THERMODYNAMICS

ERNEST YEUNG ERNESTYALUMNI@GMAIL.COM

Contents

ABSTRACT. Everything about thermodynamics.
I also look at thermodynamics for engineers from a (theoretical and mathematical) physicists' point of view. I would like to seek more cross-polination between physicists and mathematicians and engineers in thermodynamics.

1. BACKGROUND

[1]

1.1. Heating and Temperature.
Heating: keep in mind 3 different types of heating for energy exchange between two systems:

(1) Heating by conduction - literal contact, molecules jiggle faster from molecules jiggling faster by bouncing off them
(2) Heating by radiation - em waves from hot source strike and excite target
(3) heating by convection - energy transport by flow (perhaps a fluid)

This all relates to

Q

1.2. Some dilute gas relationships.

Pressure according to kinetic theory. i.e. some kinetic theory

$F \equiv$ force on area A due to molecules

$\Delta p \equiv$ momentum transferred to wall per collision

$n \equiv$ number of collisions in time Δt

Thus

$$F = \frac{(\Delta p)n}{\Delta t}$$

Now $\Delta p = 2mv_x$ since $\Delta p = mv_x - (-mv_x) = 2mv_x$ (elastic collision with momentum conversation)

$v_x \Delta t A$ is a volume, inside of which gas molecules can be within distance $v_x \Delta t$ toward the wall.

$\frac{N}{V}$ number density of molecules

Assume equal distribution of velocities: Thus $\frac{1}{2}$

$$n = (v_x \Delta t A)\frac{1}{2}\frac{N}{V}$$

$$P = \frac{F}{A} = \frac{(2mv_x)(v_x\Delta t A)\frac{1}{2}\frac{N}{V}}{A\Delta t} = mv_x^2\frac{N}{V}$$

Suppose $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle = d\langle v_x^2 \rangle$.

$$\implies P = \frac{mN}{dV}\langle v^2 \rangle = \frac{2}{d}\frac{1}{2}m\langle v^2 \rangle\frac{N}{V}$$

An empirical gas law. Now

$$P = \frac{N\tau}{V} \quad \text{(empirical)}$$

$$\implies \frac{1}{2}m\langle v^2 \rangle = \frac{d}{2}\tau$$

1.3. The First Law of Thermodynamics.

$$dU = Q - W \text{ or } Q = dU + W$$

Consider $W = Q - dU$.

Consider path in M, γ, $\gamma : \mathbb{R} \to M = (U, V)$

$$\gamma(t) = (U(t), V(t))$$

$$\dot{\gamma} \in \mathfrak{X}(M), \dot{\gamma} = \dot{U}\frac{\partial}{\partial U} + \dot{V}\frac{\partial}{\partial V}$$

$$W(\dot{\gamma}) = pdV(\dot{\gamma}) = p\dot{V} = Q(\dot{\gamma}) - dU(\dot{\gamma}) = Q(\dot{\gamma}) - \dot{U}$$

Suppose $Q(\dot{\gamma}) = Q(t)dt(\dot{\gamma}\frac{\partial}{\partial t}) = Q(t)\dot{\gamma}$.

$$\int p\dot{V}dt = \int Q(t)\dot{\gamma}dt - \int \dot{U}dt$$

$$\implies p\Delta V = \Delta Q - \Delta U$$

$p\Delta V$ interpreted as work done by gas. ΔQ is heat transferred to gas system. $-\Delta U$ is the drop in internal energy of gas system as it does work.

1.4. Heat capacity.

$$Q = Q(\tau, V) = \left(\frac{\partial Q}{\partial \tau}\right)_V d\tau + \left(\frac{\partial Q}{\partial V}\right)_\tau dV$$

So define $C_V \equiv \left(\frac{\partial Q}{\partial \tau}\right)_V$ or interpret C_V as energy input by heating at constant volume over ensuing change in temperature.

In this case, $\left(\frac{\partial U}{\partial \tau}\right)_V$.

For the case of a monatomic gas, $U = \frac{d}{2}\tau N$, $\frac{\partial U}{\partial \tau} = \frac{d}{2}N$.

$$C_V = \frac{d}{2}N$$

$N \equiv$ number of molecules.

Now

$$\begin{array}{ll} Q = \Lambda_p dp + C_p d\tau & Q \wedge dp = C_p d\tau \wedge dp \\ Q = \Lambda_V dV + C_V d\tau & \implies Q \wedge dp = \Lambda_V dV \wedge dp + C_V d\tau \wedge dp \end{array}$$

Now from the thermodynamic identity, $Q = W + dU = pdV + dU$,

$$Q \wedge dp = pdV \wedge dp + dU \wedge dp$$

and from (empirical) ideal gas law, $pV = N\tau$ (which defines a hypersurface on M),

$$dpV + pdV = Nd\tau \implies pdV \wedge dp = Nd\tau \wedge dp$$

so then

$$Q \wedge dp = Nd\tau \wedge dp + dU \wedge dp$$

In the case of the monatomic gas, $U = \frac{d}{2}\tau N$, and so $dU = \frac{d}{2}Nd\tau = C_V d\tau$ and so comparing all the equations above, one recovers

$$C_p = N + C_V = \frac{2+d}{2}N$$

EY: 20151019 I'm curious to know how this all generalizes for C_V, C_P heat capacities, regardless of the type of molecule we consider.

The adiabatic relation for a classical ideal gas. Consider the adiabatic expansion (or contraction!) of a classical ideal gas. This means that $Q = 0$; there is no heat exchange to or from the gas system.

Recall $Q = dU + W$.

If $Q = 0$, and supposing $W = pdV$, then $0 = dU + pdV$.

EY : 20151019 Either by definition, or the thermodynamic identity, $\tau d\sigma = dU + pdV$, then $C_V := \left(\frac{\partial U}{\partial \tau}\right)_V$. My question is this: for manifold of thermodynamic states M, $M = (U, V)$, i.e. U is a global coordinate and V is a "local" coordinate. One can make a Legendre transformation such that M is parametrized by (τ, V), where τ is the temperature. In general, one should say that $U = U(\tau, V) \in C^\infty(M)$, and so $dU = \frac{\partial U}{\partial \tau} d\tau + \frac{\partial U}{\partial V} dV$, $dU \in \Omega^1(M)$.

However, for this adiabatic process, we want

$$Q = 0 = dU + W = dU + pdV = C_V d\tau + pdV$$

which implies that $dU = C_V d\tau$. What happened to the $\frac{\partial U}{\partial V} dV$? Is it that in this adiabatic process, the internal energy of the gas system goes to either doing work (expansion) or increases due to work being done on it (contraction), and is characterized completely by a drop or increase in its temperature, respectively? And so $dU = C_V \tau$, and pdV completely describes what's going on with work done or work done on it?

Nevertheless, using the (empirical) ideal gas law, $pV = N\tau$,

$$0 = C_V d\tau + pdV = C_V d\tau + \frac{N\tau}{V} dV$$

Consider a path $\gamma : \mathbb{R} \to M \qquad$ in M, so that $\dot\gamma(t) = \dot\tau \frac{\partial}{\partial \tau} + \dot V \frac{\partial}{\partial V} \in \mathfrak{X}(M)$.

$$\gamma(t) = (\tau(t), V(t))$$

Thus,

$$0 = C_v \dot\tau + \frac{N\tau}{V} \dot V \text{ so } \frac{\dot\tau}{\tau} + \frac{N}{C_V} \frac{\dot V}{V}$$

$$\xrightarrow{\int dt} \ln \frac{\tau_f}{\tau_i} + \frac{N}{C_V} \ln \frac{V_f}{V_i} = 0 \text{ or } \ln \tau V^{\frac{N}{C_V}} = \text{ const.}$$

Now

$$\frac{N}{C_V} = \frac{C_P - C_V}{C_V} = \gamma - 1$$

which is true, assuming the (empirical) ideal gas law, the thermodynamic identity, and, surely, for the case of a monatomic gas.

Thus

$$\tau_f V_f^{\gamma-1} = \tau_i V_i^{\gamma-1}$$

Problems. Problem 4. *Adiabatic compression.*

A diesel engine doesn't have a spark plug to ignite and explode the fuel. Instead, the air in the cylinder is compressed so highly that the fuel ignites spontaneously when sprayed into the cylinder.

(a)

$$\frac{\tau_f V_f^{\gamma-1}}{\tau_i V_i^{\gamma-1}} = \frac{P_f V_f^\gamma}{P_i V_i^\gamma} = 1$$

$$\tau_f = \left(\frac{V_i}{V_f}\right)^{\gamma-1} \tau_i$$

Run the Python script `thermo.py` to do the calculations. Here is (some of) the code from `thermo.py` for doing so (one still needs to import the necessary libraries):

```
roomtemp_K = KCconv.subs(T_C,20).rhs # room temperature in Kelvin

Prob0104ans = adia_tV.subs(gamma,1.4).subs(V_f,1).subs(V_i,15).subs(tau_i, roomtemp_K) # answer to Problem 4 of Chapter 1

Prob0104ans = N( Prob0104ans.lhs ) # 866.016969686253 K
Prob0104ansC = solve( KCconv.subs( T_K, Prob0104ans), T_C )[0] # 592.866969686253 C
```

```
solve( FCconv.subs( T_C, Prob0104ansC ), T_F)[0] # 1099.16054543526 F
```

The final temperature is $866.01\,K$ or $592.87\,C$ or $1099.16\,F$

(b) Now from the ideal gas law, which is obeyed at all thermodynamic states

$$\frac{P_f}{P_i} = \frac{V_i\,\tau_f}{V_f\,\tau_i}$$

and so $\frac{P_f}{P_i} = 44.31$

2. PRESSURE

cf. pp. 64 of Ch. 3 "Boltzmann Distribution and Helmholtz Free Energy", Kittel and Kroemer (1980) [2].

Consider a system of quantum states of energy ϵ_s.
Assume ϵ_s is a function of volume of the system.
Volume is decreased slowly from V to $V - \Delta V$ by an applied external force.
Let volume change take place sufficiently slowly so that system remains in the same quantum state s throughout compression.

$$\epsilon_s(V - \Delta V) = \epsilon_s(V) - \frac{d\epsilon_s}{dV}\Delta V + \cdots \equiv \text{energy of states after reversible volume change}$$

cf. Eq. (21) of Kittel and Kroemer (1980) [2], pp. 64, Ch. 3.

Now

$$U(V - \Delta V) - U(V) = \Delta U = -\left(\frac{d\epsilon_s}{dV}\right)\Delta V$$

cf. Eq. (22) of Kittel and Kroemer (1980) [2], pp. 64, Ch. 3.

Let A = area of 1 face of a cube.

Then

$$\Delta V = A(\Delta x + \Delta y + \Delta z) = A\Delta x + A\Delta y + A\Delta z$$

cf. Eq. (23) of Kittel and Kroemer (1980) [2], pp. 66, Ch. 3.

(Total) work done in compression is

$$\Delta U = p_s A(\Delta x + \Delta y + \Delta z) = p_s \Delta V$$

cf. Eq. (24) of Kittel and Kroemer (1980) [2], pp. 66, Ch. 3.

Then

$$p_s = -\left(\frac{\partial \epsilon_s}{\partial V}\right)$$

cf. Eq. (25) of Kittel and Kroemer (1980) [2], pp. 66, Ch. 3.

Take the average of $p_s = -\left(\frac{\partial \epsilon_s}{\partial V}\right)$ over all states of the ensemble to obtain the average pressure p:

(1)
$$\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$$

cf. Eq. (26) of Kittel and Kroemer (1980) [2], pp. 66, Ch. 3.

Entropy is held constant because the number of states in ensemble is unchanged in reversible compression.

Alternatively, consider that

$$dU = Q - pdV$$

Let $c = c(t) = (U, V) = (U(t), V(t))$ s.t. σ const. $\dot c = \dot U \frac{\partial}{\partial U} + \dot V \frac{\partial}{\partial V}$.

Let $t = V$. Then $\dot c = \left(\frac{\partial U}{\partial V}\right)_\sigma + \frac{\partial}{\partial V}$,

(2)
$$\implies dU(\dot c) = \left(\frac{\partial U}{\partial V}\right)_\sigma = -pdV(\dot c) = -p \implies \boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$$

We can also derive the following thermodynamic identity: for $U - U(\sigma, V)$, $dU = \tau d\sigma - pdV$, then for

$$\left(\frac{\partial U}{\partial \sigma}\right)_V = \tau$$

$$\left(\frac{\partial U}{\partial V}\right)_\sigma = -p$$

(3)
$$\Longrightarrow \boxed{-\left(\frac{\partial p}{\partial \sigma}\right)_V = \left(\frac{\partial \tau}{\partial V}\right)_\sigma}$$

For *another expression* for pressure p, consider that entropy σ is a function of internal energy U and volume V:

$$\sigma = \sigma(U, V)$$

$$d\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV$$

Let $c = (U, V)$ s.t. σ const., then

$$d\sigma(\cdot c) = 0 = \left(\frac{\partial \sigma}{\partial U}\right)_V \dot{U} + \dot{V}\left(\frac{\partial \sigma}{\partial V}\right)_U$$

Now

$$\frac{1}{\tau} := \left(\frac{\partial \sigma}{\partial U}\right)_V$$

Let $c = c(t) = (U(t), V(t))$ and $t = V$

$$\frac{1}{\tau}\left(\frac{\partial U}{\partial V}\right)_\sigma + \left(\frac{\partial \sigma}{\partial V}\right)_U = \frac{-p}{\tau} + \left(\frac{\partial \sigma}{\partial V}\right)_U = 0$$

$$p = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U$$

3. Phase Equilibrium

3.1. **Condition of coexistence; Coexistence of phases.** cf. Chapter 10: Phase Transformation, earlier sections of Kittel and Kroemer (1980) [2]; Subsection 3.5.2. "Coexistence of phases" of Le Bellac, Mortessagne, Batrouni (2004) [7]

The *condition of coexistence* is

$$\mu_1(\tau, p) = \mu_2(\tau, p)$$

For example $1 = g =$ gas

$2 = l =$ liquid

Then Taylor expand:

$$\mu_1(\tau_0, p_0) = \mu_2(\tau_0, p_0) = \mu_1(\tau_0, p_0) + \left(\frac{\partial \mu_1}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_1}{\partial \tau}\right)_p d\tau + \cdots = \mu_2(\tau_0, p_0) + \left(\frac{\partial \mu_2}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_2}{\partial \tau}\right)_p d\tau + \ldots$$

$$\Longrightarrow \frac{dp}{d\tau} = \frac{\left(\frac{\partial \mu_1}{\partial \tau}\right)_p - \left(\frac{\partial \mu_2}{\partial \tau}\right)_p}{\left(\frac{\partial \mu_2}{\partial p}\right)_\tau - \left(\frac{\partial \mu_1}{\partial p}\right)_\tau}$$

Now

$$G = N\mu(\tau, p)$$

and so define

$$\frac{1}{N}\left(\frac{\partial G}{\partial \tau}\right)_{N,p} = \frac{-\sigma}{N} \equiv -\widehat{\sigma} = \left(\frac{\partial \mu}{\partial \tau}\right)_{N,p}$$

$$\frac{1}{N}\left(\frac{\partial G}{\partial p}\right)_{N,\tau} = \frac{V}{N} \equiv v = \left(\frac{\partial \mu}{\partial p}\right)_{N,\tau}$$

and so

$$\Longrightarrow \frac{dp}{d\tau} = \frac{\widehat{\sigma}_2 - \widehat{\sigma}_1}{v_2 - v_1}$$

Equation 11 in Chapter 10 of Kittel and Kroemer (1980) [2] and Eq. 3.96 of Le Bellac, Mortessagne, Batrouni (2004) [7] agree.

Now consider $\tau N d\widehat{\sigma}$ for constant τ,

$$Q = \tau N d\widehat{\sigma} \Longrightarrow \int Q = \tau N(\widehat{\sigma}_2 - \widehat{\sigma}_1) \text{ or } \frac{\int Q}{N} = \tau(\widehat{\sigma}_2 - \widehat{\sigma}_1)$$

which is the heat added in the transfer.

Define the **latent heat of vaporization**

(4)
$$L := \tau(\widehat{\sigma}_2 - \widehat{\sigma}_1) \qquad \text{(latent heat of vaporization)}$$

For the change of volume when 1 molecule is transferred from liquid to gas or 1 to 2, Δv, $\Delta v \equiv v_2 - v_1$, and so

(5)
$$\left.\frac{dp}{d\tau}\right|_{\text{coexist}} = \frac{L}{\Delta v \tau}$$

3.2. **Latent heat.** p, T const., liquid $\to$ gas, e.g. $p = 1$ atm

$$T = 373\, K$$

latent heat of vaporization L_{vap} (by def.) amount of energy supplied by heating.

$Q = dU + W$

$\epsilon := U/N =$ average (internal) energy per molecule

$v := V/N =$ volume per molecule

$\quad L_{\text{vap}} = d\epsilon + pdV$

$\quad d\epsilon(\dot{\gamma}) = \epsilon_{\text{vap}} - \epsilon_{\text{liq}}$

$\quad dv(\dot{\gamma}) = v_{\text{vap}} - v_{\text{liq}} > 0$

if p const., $L_{\text{vap}} = d(\epsilon + pV) = dh$, $h := H/N = \frac{U+pV}{N}$

EY : 20151031 Another way to think about it is this: recall that

$$Q = dU + W = dU + pdV = \tau d\sigma$$

$$H = U + pV \text{ so } dH = dU + pdV + Vdp = Q + Vdp$$

Consider a path $\gamma \in M$ s.t. $d\tau(\dot{\gamma}) = 0$ \quad (constant τ, p)

$$dp(\dot{\gamma}) = 0$$

$$Q(\dot{\gamma}) = dH(\dot{\gamma}) - Vdp(\dot{\gamma}) = dH(\dot{\gamma}) - 0 = dH(\dot{\gamma}) \quad Q(\dot{\gamma}) = \tau d\sigma(\dot{\gamma})$$

$$\int Q(\dot{\gamma}) = \int \tau d\sigma(\dot{\gamma}) = \tau(\sigma_g - \sigma_l)$$

Thus

$$\frac{\int Q(\dot{\gamma})}{N} = \tau(s_g - s_l) = \frac{H_g}{N} - \frac{H_l}{N}$$

$$L \equiv \tau(s_g - s_l) = \frac{\int Q(\dot{\gamma})}{N} = \frac{1}{N}(H_g - H_l)$$

Latent heat versus heat capacity. Take slow, reversible process.

Now

$$C_V := \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_V$$

$$C_P := \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_P$$

It's stated in Kittel and Kroemer (1980), pp. 166, Equation (37), Chapter 6: Ideal Gas, Subsection "Heat capacity" [2], that

(6)
$$C_P = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_P = \left(\frac{\partial U}{\partial \tau}\right)_P + p \left(\frac{\partial V}{\partial \tau}\right)_p$$

Suppose $\sigma = \sigma(\tau, V)$. With $\tau d\sigma = dU + W = \tau d\sigma = dU + pdV$,

$$d\sigma = \frac{\partial \sigma}{\partial \tau} d\tau + \frac{\partial \sigma}{\partial V} dV = \frac{dU}{\tau} + \frac{p}{\tau} dV$$

$$d\sigma(\dot{\gamma}) = \left(\frac{\partial \sigma}{\partial \tau}\right)_V + 0 = \frac{1}{\tau} dU(\dot{\gamma}) = \frac{1}{\tau} \left(\frac{\partial U}{\partial \tau}\right)_V$$

Then it's clear that

$$\tau \left(\frac{\partial \sigma}{\partial \tau}\right)_V = \left(\frac{\partial U}{\partial \tau}\right)_V = C_V$$

Now suppose $\sigma = \sigma(\tau, p)$.

Consider also the enthalpy, $H = U + pV$, and so

$$dH = dU + V dp + pdV = \tau d\sigma + V dp$$

Now for $\sigma = \sigma(\tau, p)$,

$$\sigma = \sigma(\tau, p)$$
$$d\sigma = \frac{\partial \sigma}{\partial \tau} d\tau + \frac{\partial \sigma}{\partial p} dp = \frac{dH}{\tau} - \frac{V}{\tau} dp \implies d\sigma(\dot{\gamma}) = \left(\frac{\partial \sigma}{\partial \tau}\right)_p + 0 = \frac{1}{\tau}\left(\frac{\partial H}{\partial \tau}\right)_p - 0$$

So

$$C_p := \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial H}{\partial \tau}\right)_p$$

Now

$$dH(\dot{\gamma}) = dU(\dot{\gamma}) + V dp(\dot{\gamma}) + pdV(\dot{\gamma}) = \left(\frac{\partial U}{\partial \tau}\right)_p + 0 + p\left(\frac{\partial V}{\partial \tau}\right)_p = \left(\frac{\partial H}{\partial \tau}\right)_p \text{ so}$$

$$C_p = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p$$

Kittel and Kroemer (1980) [2] argues that for ideal gas,

$$\left(\frac{\partial U}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_V$$

since $U = U(\tau)$.

3.3. **Conditions for coexistence.** Sec. 12.3 of Baierlein (1999) [1].

Recall

$$G = F + pV = U + pV - \tau\sigma = G(\tau, p, N)$$

Now

$$G = G(\tau, p, N_{\text{vap}}, N_{\text{liq}}) \implies dG = \frac{\partial G}{\partial N_{\text{vap}}} dN_{\text{vap}} + \frac{\partial G}{\partial N_{\text{liq}}} dN_{\text{liq}} = \mu_{\text{vap}} 1 + \mu_{\text{liq}}(-1) = 0$$

$$\implies \mu_{\text{vap}}(\tau, p) = \mu_{\text{liq}}(\tau, p)$$

[4]

4. Properties of a Pure Substance

EY : 20151030 Is the word vapor the same as gas? vapour, gaz, gas, vapore

For coexistence equilibrium,

$$\mu_g(p_0, \tau_0) = \mu_l(p_0, \tau_0) \text{ and}$$
$$\mu_g(p_0 + dp, \tau_0 + d\tau) = \mu_l(p_0 + dp, \tau_0 + d\tau)$$

and so

(7)
$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v}$$

where $v \equiv \frac{V}{N}$, the so-called **vapor pressure equation** or **Clausius-Clapeyron** equation.

For (2) approximations, $\Delta v = v_g - v_l \approx v_g = \frac{V_g}{N_g}$ and idealize vapor as ideal gas, $pV = N\tau$ so $\frac{dp}{d\tau} = \frac{L}{\tau^2/p}$.

Second, if L constant,

(8)
$$p(\tau) = p_0 \exp\left(-L_0/\tau\right) \text{ or } \ln\left(\frac{p(\tau)}{p_0}\right) = \frac{-L_0}{\tau}$$

cf. Ch. 10 Phase Transformations, pp. 278-284, "Derivation of the Coexistence Curve, p Versus τ" of Kittel and Kroemer (1980) [2].

Eq. 8 explains the shape of the coexistence curve between solid and gas (vapor) (sublimation) and liquid and gas (vapor) (vaporization; vaporization curve).

Saturation is this $p = p(\tau)$ coexistence curve.

Isotherms, Isothermals

Recall $G = F + pV$ and so $dG = dF + V dp + pdV = dU - \tau d\sigma - \sigma d\tau + pdV + V dp = -\sigma d\tau + V dp$

$$F = U - \tau\sigma \qquad dG = -\sigma d\tau + V dp$$

So then $G = G(\tau, p)$

$$G = G(\tau, p, N)$$

where the latter statement is when we include particle transfer, so that

$$dG = -\sigma d\tau + V dp + \mu dN \text{ for } \mu = \mu(\tau, p)$$

For the *ideal gas*:

$$F(\tau, V) = F = -N\tau \left(\ln\left(\frac{n_Q}{n}\right) + 1\right)$$

$$\text{where } n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$$

$$n \equiv N/V = \frac{p}{\tau}$$

$$G(\tau, p, N) = -N\tau(\ln\left(\frac{n_Q}{n}\right) + 1) + N\tau = -N\tau(\ln\left(\frac{n_Q}{n}\right)) = -N\tau \ln\left(\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}\frac{\tau}{p}\right)$$

$$\text{so then } \left(\frac{\partial G}{\partial N}\right)_{\tau, p} = \mu = -\tau \ln\left(\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}\frac{\tau}{p}\right)$$

For the *Van der Waals gas*

$$F(vdW) = -N\tau\left(\ln\left(\frac{n_Q(V-Nb)}{N}\right)+1\right)-\frac{N^2a}{V}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = \frac{N\tau}{V-Nb}-\frac{N^2a}{V^2}$$

$$G(\tau,V,N) = \frac{N\tau V}{V-Nb}-\frac{2N^2a}{V}-N\tau(\ln\left(\frac{n_Q(V-Nb)}{N}\right)+1)$$

Nevertheless, consider, when considering isotherms, isothermals,

$$dG = -\sigma d\tau + V dp + \mu dN$$

Consider a path γ on constant τ, constant total number of particles N, and so

$$dG(\dot\gamma) = V dp(\dot\gamma) = G_g - G_l = \int_\gamma V dp$$

Part 1. **Thermodynamics (Revisited)**

Let Σ be a (topological) manifold of dim. 2.
Suppose U is a global coordinate on Σ. Then consider 1 chart (U,V).
Consider $\sigma = \sigma(U,V) \in C^\infty(\Sigma)$.
Recall the thermodynamic identity

$$\tau d\sigma = dU + pdV$$

Thus

$$d\sigma = \frac{1}{\tau}dU + \frac{p}{\tau}dV \implies \begin{array}{l} \frac{p}{\tau} = \left(\frac{\partial\sigma}{\partial V}\right)_U \\[2mm] \frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_V \end{array}$$

5. Heat Capacity

From Kittel and Kroemer (1980) [2], pp. 165-166, Chapter 6: Ideal Gas, "Heat Capacity",

$$Q = Q(\tau,p) = \Lambda_p dp + C_p d\tau = dU + W = dU + pdV$$

Let $c \in \Sigma$ s.t. $dp(\dot c) = 0$ (constant pressure). And so

$$Q(\dot c) = 0 + C_p d\tau(\dot c) = \tau d\sigma(\dot c) = dU(\dot c) + pdV(\dot c)$$

for $c = (\tau,0)$, $\dot c = \frac{\partial}{\partial\tau} \in T\Sigma$.

$$\implies C_p = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_p = \left(\frac{\partial U}{\partial\tau}\right)_p + p\left(\frac{\partial V}{\partial\tau}\right)_p$$

for heat capacity at constant pressure is larger than C_V because additional heat must be added to perform the work needed to expand volume of gas against constant pressure.

Now recall for enthalpy

$$H = U + pV$$
$$H = H(\sigma,p)$$

Then

$$dH = dU + pdV + Vdp = Q + Vdp$$

Thus, for $c \in \Sigma$, $dp(\dot c) = 0$ (constant pressure). Hence

$$dH(\dot c) = \left(\frac{\partial H}{\partial\tau}\right)_p = Q(\dot c) + 0 = C_p$$

Hence,

$$C_p = \left(\frac{\partial H}{\partial\tau}\right)_p = \left(\frac{\partial Q}{\partial\tau}\right)_p$$

6. Reactions

6.1. **Gibbs (review).** cf. Chapter 5: Chemical Potential and Gibbs Distribution of Kittel and Kroemer (1980) [2]
Recall that

$$F = U - \tau\sigma$$
$$dF = dU - \tau d\sigma - \sigma d\tau = -pdV - \sigma d\tau \text{ or } dF = +\mu dN - pdV - \sigma d\tau$$

so $F = F(\tau,V)$.
Total entropy of system + reservoir $\sigma = \sigma_\mathcal{R} + \sigma_\mathcal{S}$

$$\sigma = \sigma_\mathcal{R} + \sigma_\mathcal{S} = \sigma_\mathcal{R}(U - U_\mathcal{S}) + \sigma_\mathcal{S}(U_\mathcal{S}) \simeq \sigma_\mathcal{R}(U) - U_\mathcal{S}\left(\frac{\partial\sigma_\mathcal{S}}{\partial U_\mathcal{R}}\right)_{V,N} + \sigma_\mathcal{S}(U_\mathcal{S})$$

Now

$$\left(\frac{\partial\sigma_\mathcal{R}}{\partial U_\mathcal{R}}\right)_{V,N} \equiv \frac{1}{\tau}$$

and so

$$\sigma = \sigma_\mathcal{R}(U) - \frac{1}{\tau}U_\mathcal{S} + \sigma_\mathcal{S} = \sigma_\mathcal{R}(U) - F_\mathcal{S}/\tau$$

$F_\mathcal{S}$ must be a minimum with respect to $U_\mathcal{S}$ when system in its most probable state.
EY : 20151218 Consider $\sigma = \frac{U}{\tau} - \frac{F}{\tau}$, so

$$d\sigma = \frac{dU}{\tau} - \frac{U d\tau}{\tau^2} - \frac{dF}{\tau} + \frac{F}{\tau^2}d\tau$$

Consider curve $\gamma : \mathbb{R} \to \Sigma$, s.t. $d\tau(\dot\gamma) = 0$, i.e. γ represents a thermodynamic process at constant temeprature. System in thermal equilibrium with reservoir.
Now for every thermodynamic process, entropy must increase, and so

$$d\sigma(\dot\gamma) = \frac{dU}{\tau}(\dot\gamma) - \frac{dF(\dot\gamma)}{\tau} \geq 0$$

Thus, if $\int dU(\dot\gamma) < 0$, $\int dF(\dot\gamma) < 0$, and so F is a minimum.
If $d\sigma(\dot\gamma) = 0$, $dU(\dot\gamma) = dF(\dot\gamma)$. U is minimized, so F is minimized.
Consider $\mathcal{S}_1$, $\mathcal{S}_2$ in thermal and diffusive contact, $\mathcal{S}_1$, $\mathcal{S}_2$ in thermal contact with large reservoir, with V_1,V_2 held constant,

$$F = F_1 + F_2$$
$$N = N_1 + N_2 \text{ constant}$$

$$dF = \left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2} dN_2 = \left[\left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} - \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2}\right]dN_1 = 0$$

and so $\mu_1 = \mu_2$ for diffusive equilibrium.
Note that

$$(9)\qquad \mu(\tau,V,N) := \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$$

Example: Chemical potential of ideal gas. If $\mu_1 > \mu_2$, then $dF < 0$, when $dN_1 < 0$, *particles flow from high chemical potential to low chemical potential.*

Recall

$$F = -\tau[N \ln Z_1 - \ln N!]$$

$$Z_1 = n_Q V = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} V$$

Then

$$\mu = -\tau(\ln Z_1 - \ln N) = \tau \ln (N/Z_1)$$

$$\mu = \tau \ln (n/n_Q)$$

$$\mu = \tau \ln \left(\frac{p}{\tau n_Q}\right)$$

Note that the *total chemical potential* μ is

$$\mu = \mu_{\text{tot}} = \mu_{\text{ext}} + \mu_{\text{int}}$$

Examples of μ:

$$\mu = \tau \ln \left(\frac{n}{n_Q}\right) + q\Delta V$$

Example: Variation of barometric pressure with altitude.

$$\mu = \tau \ln \left(\frac{n}{n_Q}\right) + Mgh$$

6.1.1. *Chemical Potential and Entropy.* cf. pp. 131 of Kittel and Kroemer (1980) [2], Ch.5.

$$\sigma = \sigma(U, V, N)$$

$$\tau d\sigma = dU + pdV - \mu dN$$

$$-\left(\frac{\partial \sigma}{\partial N}\right)_{U,V} = \frac{\mu}{\tau}$$

6.2. **Gibbs Factor and Gibbs Sum.** cf. pp. 134 of Kittel and Kroemer (1980) [2], Ch.5. Consider system $\mathcal{S}$, with (N, ϵ_S), number of particles and internal energy, respectively, and reservoir $\mathcal{R}$, with $(N_0 - N, U_0 - \epsilon_S)$, in thermal and diffusive contact.

System probability $P(N, \epsilon_S) \propto g(N_0 - N, U_0 - \epsilon_S)$

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \frac{g(N_0 - N_1, U_0 - \epsilon_1)}{g(N_0 - N_2, U_0 - \epsilon_2)}$$

Now by definition of entropy, $g(N_0, U_0) \equiv \exp[\sigma(N_0, U_0)]$,

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \exp(\Delta\sigma) = \exp(\sigma(N_0 - N_1, U_0 - \epsilon_1) - \sigma(N_0 - N_2, U_0 - \epsilon_2)) = \exp\left[(N_1 - N_2)\frac{\mu}{\tau} - \frac{(\epsilon_1 - \epsilon_2)}{\tau}\right]$$

so

$$\exp\left[\frac{(N\mu - \epsilon)}{\tau}\right]$$

is the Gibbs factor.

Gibbs sum or grand sum or grand partition function $\mathcal{Z}$ is

$$\mathcal{Z}(\mu, \tau) = \sum_{N=0}^{\infty} \sum_{s(N)} \exp\left[(N\mu - \epsilon_{s(N)})/\tau\right] = \sum_{ASN} \exp\left[\frac{(N\mu - \epsilon_{s(N)})}{\tau}\right]$$

where ASN = overall states of the system for all number of particles.

Problem 3 **Potential energy of gas in gravitational field** of Chapter 5: Chemical Potential and Gibbs Distribution from Kittel and Kroemer (1980) [2]: "Consider a column of atoms each of mass M at temperature τ in a uniform gravitational field g."

Consider an infinitesimal layer at height h and at height $h + dh$. At each height h, the layers of atoms are in *diffusive* and *thermal equilibrium*, and so

$$\tau(h + dh) = \tau(h) = \tau$$

(thermal equilibrium) and

$$\mu(h + dh) = \mu(h)$$

(diffusive equilibrium).

Now for chemical potential $\mu = \mu(\tau, V, N)$,

$$\mu = \mu_{\text{int}} + \mu_{\text{ext}} = \tau \ln \left(n \left(\frac{2\pi\hbar^2}{M\tau}\right)^{3/2}\right) + Mgh$$

Thus, to first order,

$$\tau \frac{1}{n(h)} \frac{dn(h)}{dh} = -Mg \text{ or } n(h) = n(0) \exp\left(\frac{-Mgh}{\tau}\right)$$

The thermal average potential energy per atom is

$$\langle U \rangle = \frac{\int_0^\infty dh Mgh n(h)}{\int_0^\infty dh n(h)} = Mg \frac{\left[\frac{h\exp\left(\frac{-Mgh}{\tau}\right)}{-Mg/\tau} + -\frac{\exp\left(\frac{-Mgh}{\tau}\right)}{(-Mg/\tau)^2}\right]\Big|_0^\infty}{\left(\frac{\exp\left(\frac{-Mgh}{\tau}\right)}{-Mg/\tau}\right)\Big|_0^\infty} = Mg\frac{\tau}{Mg} = \boxed{\tau = \langle U \rangle}$$

From Ch.3, Eq. (64) of Kittel and Kroemer (1980) [2],

$$U = \frac{\sum_{\mathbf{n}} \epsilon_{\mathbf{n}} \exp[-\epsilon_{\mathbf{n}}/\tau]}{Z_1} = \tau^2 \frac{\partial \ln Z_1}{\partial \tau} = \frac{3\tau}{2}$$

So the total heat capacity per atom C is

$$C = \frac{\partial E}{\partial \tau} = \frac{\partial(\langle U \rangle + U)}{\partial \tau} = \frac{\partial}{\partial \tau}\left(\tau + \frac{3\tau}{2}\right) = \boxed{\frac{5}{2} = C}$$

6.3. **Gibbs Free Energy.** cf. Section "Gibbs Free Energy" of Ch. 9 Gibbs Free Energy and Chemical Reactions from Kittel and Kroemer (1980) [2]

Recall

$$F = U - \tau\sigma$$

$$dF = dU - \tau d\sigma - \sigma d\tau = -\sigma d\tau - pdV + \mu dN$$

where the *generalized* thermodynamic identity

$$dU = Q + W + \mu dN = \tau d\sigma - pdV + \mu dN$$

was used.

Now

$$G \equiv U - \tau\sigma + pV = F + pV$$

$$dG = dU - \tau d\sigma - \sigma d\tau + pdV + Vdp = \mu dN - \sigma d\tau + Vdp$$

and so $G = G(N, \tau, p)$.

Now

$$\sigma = \frac{1}{\tau}[U + pV - G]$$

$$\implies d\sigma = \frac{-1}{\tau^2}d\tau(U + pV - G) + \frac{1}{\tau}(dU + Vdp + pdV - dG)$$

Consider a curve $\gamma : \mathbb{R} \to \Sigma$ s.t. $dU(\dot\gamma) = dp(\dot\gamma) = dV(\dot\gamma) = 0$ corresponding to minimized internal energy, constant pressure, and constant volume. Then

$$d\sigma(\dot\gamma) = 0 + 0 + 0 + -dG(\dot\gamma) \geq 0$$

and so $dG(\dot\gamma) \leq 0$, so G must be a minimum, because $d\sigma(\dot\gamma) \geq 0$ represents the fact that entropy must always increase for any thermodynamic process. G must move to a minimum at equilibrium, i.e. "For any irreversible change taking place entirely within $\mathcal{S}$ will increase σ and thus decrease $G_{\mathcal{S}}$" [2] for $\mathcal{S}$ signifying the system.

τ, p are **intensive quantities**; they do not change value when 2 identical systems are put together.

U, σ, V, G are linear in N; their values doubles when 2 identical systems are put together; apart from interface effects U, σ, V, N, G are **extensive quantities**.

$$G = N\varphi(\tau, p)$$

$$\left(\frac{\partial G}{\partial N}\right)_{p,\tau} = \varphi(\tau,p) = \mu \implies G(N,\tau,p) = N\mu(\tau,p)$$

If more than 1 chemical species present,

(10)
$$\boxed{\begin{aligned} G &= \sum_j N_j \mu_j \\ \tau d\sigma &= dU + pdV - \sum_j \mu_j dN_j \\ dG &= \sum_j \mu_j dN_j - \sigma d\tau + V dp \end{aligned}}$$

6.4. **Summary of Thermodynamic Potentials.** With Eq. 10, I will summarize the thermodynamic potentials we have, obtained through Legendre transformations:

$$Q = dU - W = dU + pdV$$

For curve or thermodynamic process in Σ, γ, s.t. $dp(\dot\gamma) = 0$ (thermodynamic process at *constant pressure*),

$$Q(\dot\gamma) = dH(\dot\gamma) - V dp(\dot\gamma) = dH(\dot\gamma) - 0$$
$$\implies \int_\gamma Q(\dot\gamma) = \int dH(\dot\gamma) = H_f - H_i \qquad \text{for constant } p$$

with

$$H = U + pV$$
$$dH = dU + pdV + V dp = Q + V dp$$

For the thermodynamic potential

$$dU = \tau d\sigma - pdV$$
$$\boxed{U = U(\sigma, V)}$$
$$dU = \tau d\sigma - pdV + \sum_j \mu_j dN_j \qquad U = U(\sigma, V, N_j)$$
$$F = U - \tau\sigma$$

(11)
$$dF = dU - \tau d\sigma - \sigma d\tau = -pdV - \sigma d\tau \implies \boxed{F = F(\tau, V)}$$
$$dF = Q + W - d(\tau\sigma)$$
$$G = F + pV$$
$$dG = -\sigma d\tau + V dp \implies \boxed{G = G(\tau, p)}$$
$$dG = (Q - pdV) + pdV + V dp - d(\tau\sigma) = Q + V dp - d(\tau\sigma)$$

Let $\Delta H := H_f - H_i$.
If $\Delta H < 0$, $\int_\gamma Q(\dot\gamma) < 0$, heat transferred to surroundings: reaction is *exothermic*.

If $\Delta H > 0$, $\int_\gamma Q(\dot\gamma) > 0$, heat transferred to system: reaction is *endothermic*. Now $dH = Q + V dp$. Suppose $Q = C_p(\tau)d\tau$. then for constant presure, $dp(\dot\gamma) = 0$ and so

$$\int_\gamma dH = \Delta H = \int_\gamma C_p(\tau)d\tau$$

For constant volume, $dV(\dot\gamma_V) = 0$, and so

$$Q(\dot\gamma_V) \equiv Q_V = dU(\dot\gamma_V)$$

6.4.1. *Relations between derivatives of thermodynamic quantities.* For an adiabatic process, $Q = 0$.
For $Q = Q(\tau, V)$,

(12)
$$Q = \tau d\sigma = C_V d\tau + \left(\frac{\partial Q}{\partial V}\right)_\tau dV$$

and $\sigma = \sigma(\tau, V)$, so

(13)
$$\tau d\sigma = \tau \left(\frac{\partial\sigma}{\partial\tau}\right)_V d\tau + \tau \left(\frac{\partial\sigma}{\partial V}\right)_\tau dV$$

So by comparing terms between Eq. 12 and Eq. 13, conclude that

(14)
$$\left(\frac{\partial Q}{\partial V}\right)_\tau = \tau \left(\frac{\partial\sigma}{\partial V}\right)_\tau$$

For curve $c = c(t) = (\tau(t), V(t))$ s.t. $\sigma = \sigma(\tau, V) = $ constant,

$$\dot c = \dot\tau \frac{\partial}{\partial\tau} + \dot V \frac{\partial}{\partial V}$$
$$Q(\dot c) = 0 = C_V \dot\tau + \dot V \left(\frac{\partial Q}{\partial V}\right)_\tau \text{ or } \dot\tau = \frac{-\dot V}{C_V}\left(\frac{\partial Q}{\partial V}\right)_\tau$$

Let $t = V$. Let $\dot\tau = \left(\frac{\partial\tau}{\partial V}\right)_\sigma$, $\dot V = 1$. So using Eq. 14,

(15)
$$\left(\frac{\partial\tau}{\partial V}\right)_\sigma = \frac{-\tau}{C_V}\left(\frac{\partial\sigma}{\partial V}\right)_\tau$$

Likewise, for $Q = Q(\tau, p)$, $\sigma = \sigma(\tau, p)$,

$$Q = Q(\tau, p) = C_p d\tau + \left(\frac{\partial Q}{\partial p}\right)_\tau dp = \tau d\sigma = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_p d\tau + \tau\left(\frac{\partial\sigma}{\partial p}\right)_\tau dp$$

and repeating all steps for p, but instead using V (what I call "label symmetry"),

(16)
$$\left(\frac{\partial\tau}{\partial p}\right)_\sigma = \frac{-\tau}{C_p}\left(\frac{\partial\sigma}{\partial p}\right)_\tau$$

Divide Eq. 16 by Eq. 15:

(17)
$$\frac{\left(\frac{\partial\tau}{\partial p}\right)_\sigma}{\left(\frac{\partial\tau}{\partial V}\right)_\sigma} = \frac{C_V}{C_p}\frac{\left(\frac{\partial\sigma}{\partial p}\right)_\tau}{\left(\frac{\partial\sigma}{\partial V}\right)_\tau}$$

Since $F = F(\tau, V)$,

$$dF = -pdV - \sigma d\tau$$
$$\left(\frac{\partial F}{\partial\tau}\right)_V = -\sigma$$
$$\left(\frac{\partial F}{\partial V}\right)_\tau = -p$$

and it is sufficient that $\left(\frac{\partial F}{\partial \tau}\right)_V$, $\left(\frac{\partial F}{\partial V}\right)_\tau$ are continuous on a neighborhood of (τ, V) and $\frac{\partial^2 F}{\partial \tau \partial V}$ exists and is continuous on neighborhood of (τ, V), then

$$\left(\frac{\partial^2 F}{\partial \tau \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial \tau}\right)$$

(cf. search for Clairaut's Thm., mean value Thm., or Fubini's Thm.)

(18) $$\implies \left(\frac{\partial \sigma}{\partial V}\right)_\tau = \left(\frac{\partial p}{\partial \tau}\right)_V \qquad \text{(from Helmholtz's free energy } F)$$

Similarly, with the Gibbs free energy G given in Eq. 11, since $G = G(\tau, p)$,

$$dG = -\sigma d\tau + V dp$$

then

$$\left(\frac{\partial G}{\partial \tau}\right)_p = -\sigma$$

$$\left(\frac{\partial G}{\partial p}\right)_\tau = V$$

so

(19) $$-\left(\frac{\partial \sigma}{\partial p}\right)_\tau = \left(\frac{\partial V}{\partial \tau}\right)_p \qquad \text{(from Gibbs free energy } G)$$

Use Eqns. 18, 19 in Eq. 17:

(20) $$\frac{\left(\frac{\partial \tau}{\partial p}\right)_\sigma}{\left(\frac{\partial \tau}{\partial V}\right)_\sigma} = \frac{-C_V}{C_p} \frac{\left(\frac{\partial V}{\partial \tau}\right)_p}{\left(\frac{\partial p}{\partial \tau}\right)_V}$$

Consider an *adiabatic* process, such as adiabatic compression. Then $Q = \tau d\sigma = 0$. So choose curves in Σ s.t. σ is constant along the curve.

Let $\sigma(\tau, V), d\sigma = \left(\frac{\partial \sigma}{\partial \tau}\right)_V d\tau + \left(\frac{\partial \sigma}{\partial V}\right)_\tau dV$.
Let $c = c(t) = (\tau, p) = (\tau(t), p(t))$ s.t. σ constant. Then

(21) $$d\sigma(\dot{c}) = 0 = \left(\frac{\partial \sigma}{\partial \tau}\right)_V \dot{\tau} + \left(\frac{\partial \sigma}{\partial V}\right)_\tau \dot{p} \left(\frac{\partial V}{\partial p}\right)_\sigma \implies$$

$$\left(\frac{\partial V}{\partial p}\right)_\sigma = \frac{-\dot{\tau}\left(\frac{\partial \sigma}{\partial \tau}\right)_V}{\dot{p}\left(\frac{\partial \sigma}{\partial V}\right)_\tau} \xrightarrow{t=p} \frac{-\left(\frac{\partial \tau}{\partial p}\right)_\sigma \left(\frac{\partial \sigma}{\partial \tau}\right)_V}{\left(\frac{\partial \sigma}{\partial V}\right)_\tau}$$

Now let $c = c(t) = (\tau, V) = (\tau(t), V(t))$ s.t. σ constant.

$$d\sigma(\dot{c}) = 0 = \left(\frac{\partial \sigma}{\partial \tau}\right)_V \dot{\tau} + \left(\frac{\partial \sigma}{\partial V}\right)_\tau \dot{V} \text{ or } \frac{\left(\frac{\partial \sigma}{\partial \tau}\right)_V}{\left(\frac{\partial \sigma}{\partial V}\right)_\tau} = \frac{-\dot{V}}{\dot{\tau}} \xrightarrow{t=V} \frac{-1}{\left(\frac{\partial \tau}{\partial V}\right)_\sigma}$$

Then plugging in the previous expression into Eq. 21, we obtain

(22) $$\implies \left(\frac{\partial V}{\partial p}\right)_\sigma = \frac{\left(\frac{\partial \tau}{\partial p}\right)_\sigma}{\left(\frac{\partial \tau}{\partial V}\right)_\sigma}$$

Using label symmetry for $p, V \mapsto V, p$, then

$$\left(\frac{\partial p}{\partial V}\right)_\sigma = \frac{-\left(\frac{\partial \tau}{\partial V}\right)_\sigma \left(\frac{\partial \sigma}{\partial \tau}\right)_p}{\left(\frac{\partial \sigma}{\partial p}\right)_\tau} = \frac{\left(\frac{\partial \tau}{\partial V}\right)_\sigma}{\left(\frac{\partial \tau}{\partial p}\right)_\sigma} \text{ since}$$

$$\frac{\left(\frac{\partial \sigma}{\partial \tau}\right)_p}{\left(\frac{\partial \sigma}{\partial p}\right)_\tau} = \frac{-1}{\left(\frac{\partial \tau}{\partial p}\right)_\sigma}$$

The previous expression and its derivation from first principles (namely that $d\sigma$ is a 1-form on 2-dim. Σ and thermodynamic quantities are coordinates for Σ) leads me to strongly exhort the following: stop memorizing and using "hand-wavey" formulae that claim to transform partial derivatives "to different independent variables" such as the "Jacobians" in Landau and Lifshitz (1980) [5]), pp. 53, Ch. 11 "Thermodynamic Quantities", Sec. 16 "Relations between the Derivatives of Thermodynmaic Quantities", Eq. (IV) and related:

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(t, s)} \cdot \frac{\partial(t, s)}{\partial(x, y)}$$

or in Appendix 4, "Summary of Thermodynamic Relations", pp. 577 of Sabersky, et. al. (1998) [6], which claim that the "rules of differential calculus" (???) allows for some to write, for $z = z(x, y)$,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \text{ or}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

For the latter, the "differential", dx, dy is ill-defined. It is "an outdated concept from the time of Liebniz which was used to define derivatives and integrals before limits came along.". For the former, the "Jacobian" is not general enough (at least for me), being only applicable to Euclidean spaces and is another unnecessary formula to memorize.

Instead, consider the coordinate transformation of 2-dim. manifold Σ:

$$(\tau, V) \mapsto (\tau, p)$$

Consider then that in general, $p = p(\tau, V)$, so that

$$dp = \left(\frac{\partial p}{\partial \tau}\right)_V d\tau + \left(\frac{\partial p}{\partial V}\right)_\tau dV$$

Consider curve $c \subset \Sigma$, $c = c(t) = (\tau, p) = (\tau(t), p(t))$, so that

$$\dot{c} = (\dot{\tau}, \dot{p}) = \dot{\tau}\frac{\partial}{\partial \tau} + \dot{p}\frac{\partial}{\partial p}$$

Then

(23) $$dp(\dot{c}) = \dot{p} = \dot{\tau}\left(\frac{\partial p}{\partial \tau}\right)_V + \dot{p}\left(\frac{\partial p}{\partial V}\right)_\tau \left(\frac{\partial V}{\partial p}\right)_\tau$$

where we used the fact that $dV\left(\frac{\partial}{\partial \tau}\right) = 0$ (τ and V are still independent coordinates for Σ) and $dV\left(\frac{\partial}{\partial p}\right) = \left(\frac{\partial V}{\partial p}\right)_\tau$ since τ is held constant for the component of $\dot{c} \in \mathfrak{X}(\Sigma)$ in p (i.e. $\frac{\partial}{\partial p}$).

Consider letting parameter $t = V$ for c. Then

$$\dot{\tau} = \left(\frac{\partial \tau}{\partial V}\right)_p, \qquad \dot{p} = \left(\frac{\partial p}{\partial V}\right)_\tau$$

Consider letting $t = p$. Then $\dot{\tau} = \left(\frac{\partial \tau}{\partial p}\right)_V$ and $\dot{p} = 1$. V is help constant for $\dot{\tau} = \left(\frac{\partial \tau}{\partial p}\right)_V$ because of how $p = p(\tau, V)$ for

$$dp = \left(\frac{\partial p}{\partial \tau}\right)_V d\tau + \left(\frac{\partial p}{\partial V}\right)_\tau dV$$

so

(24)
$$\implies 1 = \left(\frac{\partial \tau}{\partial p}\right)_V \left(\frac{\partial p}{\partial \tau}\right)_V + \left(\frac{\partial p}{\partial V}\right)_\tau \left(\frac{\partial V}{\partial p}\right)_\tau$$

Plug in Eq. 24 into Eq. 23:

$$\dot{p} = \dot{\tau}\left(\frac{\partial p}{\partial \tau}\right)_V + \dot{p}\left[1 - \left(\frac{\partial \tau}{\partial V}\right)_p \left(\frac{\partial p}{\partial \tau}\right)_V\right] \implies \dot{p}\left(\frac{\partial \tau}{\partial V}\right)_p \left(\frac{\partial p}{\partial \tau}\right)_V = \dot{\tau}\left(\frac{\partial p}{\partial \tau}\right)_V \text{ or}$$

(25)
$$\boxed{\left(\frac{\partial p}{\partial V}\right)_\tau = \frac{\left(\frac{\partial \tau}{\partial V}\right)_p}{\left(\frac{\partial \tau}{\partial p}\right)_V}}$$

Consider the coordinate transformation $(\tau, p) \mapsto (\tau, V)$. By "label symmetry" (i.e. substitute p for V, V for p, for example),

(26)
$$\boxed{\left(\frac{\partial V}{\partial p}\right)_\tau = \frac{\left(\frac{\partial \tau}{\partial p}\right)_V}{\left(\frac{\partial \tau}{\partial V}\right)_p}}$$

In fact, furthermore, by label symmetry, consider $(\tau, p) \mapsto (\tau, \rho)$, $\rho \equiv$ density, then

(27)
$$\boxed{\left(\frac{\partial p}{\partial \rho}\right)_\tau = \frac{\left(\frac{\partial \tau}{\partial \rho}\right)_p}{\left(\frac{\partial \tau}{\partial p}\right)_\rho}}$$

Compare the previous expressions to the equation before (16.14) and (16.14) of Landau and Lifshitz (1980) [5], pp. 54,

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\partial(V,S)}{\partial(P,S)} = \frac{\partial(V,S)/\partial(V,T)}{\partial(P,S)/\partial(P,T)} \cdot \frac{\partial(V,T)}{\partial(P,T)} = \frac{(\partial S/\partial T)_V}{(\partial S/\partial T)_P} \cdot \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{C_V}{C_p}\left(\frac{\partial V}{\partial P}\right)_T$$

Similarly with Eq. (A-4.9a) on pp. 577 with Appendix 4 of Sabersky, et. al. (1998) [6]:

$$\left(\frac{\partial p}{\partial \rho}\right)_s = -\frac{(\partial s/\partial \rho)_p}{(\partial s/\partial p)_\rho} = -\frac{(\partial s/\partial T)_p(\partial T/\partial \rho)_p}{(\partial s/\partial p)_\rho(\partial T/\partial p)_\rho} = \frac{(\partial s/\partial T)_p}{(\partial s/\partial T)_\rho}\left(\frac{\partial p}{\partial \rho}\right)_T$$

The expression we'll need uses V:

$$V = V(\tau, p) \implies$$

$$dV = \left(\frac{\partial V}{\partial \tau}\right)_p d\tau + \left(\frac{\partial V}{\partial p}\right)_\tau dp$$

Let $c = (\tau, p)$ be a curve for when V is constant.

$$dV(\dot{c}) = 0 = \left(\frac{\partial V}{\partial \tau}\right)_p \dot{\tau} + \left(\frac{\partial V}{\partial p}\right)_\tau \tau\dot{p} \xrightarrow{t=\tau} -\left(\frac{\partial V}{\partial \tau}\right)_p = \left(\frac{\partial V}{\partial p}\right)_\tau \left(\frac{\partial p}{\partial \tau}\right)_V \text{ or}$$

(28)
$$\left(\frac{\partial V}{\partial p}\right)_\tau = -\frac{\left(\frac{\partial V}{\partial \tau}\right)_p}{\left(\frac{\partial p}{\partial \tau}\right)_V}$$

Using label symmetry for $V, p \mapsto p, V$, then also

$$\left(\frac{\partial p}{\partial V}\right)_\tau = -\frac{\left(\frac{\partial p}{\partial \tau}\right)_V}{\left(\frac{\partial V}{\partial \tau}\right)_p}$$

Then using both Eq. 22 and the previous equation in Eq. 20, then we get

(29)
$$\boxed{\left(\frac{\partial V}{\partial p}\right)_\sigma = \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_\tau}$$

This is the equation for the *adiabatic compressibility* $\left(\frac{\partial V}{\partial P}\right)_\sigma$ of a body. The inequality $C_p > C_v$ implies that adiabatic compressibility is always smaller in absolute value than isothermal compressibility. Compare this to Eq. (16.14) of Landau and Lifshitz (1980) and Eq. (A-4.10) of Appendix 4, "Summary of Thermodynamic Relations", pp. 577 of Sabersky, et. al. (1998) [6].

The previous equation can be expressed as

$$\left(\frac{\partial p}{\partial V}\right)_\sigma = \frac{C_p}{C_V}\left(\frac{\partial p}{\partial V}\right)_\tau$$

From the definition of density ρ, $\rho := \frac{MN}{V}$ or $V = \frac{MN}{\rho}$, and assuming N constant, then

$$\frac{\partial}{\partial V} = \frac{\partial \rho}{\partial V}\frac{\partial}{\partial \rho} = \frac{-MN}{V^2}\frac{\partial}{\partial \rho} = \frac{-\rho^2}{MN}\frac{\partial}{\partial \rho}$$

so that

$$\left(\frac{\partial p}{\partial \rho}\right)_\sigma = \frac{C_p}{C_V}\left(\frac{\partial p}{\partial \rho}\right)_\tau$$

6.5. Equilibrium in Reactions.
cf. Section Equilibrium in Reactions for Chapter 9: Gibbs Free Energy and Chemical Reactions of Kittel and Kroemer (1980) [2]

(30)
$$\nu_1 A_1 + \nu_2 A_2 + \cdots + \nu_l A_l = 0 \text{ or } \sum_j \nu_j A_j = 0$$

where $\nu_j \in \mathbb{Z}$, A_j chemical species, where we consider the finite set of chemical elements, and nonnegative integers $\mathbb{Z}^+$ for each element, signifying how many of the element in the molecule.

Now clearly,

$$dN_j = \nu_j d\widehat{N}$$

where $d\widehat{N} \equiv$ how many times reaction takes place.

Now

$$dG = \sum_j \mu_j dN_j - \sigma d\tau + V dp$$

and so for constant temperature, constant pressure,

$$dG = \sum_j \mu_j dN_j = \sum_j \mu_j \nu_j d\widehat{N}$$

then for equilibrium $dG = 0$,

(31)
$$\boxed{\sum_j \nu_j \mu_j = 0}$$

6.5.1. *Equilibrium for Ideal Gases.* cf. Subsection Equilibrium for Ideal Gases for Chapter 9: Gibbs Free Energy and Chemical Reactions of Kittel and Kroemer (1980) [2].

From Eq. (6.48) of Kittel and Kroemer (1980) [2],

$$\mu = \tau[\ln\left(\frac{n}{n_Q}\right) - \ln Z_{\text{int}}]$$

and so

$$\mu_j = \tau(\ln n_j - \ln c_j)$$

where

$$c_j \equiv n_{Q_j} Z_j(\text{int})$$

where

$$Z_j(\text{int}) = \sum_{\text{int}} \exp\left(\frac{-\epsilon_{\text{int}}}{\tau}\right)$$

Thus

$$\Longrightarrow \sum_j \nu_j \ln n_j = \sum_j \nu_j \ln c_j$$

and so the **law of mass action** is obtained:

(32)
$$\boxed{\prod_j n_j^{\nu_j} = K(\tau) \equiv \prod_j n_{Q_j}^{\nu_j} \exp\left(-\nu_j F_j(\text{int})/\tau\right)}$$

where

$$F_j(\text{int}) = -\tau \ln Z_j(\text{int})$$

From Problem 6 **Rotation of diatomic molecules** of Chapter 3: Boltzmann Distribution and Helmholtz Free Energy, Kittel and Kroemer [2],
rotational energy at level $j \in \mathbb{Z}^+$, $\epsilon(j) = j(j+1)\epsilon_0$
multiplicity $g(j) = 2j + 1$

$$Z_R = \sum_{j=0}^{\infty}(2j+1)\exp\left(\frac{1}{-\tau}j(j+1)\epsilon_0\right) = \frac{-\tau}{\epsilon_0}\sum_{j=0}^{\infty}\frac{d}{dj}\left[(e^{-\epsilon_0/\tau})^{j^2+j}\right]$$

For $1 \gg \frac{\epsilon_0}{\tau}$,

$$Z_R(\tau) = \frac{-\tau}{\epsilon_0}\int_0^{\infty}\frac{d}{dx}\left[(e^{-\epsilon_0/\tau})^{x^2+x}\right] = \frac{\tau}{\epsilon_0}$$

So

$$F_R = -\tau \ln Z_R = -\tau \ln\left(\frac{\tau}{\epsilon_0}\right)$$

and

$$\exp\left(-\nu_j F_j(\text{int})/\tau\right) = \exp\left(\nu_j \ln\left(\frac{\tau}{\epsilon_{0;j}}\right)\right) = \exp\left(\nu_j \ln\left(\frac{\tau}{\epsilon_{0;j}}\right)\right) = \left(\frac{\tau}{\epsilon_{0;j}}\right)^{\nu_j}$$

and so

$$K(\tau) = \prod_j (n_{Q_j})^{\nu_j}\left(\frac{\tau}{\epsilon_{0;j}}\right)^{\nu_j} = \prod_j \left[\left(\frac{M_j\tau}{2\pi\hbar^2}\right)^{d/2}\frac{\tau}{\epsilon_{0;j}}\right]^{\nu_j}$$

---

[1] Phase change data for Oxygen
[2] http://webbook.nist.gov/cgi/cbook.cgi?ID=C7782447&Mask=4#Thermo-Phase

7. PHASE EQUILIBRIUM

: Phase Equilibrium
: Phase Diagram
: (Phase) Coexistence Curve
: Antoine Equation (parameters)

For coexistence equilibrium, $\mu_g(p_0, \tau_0) = \mu_l(p_0, \tau_0)$ and $\mu_g(p_0 + dp, \tau_0 + d\tau) = \mu_l(p_0 + dp, \tau_0 + d\tau)$, and so $\frac{dp}{d\tau} = \frac{L}{\tau\Delta v}$ with $v \equiv \frac{V}{N}$.

Make the approximation that $\Delta v \equiv v_g - v_l \approx v_g = \frac{V_g}{N_g}$ and idealize vapor as ideal gas, $pV = N\tau$, so $\frac{dp}{d\tau} = \frac{L}{\tau^2/p}$.

If L constant,

(33)
$$p(\tau) = p_0 \exp\left(-L_0/\tau\right) \text{ or } \ln\left(\frac{p(\tau)}{p_0}\right) = \frac{-L_0}{\tau}$$

Consider the Antoine Equation Parameters given in the NIST (National Institute of Standards and Technology) Chemistry WebBook [1]

(34)
$$\log_{10}(P) = A - (B/(T + C))$$

Then

$$P = 10^{A=\frac{B}{T+C}} = 10^A 10^{-\frac{B}{T+C}} = 10^A \exp\left(\frac{-B}{T+C}\ln 10\right)$$

Now $\frac{D}{T+C} = \frac{D}{T} - \frac{DC}{T(T+C)}$, and so

$$P = 10^A \exp\left(\frac{(B\ln 10)C}{T(T+C)}\right)\exp\left(\frac{-B\ln 10}{T}\right)$$

Consider how much the pressure is changed due to this C parameter. Consider P_0, P_1, defined as such:

$$P_0 = 10^A \exp\left(\frac{-B\ln 10}{T}\right) \quad P_1 = 10^A \exp\left(\frac{(B\ln 10)C}{T(T+C)}\right)\exp\left(\frac{-B\ln 10}{T}\right) \Longrightarrow \frac{P_0}{P_1} = \exp\left(\frac{(B\ln 10)C}{T(T+C)}\right)$$

So a deviation can be estimated from $1 - \frac{P_0}{P_1}$.

Open up `thermochem.py`. The *saturation curve* or *coexistence curve* for, for example, oxygen, from liquid to gas, can be reproduced. One needs to input in the Antoine parameters from the NIST website [2]

```
>>> O2coec = CoexistCurve(3.85845, 325.675, -5.667 )
>>> plot( O2coec.curveSI.rhs, (T,54.36,100.16) )

>>> N(O2coec.curveSI.rhs.subs(T,60.))
731.804072053687
>>> N(O2coec.curveSI.rhs.subs(T,70.))
6253.42680398774
>>> N(O2coec.curveSI.rhs.subs(T,75.))
14494.1195824433
```

8. Ideal gas (summary)

The gist of concepts involving the ideal gas, from Chapters 3,5,6 of Kittel and Kroemer [2] are the following. Consider the partition function for 1 atom in a box, Z_1

$$Z_1 = \frac{n_Q}{n} = n_Q V \text{ where } n_Q := \left(\frac{M\tau}{2\pi\hbar^2} \right)^{d/2}$$

where d is the dimension of space, usually $d = 3$.

From Kittel and Kroemer (1980) [2], Example : N atoms in a box, Chapter 3: "Boltzmann Distribution and Helmholtz Free Energy",

state of energy $\epsilon_\alpha(1) + \epsilon_\beta(2) + \cdots + \epsilon_\xi(N)$, $\alpha, \beta, \ldots \xi$ denote orbital indces of atoms in successive boxes.
each entry occurs $N!$ times in Z_1^N (EY: 20151022) $N!$ ways to fill $\alpha, \beta \ldots \xi$ orbitals with N distinguishable particles. Thus,

$$Z_N = \frac{1}{N!} Z_1^N = \frac{1}{N!} (n_Q V)^N$$

Then for N *indistinguishable particles*, the partition function of the system Z_N is

(35)
$$Z_N = \frac{1}{N!} Z_1^N = \frac{1}{N!} (n_Q V)^N$$

Then the Helmholtz free energy F is

(36)
$$F = -\tau \ln Z_N = -\tau \left[N \ln (n_Q V) - (N \ln N - N) \right] = \tau N \left[\ln \left(\frac{n}{n_Q} \right) - 1 \right]$$

and so

$$\frac{\partial F}{\partial \tau} = -N \ln \left(\frac{n_Q V}{N} \right) - N - \tau N \frac{d}{2} \frac{1}{\tau} = -N \left[\ln \left(\frac{n_Q}{n} \right) + \left(\frac{d}{2} + 1 \right) \right]$$

(37)
$$\sigma = \frac{-\partial F}{\partial \tau} = N \left[\ln \left(\frac{n_Q}{n} \right) + \left(\frac{d}{2} + 1 \right) \right]$$

Also, from using

$$F := U - \tau\sigma$$
$$dF = dU - \tau d\sigma - \sigma d\tau = -pdV - \sigma d\tau$$

then

$$p = \frac{\tau N}{V} \text{ or } pV = \tau N$$

Keep in mind that

$$\mu(\tau, V, N) \equiv \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$$

I shall attempt to generalize the Sackur-Tetrode equation to consider vibrational and rotational energy modes, and so we should review its derivation.

Consider the example of a molecule with translational *and* rotational degrees of freedom. Note that $\mathbf{n} = (n_x, n_y, n_z)$ are good quantum numbers discretizing the translational degrees of freedom, and $j \in \mathbb{N} = \{0, 1, \ldots\}$ is a good quantum number discretizing the rotational degrees of freedom. Then the energy (eigenvalue) for quantum state (described by particular values of) $\mathbf{n}, j$ is

$$\epsilon_{\mathbf{n},j} = \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2 \mathbf{n}^2 + j(j+1)\epsilon_0 \equiv \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) + j(j+1)\epsilon_0$$

keeping in mind the multiplicity of the energy state from the multiplicity of the rotational energy, $g(j) = 2j + 1$.

Then

$$\exp\left(-\frac{1}{\tau} \epsilon_{\mathbf{n},j} \right) = \exp\left(-\frac{\hbar^2}{2M\tau} \left(\frac{\pi}{L} \right)^2 \mathbf{n}^2 \right) e^{j(j+1)\epsilon_0}$$

---

[3] http://www.physics.umd.edu/courses/Phys404/Anlage_Spring11/hw8solv5.pdf

Then the partition function for *1* molecule in a box is

$$Z_1 = \sum_{\mathbf{n},j} g(j) \exp\left(\frac{-\hbar^2}{2\pi\tau} \left(\frac{\pi}{L} \right)^2 \mathbf{n}^2 \right) e^{j(j+1)\epsilon_0} = \sum_{\mathbf{n}} \exp\left(\frac{-\hbar^2}{2\pi\tau} \left(\frac{\pi}{L} \right)^2 \mathbf{n}^2 \right) \sum_j g(j) e^{j(j+1)\epsilon_0} = n_Q V \cdot \sum_j g(j) e^{j(j+1)\epsilon_0} =$$

$$= n_Q V \frac{\tau}{\epsilon_0}$$

with $n_Q := \left(\frac{M\tau}{2\pi\hbar^2} \right)^2$.

From the indistinguishability of quantum particles, for N of these particles,

$$Z_N = \frac{(n_Q V \frac{\tau}{\epsilon_0})^N}{N!}$$

and noting that

$$\ln Z_N = N \left[\ln (n_Q V) + \ln \left(\frac{\tau}{\epsilon_0} \right) \right] - \ln N! \simeq N \ln \left(\frac{n_Q}{n} \right) + N \ln \left(\frac{\tau}{\epsilon_0} \right) + N$$

then

$$F := -\tau \ln Z_N = -\tau N \left[\ln \left(\frac{n_Q}{n} \right) + 1 \right] + -\tau N \ln \left(\frac{\tau}{\epsilon_0} \right) \equiv -\tau N \left[\ln \left(\frac{n_Q}{n} \right) + 1 \right] + F(\text{int})$$

$$\sigma := -\left(\frac{\partial F}{\partial \tau} \right) = N \left[\ln \left(\frac{n_Q}{n} \right) + \left(\frac{d}{2} + 1 \right) \right] + N \left(\ln \left(\frac{\tau}{\epsilon_0} \right) + 1 \right)$$

Examining the steps above, it's clear how to generalize to when the form of the energy eigenvalues in the vibrational and rotational degrees of freedom (internal degrees of freedom), described by quantum numbers $\mathbf{k}$, is unknown:

$$\epsilon_{\mathbf{n},\mathbf{k}} = \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2 \mathbf{n}^2 + \epsilon'_{\text{int}}(\mathbf{k})$$

$g(\mathbf{k}) \in \mathbb{Z}^+$ is the multiplicity of the internal degrees of freedom

$$Z_1 = n_Q V \cdot Z_{1,\text{int}} \text{ with } Z_{1,\text{int}} = \sum_{\mathbf{k}} g(k) e^{-\frac{1}{\tau} \epsilon'_{\text{int}}(\mathbf{k})}$$

$$Z_N = \frac{(n_Q V)^N}{N!} (Z_{1,\text{int}})^N \implies \ln Z_N = N \left(\ln \left(\frac{n_Q}{n} \right) + 1 \right) + N \ln Z_{1,\text{int}}$$

$$F = -\tau N \left[\ln \left(\frac{n_Q}{n} \right) + 1 \right] + F(\text{int})(\tau)$$

$$\sigma = N \left[\ln \left(\frac{n_Q}{n} \right) + \left(\frac{d}{2} + 1 \right) \right] + \sigma_{\text{int}}$$

with $F(\text{int})(\tau)$ emphasizing that we could surmise or conjecture that the Helmholtz free energy contribution due to internal degrees of freedom can be a function of temperature τ (cf. Eq. (42.4) of Landau and Lifshitz (1980) [5]).

9. Mixtures of ideal gases

9.1. Gibbs paradox.
Kittel and Kroemer (1980) [2] Problem 6 **Entropy of mixing** of Chapter 6: Ideal Gas,

Prof. Steven Anlage, Introduction to Thermodynamics and Statistical Mechanics, Spring 2011, University of Maryland Physics 404, Homework 8 Solutions, Question 9, [3]

Consider adding together the entropies of ideal gas A with initial volume V, and molecular mass M_A (so it has a n_{Q_A} quantum concentration), and of ideal gas B with initial volume V, molecular mass M_B, n_{Q_B} quantum concentration:

$$\sigma_{\text{initial}} = \sigma_A + \sigma_B = N_A \ln \left(\frac{n_{Q_A} V}{N_A} \right) + N_A \left(1 + \frac{d}{2} \right) + N_B \ln \left(\frac{n_{Q_B} V}{N_B} \right) + N_B \left(1 + \frac{d}{2} \right)$$

After diffusive equilibrium is reached means that each of the gases now occupy a volume $2V$, gas A is free to roam in volume $2V$, as is gas B. Thus, the entropy increases:

$$\sigma_{\text{final}} = N_A \ln\left(\frac{n_{Q_A} 2V}{N_A}\right) + N_A\left(1 + \frac{d}{2}\right) + N_B \ln\left(\frac{n_{Q_B} 2V}{N_B}\right) + N_B\left(1 + \frac{d}{2}\right)$$

and so

$$\Delta\sigma = (N_A + N_B)\ln 2 = 2N\ln 2 \ \text{(if } N_A = N_B = N)$$

In general,

$$\Delta\sigma = N_A \ln\left(\frac{V_A + V_B}{V_A}\right) + N_B \ln\left(\frac{V_A + V_B}{V_A}\right)$$

For identical atoms ($A \equiv B$),

$$\sigma_A = N\ln\left(\frac{n_Q V}{N}\right) + N\left(1 + \frac{d}{2}\right) = \sigma_B$$

and so

$$\sigma_{\text{initial}} = \sigma_A + \sigma_B = 2N\ln\left(\frac{n_Q V}{N}\right) + 2N\left(1 + \frac{d}{2}\right)$$

For the final entropy after mixing, treat the system as a (whole) system of $2N$ indistinguishable particles occupying a volume of $2V$:

$$\sigma_{\text{final}} = 2N\ln\left(\frac{n_Q(2V)}{2N}\right) + 2N\left(1 + \frac{d}{2}\right)$$

and so $\Delta\sigma = 0$

From Sec. 93. Mixtures of ideal gases of Landau and Lifshitz (1980) [5], additivity of thermodynamic quantities (such as energy and entropy) holds only if interaction between various parts of body is negligible.

But for mixture of several substances, e.g. mixture of liquids, thermodynamic quantities are not equal to sums of thermodynamic quantities for individual components of the mixture.

Mixtures of ideal gases are an exception, since interaction between molecules is by definition negligible.

But for partial pressure of ith gas, $p_i = \frac{N_i \tau}{V} = \frac{N_i p}{N}$, N = total number of molecules in mixture, N_i number of molecules of ith gas.

So

$$p_j = \frac{N_j \tau}{V} = \frac{N_j}{N} p = X_j p$$

where X_j is mole fraction or particle fraction.

10. Chemical Reactions

Topics:
- Heat of formation i.e. standard enthalpy of formation

I will follow Chapter 10, "Chemical Reactions", of Landau and Lifshitz (1980) [5].

From Sec. 101. The condition for chemical equilibrium of Landau and Lifshitz (1980) [5], for a chemical reaction,

$$\sum_i \nu_i A_i = 0 \qquad \nu_i \in \mathbb{Z}$$

Denote thermodynamic potential Φ.

In equilibrium, say at constant temperature and pressure,

$$d\Phi\left(\frac{\partial}{\partial N_i}\right) = \frac{\partial\Phi}{\partial N_1} + \frac{\partial\Phi}{\partial N_2}\frac{\partial N_2}{\partial N_1} + \frac{\partial\Phi}{\partial N_3}\frac{\partial N_3}{\partial N_1} + \cdots = 0 \ \text{for}$$

$$d\Phi = \frac{\partial\Phi}{\partial N_1}dN_1 + \frac{\partial\Phi}{\partial N_2}dN_2 + \ldots$$

where $N_1, N_2 \cdots$ = number of particles of particles of various substances taking place in reaction.

It's clear that

$$dN_i = \frac{\nu_i}{\nu_1}dN_1$$

so

$$\sum_i \frac{\partial\Phi}{\partial N_i}\frac{\nu_i}{\nu_1} = 0$$

Let $\mu_i := \frac{\partial\Phi}{\partial N_i}$.

(38) $$\implies \sum_i \nu_i \mu_i = 0$$

Here, I will follow Section 3.5 Chemical potential of Le Bellac, Mortessagne, Batrouni (2004) [7]. Recall that

$$G(N, \tau, p) = N\mu(\tau, p)$$

$$G = \sum_j \mu_j N_j$$

from Eq. 10, and Kittel and Kroemer (1980) [2]. Therefore,

$$dG = \sum_j \mu_j dN_j + N_j d\mu_j = -\sigma d\tau + V dp + \sum_j \mu_j dN_j$$

and so the **Gibbs-Duhem** relation is (correctly) obtained:

(39) $$0 = \sigma d\tau - V dp + \sum_j N_j d\mu_j$$

10.0.1. *Conduction and Convection.* In $\tau d\sigma$, let's distinguish the *conduction* component and *convection* component.

Consider system at equilibrium, thermal equilibrium with thermostat at temperature τ
kept at pressure p
able to exchange particles with reservoir at chemical potential μ
Define

$$\widehat{\sigma} := \frac{\sigma}{N} \qquad \textbf{entropy per particle}$$

$$\widehat{\epsilon} := \frac{E}{N} \qquad \textbf{energy per particle}$$

Then,

$$\boxed{\tau d\sigma = \tau d(\widehat{\sigma}N) = \tau N d\widehat{\sigma} + \tau\widehat{\sigma}dN}$$

where

$\tau N d\widehat{\sigma}$ is *entropy change due to change in entropy per particle*, i.e. *conduction term* and

$\tau\widehat{\sigma}dN$ is *entropy change due to change in number of particles* i.e. *convection term.*

So

$$dE = Q + W + \mu dN = \tau d\sigma + 0 + \mu dN = \tau N d\widehat{\sigma} + (\tau\widehat{\sigma} + \mu)dN = \tau N d\widehat{\sigma} + \widehat{h}dN$$

where

$$\widehat{h} := \frac{H}{N} = \widehat{\epsilon} + pV \ \text{is } \textbf{enthalpy per particle}$$

since

$$H = E + pV$$

$$G = E - \tau\sigma + pV = \mu N = H - \tau\sigma \implies \tau\widehat{\sigma} + \mu = \frac{H}{N} = \widehat{h}$$

Interpretation of $\widehat{h}dN$: If dN particles are transported into a given volume by convection, energy increases by $\widehat{\epsilon}dN$. However, to return to initial volume, it's necessary to compress by $vdN =: \frac{V}{N}dN$ and add work done by pressure $pvdN$

$$\implies \widehat{h}dN = (\widehat{\epsilon} + pv)dN$$

An example of this is *Joule-Thomson expansion*.

11. Joule-Thomson Effect

cf. Problem 1.7.6 of Le Bellac, Mortessagne, Batrouni (2004) [7], Lecture 18, Sections "Throttling Processes", "The Joule-Thomson Effect" of Groth, Phys301 Fall 1999 [4]

From Prob. 1.7.6 of Le Bellac, Mortessagne, Batrouni (2004) [7], their setup is the following:
gas initially confined in fixed volume escapes freely without exchanging heat with its environment,

- initially, gas in compartment and (T_1, V_1, p_1)
- expands into container of volume V_2 under constant pressure p_2 $(p_2 < p_1)$
- 2 compartments are thermally isolated; connected by porous plug to maintain pressure difference
- adiabatic (but not quasi-static) expansion.

$Q = 0$. So $Q = 0 = dU - W$. Then

$$\int dU - \int W = \Delta U - \int W = 0$$

Now

$$\Delta H = H_2 - H_1 = u_2 + p_2 V_2 - U_1 - p_1 V_1 = \Delta U + p_2 V_2 - p_1 V_1$$

Treat the process of gas evacuating, or going from compartment 1 to container 2 as 2 processes: $\int W = W_1 + W_2$ where
$W_1 = -p_1(0 - V_1) = p_1 V_1 \equiv$ work done on gas as the gas evacuates the compartment.
$W_2 = -p_2(V_2 - 0) = -p_2 V_2 =$ work done by gas as gas expands into container at constant pressure p_2.

Thus $\int W = W_1 + W_2 = p_1 V_1 - p_2 V_2$ and so

$$\boxed{\Delta H = 0}$$

The enthalpy is constant for this expansion.

For an ideal gas, $H = U + pV = \frac{\gamma}{\gamma-1}N\tau$, for an ideal gas has $U = \frac{1}{\gamma-1}N\tau$. $\gamma = \frac{5}{3}$ and $\frac{\gamma}{\gamma-1} = \frac{5/3}{2/3} = 5/2$. Nevertheless, since H is constant, T is constant, and so there's no cooling of an ideal gas in a Joule-Thomson apparatus! But an ideal gas has no interaction energy, and it can be argued that one has to consider interaction energy between molecules for liquefaction (cf. Groth (1999) [8], Lecture 18 Physics 301 Fall 1999).

From the "Derivation of the Joule-Thomson (Kelvin) coefficient" section of the *Joule-Thomson effect* article in Wikipedia, recall the definition of enthalpy $H := U + pV$, and so that $dH = dU + pdV + Vdp = \tau d\sigma + Vdp$.

Let $\sigma = \sigma(\tau, p)$.

$$dH = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_p d\tau + (V + \tau\left(\frac{\partial\sigma}{\partial p}\right)_\tau)dp = C_p d\tau + (V + \tau\left(\frac{\partial\sigma}{\partial p}\right)_\tau)dp$$

since

$$Q = Q(\tau, p) = \frac{\partial Q}{\partial\tau}d\tau + \frac{\partial Q}{\partial p}dp = C_p d\tau + \frac{\partial Q}{\partial p}dp$$

and so for a thermodynamic process γ such that $dp(\dot{\gamma}) = 0$ (i.e. constant pressure), then we can say

$$\frac{C_p}{\tau}d\tau = d\sigma \xrightarrow{\int_\gamma} \int_\gamma \frac{C_p}{\tau}d\tau = \Delta\sigma \implies \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_p = C_p$$

And now

$$dG = -\sigma d\tau + Vdp = \left(\frac{\partial G}{\partial\tau}\right)_p d\tau + \left(\frac{\partial G}{\partial p}\right)_\tau dp$$

and since $\frac{\partial^2 G}{\partial\tau\partial p} = \frac{\partial^2 G}{\partial p\partial\tau}$,

$$\left(\frac{\partial\sigma}{\partial p}\right)_\tau = -\left(\frac{\partial V}{\partial\tau}\right)_p = -V\alpha$$

Then

$$dH = C_p d\tau + V(1 - \tau\alpha)dp$$

and so

(40)
$$\left(\frac{\partial\tau}{\partial p}\right)_H = \frac{V(1 - \tau\alpha)}{-C_p}$$

is the **Joule-Thomson coefficient**, where α is the coefficient of thermal expansion.

For an ideal gas,

$$pV = N\tau$$
$$V = \frac{N\tau}{p} \implies \frac{\partial V}{\partial\tau} = \frac{N}{p} = \frac{V}{\tau}$$

so

$$dH = C_p d\tau + (V + \tau\left(\frac{-V}{\tau}\right))dp = C_p d\tau$$

so that

$$\left(\frac{\partial\tau}{\partial p}\right)_H = 0$$

for an ideal gas.

For every real gas, every real gas has an *inversion temperature* such that below the inversion temperature, $\left(\frac{\partial T}{\partial p}\right)_H$ is positive, and so $dp < 0$ always in an expansion, and so $dT < 0$ and the gas cools, and above the inversion temperature, $\left(\frac{\partial T}{\partial p}\right)_H$ is negative, and so $dp < 0$ always in an expansion, and so $dT < 0$ and the gas warms.

An inversion temperature must exist because when the molecules are close enough, there are intermolecular forces that'll make them attract each other (such as temporary configurations so a slightly (electrically) negative cloud of electrons attract slightly positively charged part of another molecule) so the interaction energy is negative.

However, it appears that this inversion temperature is not found from the Joule-Thomson coefficient expression, Eq. 40, but from, possibly, the Van der Waals expression or another model (cf. Lecture 18 of Groth (1999) [8]).

Looking at Figure 1.16 of Le Bellac, Mortessagne, Batrouni (2004) [7], for isenthalpy curves ($H = $ const.), in (T, p) plane, T vs. p, the dashed line intersects the points on each isenthalpy curves where $\left(\frac{\partial T}{\partial p}\right)_H = 0$ and for lower pressures ($dp < 0$, gas expands), cooling occurs.

There's a maximum temperature, about $300°\,C$ for nitrogen, where the dashed line meets the $p = 0$ atm axis, meaning $\left(\frac{\partial\tau}{\partial p}\right)_H < 0 \quad \forall\, p > 0$, so no cooling occurs.

12. Hydrodynamics

Another example: hydrodynamics; Eulerian description in fixed volume.
Define $\epsilon := \frac{E}{V} = \widehat{\epsilon} \cdot \left(\frac{N}{V}\right) \equiv \widehat{\epsilon}n$.

$$dE = \tau N d\widehat{\sigma} + \widehat{h}dN \xrightarrow{\frac{1}{V}} d\epsilon = \tau n d\widehat{\sigma} + \widehat{h}dn$$

in isentropic process, $\left(\frac{1}{2}\rho u^2 + h\right)\mathbf{u}$ is energy current; $h = \frac{H}{V}$, $\mathbf{u}$ velocity of fluid

---

[4] Edward J. Groth, 1999, Fall 1999 Physics 301, Phys301 23-Nov-1999 18-10

Part 2. **Nonequilibrium**

13. Irreversible processes: macroscopic theory

Chapter 6 of Le Bellac, Mortessagne, Batrouni (2004) [7]

13.1. **Flux, affinities, transport coefficients.** Section 6.1 of Le Bellac, Mortessagne, Batrouni (2004) [7].
Assume system composed of homogeneous cells, small on macroscopic scale, but large on microscopic, labelled $(a, b, \dots)$.
Assume cells weakly interacting, so each cell independently attains local equilibrium with microscopic relaxation time τ_{micro}
Assume $\tau_{\text{micro}} \ll \tau_{\text{macro}}$ where
$\qquad \tau_{\text{macro}}$ macroscopic relaxation time, for global equilibrium

13.1.1. *Affinities and transport coefficients.* Suppose neighboring cells a, b have different intensive variables γ_i, an exchange of A_i will take place between them.
Recall, from the Gibbs-Duhem relation, 39,
$$N d\mu + \sigma d\tau - V dp = 0$$

For the $d\tau = 0$ isothermal case, define

(41)
$$n := \frac{N}{V} \equiv \text{ particle density}$$

Then

$$dp = n d\mu$$

(42)
$$\implies \boxed{\left(\frac{\partial p}{\partial \mu} \right)_\tau = n}$$

Recall

13.1.2. *Dissipation and Entropy Production.* cf. Subsection 6.1.5 of Le Bellac, Mortessagne, Batrouni (2004) [7].

(43)
$$\frac{dS(a)}{dt} + \sum_{b \neq a} \Phi_S(a \to b) = \frac{1}{2} \sum_{i, b \neq a} \Gamma_i(a,b) \Phi_i(a \to b)$$

since

$$\frac{dS(a)}{dt} = - \sum_{i, b \neq a} \frac{1}{2} (\gamma_i(a) + \gamma_i(b)) \Phi_i(a \to b) + \frac{1}{2} \sum_{i, b \neq a} \Gamma_i(a,b) \Phi_i(a \to b)$$

and since

(44)
$$\Phi_S(a \to b) = \frac{1}{2} \sum_i (\gamma_i(a) + \gamma_i(b)) \Phi_i(a \to b) = -\Phi_S(b \to a)$$

Calculate $\frac{dS_{\text{tot}}}{dt}$, evolution of total entropy.
$$\frac{dS_{\text{tot}}}{dt} = \frac{d}{dt} \sum_a S(a) = \sum_a \frac{dS(a)}{dt}$$

Note that
$$\Phi_S(b \to a) + \Phi_S(a \to b) = 0$$

by antisymmetry of $\Phi_S(a \to b)$.
The $\sum_a \sum_{b \neq a}$ is the summation of all the ways of making a size 2 ordered choice of 2 elements out of the possible cells $\{a, b, \dots\}$; if there are n total cells, then there are $n(n-1)$ ways of picking out 2, *in order*. Note that $n(n-1)$ *must* be even.
Then

$$\sum_a \sum_{b \neq a} \Phi_S(a \to b) = \frac{1}{2} \sum_a \sum_{b \neq a} \Phi_S(a \to b) + \frac{1}{2} \sum_b \sum_{a \neq b} \Phi_S(b \to a) = \frac{1}{2} \sum_a \sum_{b \neq a} \Phi_S(a \to b) + \frac{1}{2} \sum_b \sum_{a \neq b} -\Phi_S(a \to b) = 0$$

So Φ_S doesn't contribute to $\frac{dS_{\text{tot}}}{dt}$: $\implies$ *reversible exchange*

$$\frac{dS_{\text{tot}}}{dt} = \frac{1}{2} \sum_a \sum_{i, b \neq a} \Gamma_i(a,b) \Phi_i(a \to b)$$

entropy production, called *dissipation*; all physical phenomena accompanied by entropy production called *dissipative*.

13.1.3. *Particle Diffusion.* cf. pp. 399 of Kittel and Kroemer [2]
Consider a system.
One end in diffusive contact with reservoir at chemical potential μ_1
Other end in diffusive contact with reservoir at chemical potential μ_2
Constant temperature τ.
If $\mu_1 > \mu_2$, particle flow through system from reservoir 1 to reservoir 2; $1 \to 2$.
$n_i \equiv$ particle concentration in i
Take

(45)
$$\mathbf{j}_n = -D \text{grad} n$$

which is **Fick's law**, and where $D \equiv$ particle diffusion constant or **diffusivity**.
Mean free path l. Particles freely travel over l.
Assume in a collision at z, particles come into local equilibrium at local chemical potential $\mu(z)$, local concentration $n(z)$.
At z, particle flux density in positive z direction $\qquad \frac{1}{2} n(z - l_z) \bar{c}_z$
$\qquad$ particle flux density in negative z direction $\qquad -\frac{1}{2} n(z + l_z) \bar{c}_z$
Note $n(z - l_z)$ is particle concentration at $z - l_z$

$$J_n^z = \frac{1}{2} [n(z - l_z) - n(z + l_z)] \bar{c}_z = -\frac{dn}{dz} \bar{c}_z l_z$$

where $\bar{c}_z = \bar{c} \cos \theta$
$\qquad \bar{l}_z = \bar{l} \cos \theta$

$$\langle \bar{c}_z l_z \rangle = \bar{c} \bar{l} \frac{\int_{\text{hemisphere}} \cos^2 \theta dS}{\int_{\text{hemisphere}} dS} = \bar{c} \bar{l} \frac{\int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \cos^2 \theta \sin \theta d\theta}{\int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\varphi} = \bar{c} \bar{l} \frac{1}{3}$$

Comparing with Fick's law,

$$J_n^z = \frac{-1}{3} \bar{c} \bar{l} \frac{dn}{dz} \text{ or } \mathbf{J}_N = -\frac{1}{3} \bar{c} \bar{l} \nabla n$$

For diffusivity D is then $D = \frac{1}{3} \bar{c} \bar{l}$.
Now recall that $\bar{l}$, the *mean free path*, was derived from kinetic theory:

$$l = \frac{1}{n \pi d^2}$$

where d is the diameter of the particle.
The mean thermal velocity was derived from the Maxwell distribution:

$$\bar{c} = \left(\frac{8\tau}{M\pi} \right)^{1/2}$$

13.1.4. *Momentum conservation.* Introduce *stress tensor* $\mathcal{P}_{\alpha\beta}$, $-\mathcal{P}_{\alpha\beta}$ is α component of force per unit area applied by fluid outside parallelopiped on surface $\mathcal{S}_\beta$.

13.1.5. *Hydrodynamics of the perfect fluid.* cf. Subsection 6.5.2 Hydrodynamics of the perfect fluid, of Le Bellac, Mortessagne, Batrouni (2004) [7].

Consider a fluid where the only internal force is pressure. Assume there's no thermal conduction. In such a fluid, dissipation is absent. The fluid is a so-called "perfect fluid." Then right hand side for these transport equations (Eq. (6.87), (6.88) of Le Bellac, Mortessagne, Batrouni (2004) [7] is 0:

$$\mathbf{j}'_E = L_{EE}\nabla\frac{1}{T}$$

$$\mathcal{P}_{\alpha\beta} - \delta_{\alpha\beta}\mathcal{P} = -\xi\delta_{\alpha\beta}(\partial_\gamma u_\gamma) - 2\eta\Delta_{\alpha\beta}$$

(1) Consider the force acting on a fluid volume element $\text{vol}^n \in \Omega^n(N)$, where spatial manifold has dimension n, i.e. $\dim N = n$.

The **total force** applied by rest of fluid in fluid enclosed in parallelpipe (generalized to V), integrate over ∂V (all forces)

$$-\int_{\partial V}\mathcal{P}_{\alpha\beta}dx^\alpha \otimes dS^\beta = -\int_{\partial V}\mathcal{P}_{\alpha\beta}dS^\beta \otimes dx^\alpha = -\int_V d(\mathcal{P}_{\alpha beta}dS^\beta) \otimes dx^\alpha = -\int_V \frac{\partial(\mathcal{P}_{\alpha\beta}\sqrt{g})}{\partial x^\beta}\frac{1}{\sqrt{g}}\text{vol}^n \otimes dx^\alpha$$

Now consider the "left-hand side" which describes the dynamics (or kinematics?). For *total* momentum Π

$$\Pi = \int_V \rho u_i dx^i \otimes \text{vol}^n$$

$$\frac{d\Pi}{dt} = \dot{\Pi} = \frac{d}{dt}\int_V \rho u_i\text{vol}^n \otimes dx^i = \int_V \frac{\partial(\rho u_i)}{\partial t}\text{vol}^n \otimes dx^i + \int_V \mathcal{L}_{\mathbf{u}}\rho u_i\text{vol}^n \otimes dx^i = \int_V \frac{\partial(\rho u_i)}{\partial t}\text{vol}^n \otimes dx^i + \int_V \mathbf{d}(\rho u_i u^j dS_j)$$

Now

$$\mathbf{d}(\rho u_i u^j dS_j) = \frac{\partial\rho}{\partial x^j}u^j u_i\text{vol}^n + \rho\left[\frac{\partial u_i}{\partial x^j}u^j\text{vol}^n + u_i\frac{\partial u^j}{\partial x^j}\text{vol}^n\right]$$

where, recalling

$$dS_j = \frac{\sqrt{g}}{(n-1)!}\epsilon_{ji_2\ldots i_n}dx^{i_2} \wedge \cdots \wedge dx^{i_n}$$

then

$$dx^k \wedge dS_j = \frac{\sqrt{g}}{(n-1)!}\epsilon_{ji_2\ldots i_n}dx^k \wedge dx^{i_2} \wedge \cdots \wedge dx^{i_n} = \frac{\sqrt{g}}{(n-1)!}\epsilon_{ji_2\ldots i_n}\epsilon^{ki_2\ldots i_n}_{12\ldots n}\frac{dx^1 \wedge \cdots \wedge dx^n}{n} = \delta^k_j\text{vol}^n$$

(2) Consider the *lab frame* (with unprimed notation).
Consider the frame *at rest in the fluid's frame* (with primed notation).
Note that

$$\frac{d}{dt}\int_V \text{vol}^n = \int_V \mathcal{L}_{\frac{\partial}{\partial t}+\mathbf{u}}\text{vol}^n = \int_V 0 + \mathbf{d}i_{\mathbf{u}}\text{vol}^n + 0 = \int_{\partial V} i_{\mathbf{u}}\text{vol}^n = \int_{\partial V} u^i dS_i$$

Let $s \equiv S/V \equiv \overline{\sigma} \equiv \frac{\sigma}{V}$ entropy per unit volume in fluid's frame
$h' \equiv H/V$ enthalpy per unit volume in *fluid's frame.*
Note that $s = s'$ since entropy is Galilean invariant.
Now

$$\check{s} \equiv S/N \equiv \check{\sigma} \equiv \sigma/N$$

$$\check{h}' \equiv H/N$$

Let's review Subsubsection 10.0.1, which is on pp.137 at the end of Section 3.5.1. Basic formulae of Le Bellac, Mortessagne, Batrouni (2004) [7].

13.1.6. *Conduction and Convection.* Consider system at equilibrium, with thermostate at temperature T, kept at pressure p, able to exchange particles, with reservoir at chemical potential μ.

For 1 kind of particle, let

$$\check{s} \equiv S/N \text{ entropy per particle}$$

$$\check{\epsilon} \equiv E/N \text{ energy per particle}$$

Thus

$$\tau d\sigma = \tau d(N\check{\sigma}) = \tau N d\check{\sigma} + \tau\check{\sigma}dN$$

where

$\tau N d\check{\sigma}$ is entropy change due to change in entropy per particle, i.e. **conduction term**

$\tau\check{\sigma}dN$ is entropy change due to change in number of particles, i.e. **convection term**

For constant volume,

$$dE = TN d\check{\sigma} + (T\check{\sigma} + \mu)dN = TN d\check{\sigma} + \check{h}dN$$

where $\check{h} = \overline{H}/N = \check{\epsilon} + Pv$ is enthalpy per particle, since, recall,

$$\overline{H}(S, P) = E + PV$$

$$\mu N = E - TS + PV = G$$

physical interpretation of $\check{h}dN$: if dN particles transported into a given volume by convection, energy increases by $\check{\epsilon}dN$. But to return to initial volume, it's necessary to compress by vdN and so add energy to do work $PvdN$ by pressure.

Example: hydrodynamics, where 1 uses Eulerian description in fixed volume.
Define energy density $\epsilon = \frac{E}{V} = \check{\epsilon}n$.

$$d\epsilon = Tnd\check{s} + \check{h}dn$$

separates conduction and convection terms.
To reiterate, in my notation,

$$H = E + pV \xrightarrow{1/N} \check{h} = \check{\epsilon} + pV$$

$$G = F + pV = E - \tau\sigma + pV = \mu N = H - \tau\sigma \implies \mu = \check{h} - \tau\check{\sigma}$$

$$dE = Q + W + \mu dN \implies dE = \tau d\sigma - pdV + \mu dN = \tau N d\check{\sigma} + \tau\check{\sigma}dN - pdV + \mu dN = \tau N d\check{\sigma} + (\tau\check{\sigma} + \mu)dN = \tau N d\check{\sigma} + \check{h}dN$$

where the process considered was for constant volume, and so $dV = 0$, and one must keep in mind that the general form of the (internal) energy is as a function of $\sigma, V, \{N_i\}$, so that

$$dE = \tau d\sigma - pdV + \sum_i \mu_i dN_i$$

References

[1] Ralph Baierlein. **Thermal Physics** Cambridge University Press (July 28, 1999), ISBN-13: 978-0521658386

[2] Charles Kittel, Herbert Kroemer, **Thermal Physics**, W. H. Freeman; Second Edition edition, 1980. ISBN-13: 978-0716710882

[3] Bernard F. Schutz, **Geometrical Methods of Mathematical Physics**, Cambridge University Press, 1980. ISBN-13: 978-0521298872

[4] Claus Borgnakke, Richard E. Sonntag. **Fundamentals of Thermodynamics**, 8th Edition, Wiley, (December 26, 2012). ISBN-13: 978-1118131992

[5] L.D. Landau, E.M. Lifshitz. **Statistical Physics**, Third Edition, Part 1: Volume 5 (Course of Theoretical Physics, Volume 5). Butterworth-Heinemann; 3rd edition (January 15, 1980). ISBN-13: 978-0750633727

[6] Rolf H. Sabersky, Allen J. Acosta, Edward G. Hauptmann, E.M. Gates. **Fluid Flow: A First Course in Fluid Mechanics** (4th Edition). Prentice Hall. (August 22, 1998). ISBN-13: 978-0135763728
https://www-physics.ucsd.edu/students/courses/spring2010/physics210a/LECTURES/210_COURSE.pdf

[7] Michel Le Bellac, Fabrice Mortessagne, G. George Batrouni. **Equilibrium and Non-Equilibrium Statistical Thermodynamics**. Cambridge University Press (May 3, 2004). ISBN-13: 978-0521821438

[8] Edward J. Groth. Phys301, Physics 301.
http://grothserver.princeton.edu/~groth/phys301f99/lect18.pdf

14. CODE LISTINGS