

# Chapter 1

## ThermoS26-04

Math Thermo  
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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

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

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 1.0.1.** (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,

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

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

$\tilde{U}$  and  $\tilde{S}$  are homogeneous of degree one (also called extensive variables).  $T, P, \mu$  on the other hand are homogeneous of degree zero (also called intensive variables).

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

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

Thus,

$$T_U(S, V, N) = T_U(s, v, 1).$$

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

$$t_U(s, v) := T_U(s, v, 1) \dots$$

## 1.1 Molar Euler and Gibbs–Duhem Equation

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

$$\tilde{U}(S, V, N) = T_U(S, V, N)S - P_U(S, V, N)V + \mu_U(S, V, N)N$$

Suppose  $N > 0$  is fixed. Then,

$$\frac{1}{N}\tilde{U}(S, V, N) = T_U(S, V, N)\frac{S}{N} - P_U(S, V, N)\frac{V}{N} + \mu_U(S, V, N)$$

or, equivalently,

$$\tilde{u}(s, v) = T_U(s, v)s - P_U(s, v)v + \mu_U(s, v). \quad (4.1)$$

This is the molar version of Euler's equation. How do we get the Gibbs–Duhem equation?

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

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

But

exercise

$$\frac{\partial\tilde{u}}{\partial s}(\vec{z}(\gamma)) = T_U(s(\gamma), v(\gamma))$$

and

$$\frac{\partial\tilde{u}}{\partial v}(\vec{z}(\gamma)) = -P_U(s(\gamma), v(\gamma)).$$

Thus, the combined First and Second laws are

$$\frac{d}{d\gamma}\tilde{u}(\vec{z}(\gamma)) = T_U(\vec{z}(\gamma))s'(\gamma) - P_U(\vec{z}(\gamma))v'(\gamma). \quad (4.2)$$

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

$$\frac{d}{d\gamma}\tilde{u}(\vec{z}(\gamma)) = \frac{d}{d\gamma}T_U(\vec{z}(\gamma))s(\gamma) + T_U(\vec{z}(\gamma))s'(\gamma) \quad (1.1.1)$$

$$- \frac{d}{d\gamma}P_U(\vec{z}(\gamma))v(\gamma) - P_U(\vec{z}(\gamma))v'(\gamma) \quad (1.1.2)$$

$$+ \frac{d}{d\gamma}\mu_U(\vec{z}(\gamma)). \quad (4.3)$$

Therefore, the molar Gibbs–Duhem equation is

$$0 = \frac{d}{d\gamma} T_U(\vec{z}(\gamma))s(\gamma) - \frac{d}{d\gamma} P_U(\vec{z}(\gamma))v(\gamma) + \frac{d}{d\gamma} \mu_U(\vec{z}(\gamma)). \quad (4.4)$$

The molar entropy form of the Euler and Gibbs– Duhem equations are (as one would expect)

$$\tilde{s}(u, v) = \frac{1}{T_S(u, v)} u + \frac{P_S(u, v)}{T_S(u, v)} v - \frac{\mu_S(u, v)}{T_S(u, v)}. \quad (4.6)$$

and

$$0 = \frac{d}{d\gamma} \left( \frac{1}{T_S(\vec{z}(\gamma))} \right) u(\gamma) + \frac{d}{d\gamma} \left( \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} \right) v(\gamma) - \frac{d}{d\gamma} \left( \frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} \right). \quad (4.7)$$

The molar representation of the First and Second laws is

$$\frac{d}{d\gamma} \tilde{s}(\vec{z}(\gamma)) = \frac{1}{T_S(\vec{z}(\gamma))} u'(\gamma) + \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} v'(\gamma). \quad (4.8)$$

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

## 1.2 Examples

Let's look at a couple of examples.

**Example 1.2.1.** (4.2) Suppose that

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

$$T = \left( \frac{AU^{3/2}}{VN^{1/2}} \right)^{1/2}$$

(homog. deg. zero)

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

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

$$\frac{P_S}{T_S} = 2A^{-1/2} u^{1/4} v^{-1/2}$$

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

$$\begin{aligned}\frac{d}{d\gamma} \tilde{s}(\vec{z}(\gamma)) &= \frac{1}{T_S(\vec{z}(\gamma))} u'(\gamma) + \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} v'(\gamma) \\ &= A^{-1/2} \left( u(\gamma)^{-3/4} v(\gamma)^{1/2} u'(\gamma) + 2u(\gamma)^{1/4} v(\gamma)^{-1/2} v'(\gamma) \right) \\ &= 4A^{-1/2} \frac{d}{d\gamma} \left( (u(\gamma))^{1/4} (v(\gamma))^{1/2} \right).\end{aligned}$$

Therefore,

$$\tilde{s}(\gamma) = 4A^{-1/2} (u(\gamma))^{1/4} (v(\gamma))^{1/2} + s_0.$$

Equivalently,

$$\tilde{S}(\gamma) = 4A^{-1/2} U^{1/4} V^{1/2} N^{1/4} + Ns_0.$$

here  $s_0$  is a positive constant. ///

Let's try an alternative method.

**Example 1.2.2.** (4.3) Same problem as above. This time we will use the Gibbs–Duhem equation (4.7) as the starting point:

$$\begin{aligned}
\frac{d}{d\gamma} \left( \frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} \right) &= \frac{d}{d\gamma} \left( \frac{1}{T_S(\vec{z}(\gamma))} \right) u(\gamma) + \frac{d}{d\gamma} \left( \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} \right) v(\gamma) \\
&= A^{-1/2} \frac{d}{d\gamma} \left( (u(\gamma))^{-3/4} (v(\gamma))^{1/2} \right) u(\gamma) \\
&\quad + A^{-1/2} \frac{d}{d\gamma} \left( 2(u(\gamma))^{1/4} (v(\gamma))^{-1/2} \right) \\
&\qquad v(\gamma) \\
&= A^{-1/2} \left( -\frac{3}{4} (u(\gamma))^{-3/4} (v(\gamma))^{1/2} u'(\gamma) \right. \\
&\quad \left. + (u(\gamma))^{1/4} \frac{1}{2} (v(\gamma))^{-1/2} v'(\gamma) \right) \\
&\quad + A^{-1/2} \left( \frac{1}{2} (u(\gamma))^{-3/4} (v(\gamma))^{1/2} u'(\gamma) \right. \\
&\quad \left. - 2(u(\gamma))^{1/4} \frac{1}{2} (v(\gamma))^{-1/2} v'(\gamma) \right) \\
&= A^{-1/2} \left( -\frac{1}{4} (u(\gamma))^{-3/4} (v(\gamma))^{1/2} u'(\gamma) \right. \\
&\quad \left. - \frac{1}{2} (u(\gamma))^{1/4} (v(\gamma))^{-1/2} v'(\gamma) \right) \\
&= -A^{-1/2} \frac{d}{d\gamma} \left( (u(\gamma))^{1/4} (v(\gamma))^{1/2} \right).
\end{aligned}$$

Thus,

$$\frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} = -A^{-1/2} (u(\gamma))^{1/4} (v(\gamma))^{1/2} - s_0.$$

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

$$\begin{aligned}
\tilde{s}(u, v) &= \frac{1}{T_S(u, v)} u + \frac{P_S(u, v)}{T_S(u, v)} v - \frac{\mu_S(u, v)}{T_S(u, v)} \\
&= A^{-1/2} u^{1/4} v^{1/2} + 2A^{-1/2} u^{1/4} v^{1/2} + A^{-1/2} u^{1/4} v^{1/2} + s_0 \\
&= 4A^{-1/2} u^{1/4} v^{1/2} + s_0,
\end{aligned}$$

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 1.2.3.** (4.4) Ideal Gas law

$$PV = NRT$$

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

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

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 equation (in molar form). The Gibbs–Duhem equation is

$$\begin{aligned} \frac{d}{d\gamma} \left( \frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} \right) &= \frac{d}{d\gamma} \left( \frac{1}{T_S(\vec{z}(\gamma))} \right) u(\gamma) + \frac{d}{d\gamma} \left( \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} \right) v(\gamma) \\ &= \frac{3R}{2} \frac{d}{d\gamma} \left( \frac{1}{u(\gamma)} \right) u(\gamma) + R \frac{d}{d\gamma} \left( \frac{1}{v(\gamma)} \right) v(\gamma) \\ &= -\frac{3R}{2} \frac{u'(\gamma)}{u(\gamma)} - R \frac{v'(\gamma)}{v(\gamma)}. \end{aligned}$$

Integrating, we have

$$\frac{\mu_S(u(\gamma), v(\gamma))}{T_S(u(\gamma), v(\gamma))} - \frac{\mu_0}{T_0} = -\frac{3R}{2} \ln \left( \frac{u(\gamma)}{u_0} \right) - R \ln \left( \frac{v(\gamma)}{v_0} \right),$$

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

$$\begin{aligned} \tilde{s}(u, v) &= \frac{1}{T_S(u, v)} u + \frac{P_S(u, v)}{T_S(u, v)} v - \frac{\mu_S(u, v)}{T_S(u, v)} \\ &= \frac{3R}{2} + R + \frac{3R}{2} \ln \left( \frac{u}{u_0} \right) + R \ln \left( \frac{v}{v_0} \right) - \frac{\mu_0}{T_0} \\ &= s_0 + R \ln \left( \left( \frac{u}{u_0} \right)^{3/2} \left( \frac{v}{v_0} \right) \right). \end{aligned}$$

Thus,

$$\tilde{S}(U, V, N) = Ns_0 + NR \ln \left( \left( \frac{U}{U_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-5/2} \right),$$

where

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

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

and

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