Chapter 1

ThermoS26-05

1.1 Examples

Example 1.1.1. (3.4) Suppose that the fundamental relation for a material is given by

$$\tilde{S} = 4A\,U^{1/4}V^{1/2}N^{1/4} + BN, \qquad \Sigma_U = [0,\infty)^3,$$

where $A, B > 0$ are constants. This function must be homogenous of degree one. Suppose $\lambda > 0$. Then

$$\tilde{S}(\lambda U, \lambda V, \lambda N) = 4A\,\lambda U^{1/4}\lambda V^{1/2}\lambda N^{1/4} + B\lambda N = \lambda\tilde{S}(U, V, N).///$$

Recall that

$$T = \frac{1}{\frac{\partial\tilde{S}}{\partial U}} = \left(A\,U^{-3/4}V^{1/2}N^{1/4}\right)^{-1} = \frac{U^{3/4}}{AV^{1/2}N^{1/4}},$$

which is homogenous degree zero.

$$\frac{P}{T} = \frac{\partial\tilde{S}}{\partial V}$$

so

$$P = T\,\frac{\partial\tilde{S}}{\partial V} = \frac{U^{3/4}}{AV^{1/2}N^{1/4}}\left(\frac{2A\,U^{1/4}N^{1/4}}{V^{1/2}}\right) = \frac{2U}{V}.$$

Finally,

$$\mu = -T\,\frac{\partial\tilde{S}}{\partial N} = -\frac{U^{3/4}}{AV^{1/2}N^{1/4}}\left(\frac{A\,U^{1/4}V^{1/2}}{N^{3/4}} + B\right) = -\frac{U}{N} - \frac{BU^{3/4}}{AV^{1/2}N^{1/4}}.///$$

Example 1.1.2. (3.5) Suppose that the fundamental relation is

$$\tilde{U} = \left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^4.$$

Recall that

$$T = \frac{\partial \tilde{U}}{\partial S} = 4\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}N^{1/4}} = \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}},$$

the same as above.

$$P = -\frac{\partial \tilde{U}}{\partial V} = -4\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^3 \left(\frac{S - BN}{4AN^{1/4}}\right)\left(-\frac{1}{2}\right)\frac{1}{V^{3/2}}$$

so

$$= 2\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^4 \frac{1}{V} = \frac{2\tilde{U}}{V}.$$

Finally,

$$\begin{aligned}
\mu = \frac{\partial \tilde{U}}{\partial N} &= 4\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B) - (S - BN)\frac{1}{4}N^{-3/4}}{N^{1/2}} \\
&= 4\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B) - (S - BN)\frac{1}{4}N^{-3/4}}{N^{1/2}} \\
&= 4\tilde{U}^{3/4}\frac{N^{1/4}}{4AV^{1/2}N^{1/2}} \cdot \left(-B - \frac{S - BN}{4N}\right) \\
&= -\frac{B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}}\frac{(S - BN)}{4N} = -\frac{B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}}{N}.///
\end{aligned}$$

1.2 Euler Equation with Respect to Entropy

Theorem 1.2.1. (3.5) *Let $\tilde{S}$ be the internal energy of an isolated system. Then*

$$\tilde{S} = \frac{1}{T_S}U + \frac{P_S}{T_S}V - \sum_{i=1}^{r}\frac{\mu_{S,i}}{T_S}N_i, \tag{3.8}$$

where

$$T_S = T_S(U, V, \vec{N}), \qquad P_S = P_S(U, V, \vec{N}), \qquad \mu_{S,i} = \mu_{S,i}(U, V, \vec{N}),$$

and

$$\frac{1}{T_S} = \frac{\partial \tilde{S}}{\partial U}, \qquad \frac{P_S}{T_S} = \frac{\partial \tilde{S}}{\partial V}, \qquad \frac{\mu_{S,i}}{T_S} = \frac{\partial \tilde{S}}{\partial N_i}.$$

Proof. We again use the fact that $\tilde{S}$ is homogenous of degree one. For any $\lambda > 0$,

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

Taking the derivative with respect to λ, we have

$$\frac{U}{T_S(\lambda U, \lambda V, \lambda \vec{N})} + \frac{P_S(\lambda U, \lambda V, \lambda \vec{N})}{T_S(\lambda U, \lambda V, \lambda \vec{N})} V + \sum_{j=1}^{r} \frac{\mu_{S,j}(\lambda U, \lambda V, \lambda \vec{N})}{T_S(\lambda U, \lambda V, \lambda \vec{N})} N_j = \tilde{S}(U, V, \vec{N}),$$

and setting $\lambda = 1$ gives the desired result. /// □

1.3 Gibbs-Duhem Relation in the Entropy Form

The Gibbs-Duhem equation is similarly derived.

Theorem 1.3.1. (3.6) *Suppose that $\vec{Y} : [0, 1] \to \Sigma_U$ is a process path. Then*

$$0 = \frac{dT_S}{d\gamma}\big(\vec{Y}(\gamma)\big)\, \tilde{S}\big(\vec{Y}(\gamma)\big) - \frac{dP_S}{d\gamma}\big(\vec{Y}(\gamma)\big) V(\gamma) + \sum_{j=1}^{r} \frac{d\mu_S^j}{d\gamma}\big(\vec{Y}(\gamma)\big) N_j(\gamma). \quad (3.9)$$

This equation is called the Gibbs-Duhem relation in the entropy form.

Proof. Using (3.8), we have

$$T_S\big(\vec{Y}(\gamma)\big)\, \tilde{S}\big(\vec{Y}(\gamma)\big) = U(\gamma) + P_S\big(\vec{Y}(\gamma)\big) V(\gamma) - \sum_{j=1}^{r} \mu_{S,j}\big(\vec{Y}(\gamma)\big) N_j(\gamma).$$

Taking the γ-derivative of the last equation, we have

$$\frac{dT_S}{d\gamma}\big(\vec{Y}(\gamma)\big)\, \tilde{S}\big(\vec{Y}(\gamma)\big) + T_S\big(\vec{Y}(\gamma)\big) \frac{d\tilde{S}}{d\gamma}\big(\vec{Y}(\gamma)\big) = U'(\gamma) + \frac{dP_S}{d\gamma}\big(\vec{Y}(\gamma)\big) V(\gamma) + P_S\big(\vec{Y}(\gamma)\big) V'(\gamma) - \sum_{j=1}^{r} \left\{ \frac{d\mu_{S,j}}{d\gamma}\big(\vec{Y}(\gamma)\big) N_j(\gamma) + \mu_{S,j}\big(\vec{Y}(\gamma)\big) N_j'(\gamma) \right\}. \quad (3.10)$$

Taking the γ-derivative of $\tilde{S}\big(\vec{Y}(\gamma)\big)$ we have

$$\frac{d\tilde{S}}{d\gamma}\big(\vec{Y}(\gamma)\big) = \frac{1}{T_S(\vec{Y}(\gamma))} U'(\gamma) + \frac{P_S(\vec{Y}(\gamma))}{T_S(\vec{Y}(\gamma))} V'(\gamma) - \sum_{j=1}^{r} \frac{\mu_{S,j}(\vec{Y}(\gamma))}{T_S(\vec{Y}(\gamma))} N_j'(\gamma). \quad (3.11)$$

Substituting (3.11) into (3.10) yields (3.9). /// □

Remark: Compare (**??**) and (3.9):

$$0 = S(\gamma)\frac{dT_S(\vec{Y}(\gamma))}{d\gamma} - V(\gamma)\frac{dP_S(\vec{Y}(\gamma))}{d\gamma} + \sum_{i=1}^{r} N_i(\gamma)\frac{d\mu_S^i(\vec{Y}(\gamma))}{d\gamma},$$

$$0 = \frac{dT_S}{d\gamma}\left(\vec{Y}(\gamma)\right)\tilde{S}\left(\vec{Y}(\gamma)\right) - \frac{dP_S}{d\gamma}\left(\vec{Y}(\gamma)\right)V(\gamma) + \sum_{j=1}^{r}\frac{d\mu_S^j}{d\gamma}\left(\vec{Y}(\gamma)\right)N_j(\gamma),$$

These are essentially the same expression!
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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

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

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

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

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

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 1.3.2. (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,

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

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

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

T, P, μ 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

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

1.4 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,

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

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

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

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

$$\begin{aligned}\frac{d}{d\gamma}\tilde{u}(\vec{z}(\gamma)) = {} & \frac{d}{d\gamma}T_U(\vec{z}(\gamma))s(\gamma) + T_U(\vec{z}(\gamma))s'(\gamma) && (1.4.1)\\ & - \frac{d}{d\gamma}P_U(\vec{z}(\gamma))v(\gamma) - P_U(\vec{z}(\gamma))v'(\gamma) && (1.4.2)\\ & + \frac{d}{d\gamma}\mu_U(\vec{z}(\gamma)). && (4.3)\end{aligned}$$

Therefore, the molar Gibbs–Duhem equation is

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

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

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

and

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

The molar representation of the First and Second laws is

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

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

1.5 Examples

Let's look at a couple of examples.

Example 1.5.1. (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 1.5.2. (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 1.5.3. (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

$$\frac{1}{T_S} = \frac{3R}{2u} \qquad \frac{P_S}{T_S} = \frac{R}{v}.$$

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

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

$$U_0 = u_0N_0,\ V_0 = v_0N_0,$$

and

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