

Maths Thermo

Class # 04

01/29/2026

Suppose that \tilde{S} is the fundamental entropy relation for an isolated system containing a unary ($r=1$) material.

$$\tilde{S} = \tilde{S}(U, V, N).$$

Suppose that $N > 0$ is fixed. Define

$$u := \frac{U}{N}, \quad \text{the molar energy,}$$

$$v := \frac{V}{N}, \quad \text{the molar volume.}$$

Then, since, for any $\lambda > 0$,

$$\lambda \tilde{S}(U, V, N) = \tilde{S}(\lambda U, \lambda V, \lambda N),$$

it follows that

$$\begin{aligned} \frac{1}{N} \tilde{S}(U, V, N) &= \tilde{S}\left(\frac{U}{N}, \frac{V}{N}, \frac{N}{N}\right) \\ &= \tilde{S}(u, v, 1). \end{aligned}$$

Now, define the molar entropy relation

$$\tilde{s} = \tilde{s}(u, v) := \tilde{S}(u, v, 1).$$

It then follows that

$$\tilde{S}(U, V, N) = N \tilde{s}(u, v).$$

likewise, if we define

$$s = \frac{S}{N} \quad v = \frac{V}{N}$$

and

$$\tilde{u} = \tilde{u}(s, v) := \tilde{U}(s, v, 1),$$

then it follows that

$$\tilde{U}(s, v, N) = N \tilde{u}(s, v).$$

Example (4.1) Suppose that

$$\tilde{S}(u, v, N) = \left(\frac{NVUR^2}{v_0 \theta} \right)^{1/3},$$

where $R, v_0, \theta > 0$ are constants. Then,

$$\begin{aligned} \tilde{S}(u, v) &= \tilde{S}(u, v, 1) \\ &= \left(\frac{vuR^2}{v_0 \theta} \right)^{1/3}. \end{aligned}$$

$$\begin{aligned} N\tilde{S}(u, v) &= \left(\frac{N^3 vuR^2}{v_0 \theta} \right)^{1/3} \\ &= \left(\frac{NVUR^2}{v_0 \theta} \right)^{1/3} \\ &= \tilde{S}(U, V, N). \end{aligned}$$

\tilde{U} and \tilde{S} are homogeneous of degree one (also called extensive variables).

T, P, μ on the other hand are homogeneous of degree zero (also called intensive variables).

Recall that, for all $\lambda > 0$,

$$T_0(S, V, N) = T_0(\lambda S, \lambda V, \lambda N).$$

Thus,

$$T_0(S, V, N) = T_0(s, v, 1)$$

We could, of course, give a new symbol for $T_0(s, v, 1)$, for example

$$t_0(s, v) := T_0(s, v, 1) \dots$$

Molar Euler and Gibbs-Duhem Equations

For a unary material ($r=1$), recall

$$\tilde{U}(S, V, N) = T_0(S, V, N)S - P_0(S, V, N)V + \mu_0(S, V, N)N$$

Suppose $N > 0$ is fixed. Then,

$$\frac{1}{N} \tilde{U}(S, V, N) = T_0(S, V, N) \frac{S}{N} - P_0(S, V, N) \frac{V}{N} + \mu_0(S, V, N)$$

or, equivalently,

(4.1)

$$\tilde{u}(s, v) = T_0(s, v) s - P_0(s, v) v + \mu_0(s, v).$$

This is the molar version of Euler's equation.

How do we get the Gibbs-Duhem equation?

Let $\vec{\gamma}(r) = (s(r), v(r))$ be a path in molar state space. Then

$$\frac{d}{dr} \tilde{u}(\vec{\gamma}(r)) = \frac{\partial \tilde{u}}{\partial s}(\vec{\gamma}(r)) s'(r) + \frac{\partial \tilde{u}}{\partial v}(\vec{\gamma}(r)) v'(r).$$

But

$$\frac{\partial \tilde{u}}{\partial s}(\vec{\gamma}(r)) \stackrel{\text{exercise}}{=} T_v(s(r), v(r))$$

and

$$\frac{\partial \tilde{u}}{\partial v}(\vec{\gamma}(r)) \stackrel{\text{exercise}}{=} -P_v(s(r), v(r)).$$

Thus, the combined First and Second laws are

(4.2)

$$\frac{d}{dr} \tilde{u}(\vec{\gamma}(r)) = T_v(\vec{\gamma}(r)) s'(r) - P_v(\vec{\gamma}(r)) v'(r).$$

On the other hand, differentiate the molar Euler equation (4.1), we have

(4.3)

$$\begin{aligned} \frac{d}{dr} \tilde{u}(\vec{\gamma}(r)) &= \frac{d}{dr} T_v(\vec{\gamma}(r)) s(r) + T_v(\vec{\gamma}(r)) s'(r) \\ &\quad - \frac{d}{dr} P_v(\vec{\gamma}(r)) v(r) - P_v(\vec{\gamma}(r)) v'(r) \\ &\quad + \frac{d}{dr} \mu_v(\vec{\gamma}(r)). \end{aligned}$$

Therefore, the molar Gibbs-Duhem equation is

(4.4)

$$0 = \frac{d}{dr} T_v(\vec{\gamma}(r)) s(r) - \frac{d}{dr} P_v(\vec{\gamma}(r)) v(r) + \frac{d}{dr} \mu_v(\vec{\gamma}(r))$$

The molar entropy form of the Euler and Gibbs-Duhem equations are, as one would expect,

$$(4.6) \quad \tilde{S}(u, v) = \frac{1}{T_s(u, v)} u + \frac{P_s(u, v)}{T_s(u, v)} v - \frac{\mu_s(u, v)}{T_s(u, v)}$$

and

$$(4.7) \quad 0 = \frac{d}{dr} \left(\frac{1}{T_s(\vec{s}(r))} \right) u(r) + \frac{d}{dr} \left(\frac{P_s(\vec{s}(r))}{T_s(\vec{s}(r))} \right) v(r) - \frac{d}{dr} \left(\frac{\mu_s(\vec{s}(r))}{T_s(\vec{s}(r))} \right).$$

The molar representation of the First and Second laws is

$$(4.8) \quad \frac{d}{dr} (\tilde{S}(\vec{s}(r))) = \frac{1}{T_s(\vec{s}(r))} u'(r) + \frac{P_s(\vec{s}(r))}{T_s(\vec{s}(r))} v'(r)$$

where $\vec{s}(r) = (u(r), v(r))$ is a process path in molar state space.

Let's look at a couple of examples.

Example (4.2): Suppose that

$$P = \frac{2U}{V}$$

$$T = \left(\frac{A U^{3/2}}{V N^{1/2}} \right)^{1/2}$$

(homog. deg. zero)

✓

✓

We should be able to recover the fundamental relation using these two equations of state.

Observe that

$$\frac{1}{T_s} = A^{-1/2} u^{-3/4} v^{1/2}$$

$$\frac{P_s}{T_s} = 2 A^{-1/2} u^{1/4} v^{-1/2}$$

Using the molar 1st and 2nd law (4.8)

$$\frac{d}{dr} (\tilde{S}(\vec{r}(r))) = \frac{1}{T_s(\vec{r}(r))} u'(r) + \frac{P_s(\vec{r}(r))}{T_s(\vec{r}(r))} v'(r)$$

$$= A^{-1/2} \left(u^{-3/4} v^{1/2} u'(r) + 2 u^{1/4} v^{-1/2} v'(r) \right)$$

$$= 4 A^{-1/2} \frac{d}{dt} \left((u(r))^{1/4} (v(r))^{1/2} \right)$$

Therefore,

$$\tilde{S}(r) = 4 A^{-1/2} (u(r))^{1/4} (v(r))^{1/2} + S_0$$

Equivalently,

$$\tilde{S}(r) = 4 A^{-1/2} U^{1/4} V^{1/2} N^{1/4} + N S_0.$$

Here S_0 is a positive constant. ///

let's try an alternative method.

Example (4.3): Same problem as above. This time we will use the Gibbs-Duhem equation (4.7) as the starting point:

$$\begin{aligned}
 \frac{d}{dr} \left(\frac{\mu_s(\vec{r}(r))}{T_s(\vec{r}(r))} \right) &= \frac{d}{dr} \left(\frac{1}{T_s(\vec{r}(r))} \right) u(r) \\
 &\quad + \frac{d}{dr} \left(\frac{P_s(\vec{r}(r))}{T_s(\vec{r}(r))} \right) v(r) \\
 &= A^{-1/2} \frac{d}{dr} \left((u(r))^{-3/4} (v(r))^{1/2} \right) u(r) \\
 &\quad + A^{-1/2} \frac{d}{dr} \left(2(u(r))^{1/4} (v(r))^{-1/2} \right) v(r) \\
 &= A^{-1/2} \left(-\frac{3}{4} \right) (u(r))^{-3/4} (v(r))^{1/2} u'(r) \\
 &\quad + A^{-1/2} (u(r))^{1/4} \frac{1}{2} (v(r))^{-1/2} v'(r) \\
 &\quad + A^{-1/2} \cdot 2 \cdot \frac{1}{4} (u(r))^{-3/4} (v(r))^{1/2} u'(r) \\
 &\quad + A^{-1/2} 2 (u(r))^{1/4} \left(-\frac{1}{2} \right) (v(r))^{-1/2} v'(r) \\
 &= A^{-1/2} \left(-\frac{1}{4} \right) (u(r))^{-3/4} (v(r))^{1/2} u'(r) \\
 &\quad + A^{-1/2} \left(-\frac{1}{2} \right) (u(r))^{1/4} (v(r))^{-1/2} v'(r) \\
 &= -A^{-1/2} \frac{d}{dr} \left((u(r))^{1/4} (v(r))^{1/2} \right)
 \end{aligned}$$

Thus,

$$\frac{\mu_s(\vec{r}(r))}{T_s(\vec{r}(r))} = -A^{-1/2} (u(r))^{1/4} (v(r))^{1/2} - s_0$$

or

$$\frac{\mu_s(u,v)}{T_s(u,v)} = -A^{-1/2} u^{1/4} v^{1/2} - s_0.$$

Using Euler's equation (4.6), we have

$$\begin{aligned}\tilde{S}(u,v) &= \frac{1}{T_s(u,v)} u + \frac{P_s(u,v)}{T_s(u,v)} v - \frac{\mu_s(u,v)}{T_s(u,v)} \\ &= A^{-1/2} u^{1/4} v^{1/2} + 2A^{-1/2} u^{1/4} v^{1/2} \\ &\quad + A^{-1/2} u^{1/4} v^{1/2} + s_0 \\ &= 4A^{-1/2} u^{1/4} v^{1/2} + s_0,\end{aligned}$$

which is the same as before.

Using 2 equations of state, we can recover the 3rd and then, utilizing Euler's equation we get the fundamental relation. //

Example (4.4): Ideal Gas law

$$PV = NRT$$

$$U = \frac{3}{2} NRT$$

With these two equations of state we can find the fundamental relation.

Observe that

$$\frac{1}{T_s} = \frac{3R}{2u} \quad \frac{P_s}{T_s} = \frac{R}{v}$$

This suggests that we again use the entropy equations (in molar form). The Gibbs-Duhem equation is

$$\begin{aligned} \frac{d}{dr} \left(\frac{\mu_s(\vec{r}(r))}{T_s(\vec{r}(r))} \right) &= \frac{d}{dr} \left(\frac{1}{T_s(\vec{r}(r))} \right) u(r) \\ &\quad + \frac{d}{dr} \left(\frac{P_s(\vec{r}(r))}{T_s(\vec{r}(r))} \right) v(r) \\ &= \frac{3R}{2} \frac{d}{dr} \left(\frac{1}{u(r)} \right) u(r) \\ &\quad + R \frac{d}{dr} \left(\frac{1}{v(r)} \right) v(r) \\ &= -\frac{3R}{2} \frac{u'(r)}{u(r)} - \frac{R v'(r)}{v(r)} \end{aligned}$$

Integrating, we have

$$\begin{aligned} \frac{\mu_s(u(r), v(r))}{T_s(u(r), v(r))} - \frac{\mu_0}{T_0} &= -\frac{3R}{2} \ln \left(\frac{u(r)}{u_0} \right) \\ &\quad - R \ln \left(\frac{v(r)}{v_0} \right), \end{aligned}$$

where

$$\frac{\mu_0}{T_0} := \frac{\mu_s(u_0, v_0)}{T_s(u_0, v_0)}.$$

Using the molar Euler equation, we have

$$\begin{aligned}\tilde{S}(u,v) &= \frac{1}{T_s(u,v)} u + \frac{P_s(u,v)}{T_s(u,v)} v - \frac{\mu_s(u,v)}{T_s(u,v)} \\ &= \frac{3R}{2} + R + \frac{3R}{2} \ln\left(\frac{u}{u_0}\right)\end{aligned}$$

$$+ R \ln\left(\frac{v}{v_0}\right) - \frac{\mu_0}{T_0}$$

$$= s_0 + R \ln\left(\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{v}{v_0}\right)\right)$$

Thus,

$$\tilde{S}(U,V,N) = N s_0 + NR \ln\left(\left(\frac{U}{U_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2}\right),$$

where

$$U = uN, \quad V = vN,$$

$$U_0 = u_0 N_0, \quad V_0 = v_0 N_0,$$

and

$$s_0 = \frac{5}{2}R - \frac{\mu_0}{T_0}. \quad ///$$