Mechanics

C_p is often the measured quantity

B. $C_V(V)$?

- Ideal Gas (e.g.) $C_V = \frac{3}{2}Nk \Rightarrow$ No V-dependence in C_V OR $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$
- General Substances?

$$\left(\frac{\partial}{\partial V}C_V\right)_T = T\frac{\partial^2 S}{\partial V\,\partial T} = T\frac{\partial^2 S}{\partial T\,\partial V} = T\left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{=\left(\frac{\partial P}{\partial T}\right)_V}\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (6)$$

(Maxwell Relation)

Any substance, need equation of state $\mathcal{F}(P,T,V)=0$,
then Eq.(6) gives how C_V varies with V.

[Ideal gas: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V}$; $\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \Rightarrow$ C_V doesn't vary with V]

from $U = \frac{3}{2}NkT$ deceivingly simple!

Ex: How about $C_P(P)$?

C. Energy Equation

[Ideal Gas: $U = \frac{3}{2}NkT = U(T)$ only, but generally $U(T,V)$]

$$dU = TdS - PdV \qquad \text{identity}$$

in one step

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{(Maxwell Relation used)}$$

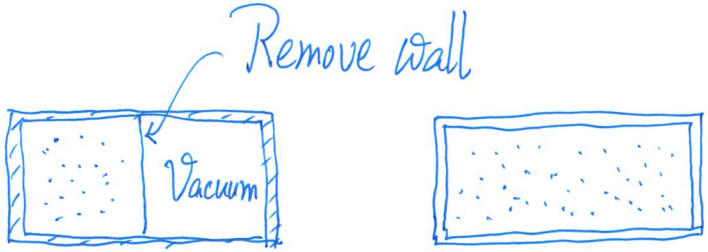
[how U varies with V]

$$\therefore \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \qquad (7) \qquad \text{(General)}$$

if equation of state is known, (7) gives information on U

[Ideal gas: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V}$; $T\frac{Nk}{V} - P = P - P = 0$] (deceivingly simple)

D. Free Expansion of Gases



[We did free expansion of ideal gas. $Q=0$, $W=0$, $\therefore \Delta U=0$, ideal gas $\Rightarrow$ T no change]

$Q=0$, $W=0$, $\therefore \Delta U=0$: true

ideal gas $\Rightarrow$ T no change: ideal gas

Real Gas: Temperature will drop

Need $\left(\frac{\partial T}{\partial V}\right)_U$ good

First, focus on what you want in applying thermodynamics

U: strange (unusual) constrain.

"-1" rule: $\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T = -1 \Rightarrow \left(\frac{\partial T}{\partial V}\right)_U = \frac{-1}{\left(\frac{\partial U}{\partial T}\right)_V} \cdot \left(\frac{\partial U}{\partial V}\right)_T$ (reciprocal rule)

$= -\frac{1}{C_V} \cdot \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$

needs eq. of state

$$\therefore \mu_J \equiv \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right] \quad (8)$$

μ_J: Joule coefficient (for Joule expansion (free expansion)) [Ideal gas: $\mu_J = 0$]

Real gas: $\frac{P}{kT} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + \cdots \Rightarrow P = \frac{NkT}{V} + B_2(T)\left(\frac{N}{V}\right)^2 kT$

$B_2(T)$: correction term†

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} + k\left(\frac{N}{V}\right)^2 B_2(T) + \left(\frac{N}{V}\right)^2 kT \frac{dB_2}{dT}$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = \underbrace{\frac{NkT}{V} + kT\left(\frac{N}{V}\right)^2 B_2(T)}_{P} + \left(\frac{N}{V}\right)^2 kT^2 \frac{dB_2}{dT}$$

$$\therefore \boxed{\mu_J = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right] = -\frac{1}{C_V}\left(\frac{N}{V}\right)^2 kT^2 \frac{dB_2}{dT}}$$

related to $B_2(T)$ ↑ due to interaction between gas molecules ["a" & "b" in Van der Waals Eq.]

Then, drop in temperature is

$$\Delta T = \int_{V_i}^{V_f} \mu_J \, dV = \int_{V_i}^{V_f} \left(\frac{\partial T}{\partial V}\right)_U dV$$ Done!

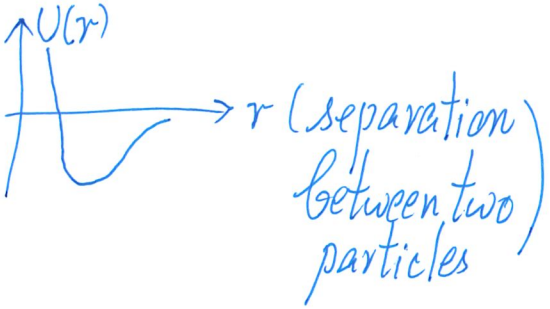
† One could start, e.g., with Van der Waals equation and obtain $B_2(T)$.

What is the physics? [Need microscopic View]

- U has k.e. + p.e. [ideal gas: k.e. only, special case!]

  p.e. due to inter-particle interaction

  p.e. is negative



- Now expansion (volume bigger) ⇒ separation farther

  p.e. less negative "increased"

To keep U, need k.e. decreases

T ≈ average k.e.

E. The Central Equation (revisited)

- dU can also be changed by introducing more matter (or taking away matter) from a system, i.e. a dN term
- Simplest Case: 1 species

$$\boxed{dU = TdS - pdV + \mu dN} \qquad (9)$$

μ is called the chemical potential

[will build up more sense on μ via Stat. Mech.]

$U(S, V, N)$

↑ ↑ ↑ all extensive

Within U,

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \qquad (10)$$

← change in U due to change in N when S and V are kept constant

Equivalently, $dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$ (11)

$S(U, V, N)$ (from Stat. Mech.) $\Rightarrow T, p, \mu$ by derivatives

all extensive

(thus Eq. of State)

Legendre Transforms

$H = U + pV$; $dH = TdS + Vdp + \mu dN$

$F = U - TS$; $dF = -SdT - pdV + \mu dN$ (12)

$F(T, V, N)$ (from Stat. Mech.) $\Rightarrow S, p, \mu$ by derivatives

Within F, $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$ ← change in F due to change in N keeping T and V constant

$$G_T = U + pV - TS, \qquad dG_T = -S\,dT + V\,dp + \mu\,dN \quad (13)$$

$G_T(T, p, N)$ — T, p: intensive; N: extensive

$$\mu = \left(\frac{\partial G_T}{\partial N}\right)_{T,p}$$

from here, there is a further development (stay tuned)

There is another one useful in Statistical Mechanics

$$\Omega = U - TS - \mu N$$

$$d\Omega = dU - T\,dS - S\,dT - \mu\,dN - N\,d\mu$$

$$= -S\,dT - p\,dV - N\,d\mu \quad (14)$$

$\Omega(T, V, \mu)$ — T, μ: intensive; V: extensive

(from Stat. Mech.) $\Rightarrow S, p, N$ from derivatives

Ω = Grand Potential

When there are several species (chemical components, e.g. $C + O_2 \rightarrow CO_2$)

(1) (2) (3)

$$dU = TdS - pdV + \sum_{i=1,2,3} \mu_i dN_i$$

(but we will treat 1 species only)

e.g. H_2O molecules

even so, still possible to consider H_2O in different phases

ice, water, vapor

F. Euler's Equation: Another Magical Moment

$U(S, V, N)$ function of extensive variables

Scaling system by λ: $S \to \lambda S$, $V \to \lambda V$, $N \to \lambda N$

U becomes λU

$$U(\lambda S, \lambda V, \lambda N) = \lambda\, U(S, V, N) \qquad (15)$$

meaning: Take the U function, substituting in the variables λS, λV, λN

meaning: Take the U function and time λ

Mathematically, Eq. (15) indicates that U is a Homogeneous Function of first order ($\because \lambda^1$ in front of $\lambda^1 U$).

Consider $\lambda = 1+\varepsilon$ $(\varepsilon \ll 1)$ (an infinitesimal increase in the system)

$$LHS = U\big((1+\varepsilon)S,\ (1+\varepsilon)V,\ (1+\varepsilon)N\big) = U(S,V,N) + \left(\frac{\partial U}{\partial S}\right)\varepsilon S + \left(\frac{\partial U}{\partial V}\right)\varepsilon V + \left(\frac{\partial U}{\partial N}\right)\varepsilon N + \cdots$$

Taylor series

$$= U(S,V,N) + T\cdot\varepsilon S - p\cdot\varepsilon V + \mu\cdot\varepsilon N + \underbrace{\cdots}_{O(\varepsilon^2)}$$

$$= U(S,V,N) + \varepsilon\,(TS - pV + \mu N)$$

Compare

$$= (1+\varepsilon)\,U(S,V,N) \qquad (RHS)$$

$$= U(S,V,N) + \varepsilon U$$

$$\therefore \quad \boxed{U = TS - pV + \mu N} \qquad (16) \quad \text{Euler's Equation}^{\dagger}$$

† This is related to the Euler's Theorem of Homogeneous Functions

Recall: Central Equation is an identity (generally true)

Its consequences are also generally true, including $C_p - C_v$, energy equation, μ_J, $\left(\frac{\partial C_v}{\partial V}\right)_T$, and Euler's Equation, and more

Another meaning of μ

- Recall: $G_T = F + pV = U - TS + pV$

Euler's Equation $\Rightarrow$ $U - TS + pV = \mu N$

$\therefore$ $G_T = \mu N$

OR $\mu = \frac{G_T}{N}$ Gibb's free energy per particle

[a "specific" (per particle) G_T] (see phase transitions)

Appendix: Homogeneous Functions (Euler's Theorem)

$$f(\underbrace{\lambda x}_{u}, \underbrace{\lambda y}_{v}, \underbrace{\lambda z}_{w}) = \lambda^p f(x,y,z)$$ Homogeneous Function of degree p

Differentiate LHS and RHS w.r.t. λ

$$\frac{\partial f}{\partial u}\cdot\frac{\partial u}{\partial \lambda} + \frac{\partial f}{\partial v}\cdot\frac{\partial v}{\partial \lambda} + \frac{\partial f}{\partial w}\cdot\frac{\partial w}{\partial \lambda} = p\lambda^{p-1} f(x,y,z)$$

$$x\frac{\partial f}{\partial u} + y\frac{\partial f}{\partial v} + z\frac{\partial f}{\partial w} = p\lambda^{p-1} f(x,y,z)$$

↳ True for any λ, including $\lambda = 1$ $(u=x,\ v=y,\ w=z)$

$$\therefore \boxed{x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = p f(x,y,z)}$$ Euler's Theorem (17)

In thermodynamics, degree 1, so $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = f(x,y,z)$

e.g. $S\cdot T - PV + \mu N = U$

G. Gibbs-Duhem Relation

$$U = TS - pV + \mu N$$

Total differential: $dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu$

$$= \underbrace{(TdS - pdV + \mu dN)}_{dU} + SdT - Vdp + Nd\mu$$

$$\therefore \boxed{SdT - Vdp + Nd\mu = 0} \quad (18)$$

↳ Gibbs-Duhem Relation[+]

[Useful in obtaining slope of phase boundary in phase transitions]

[+] There are other forms of "Gibbs-Duhem Relation", as one can start with other "forms" of the Euler Equation, such as $S = \frac{U}{T} + \frac{pV}{T} - \frac{\mu N}{T}$.