

2.E. Fundamental Equation of Thermodynamics

Since irreversible processes always involve dissipative and/or chaotic motion such as friction and/or turbulence, they are more disorderly than the reversible processes connecting the same initial and final states. Together with the property [see (2.48)]

$$dS = \frac{\bar{d}Q}{T} + d_i S \quad \begin{array}{l} d_i S = 0 \text{ for reversible processes} \\ d_i S > 0 \text{ for irreversible processes} \end{array}$$

we conclude that S can be taken as a measure of disorder. As already mentioned in §2.D.4, this interpretation will be made concrete by its definition in statistical mechanics [see (7.8) of §7.B].

Comparing the heat absorbed

$$\bar{d}Q = T dS \quad \text{for reversible processes}$$

with the work done

$$\bar{d}W = -\mathbf{Y} \cdot d\mathbf{X} \quad \text{for reversible processes}$$

we see that S & T form a conjugate pair for the heat production, with S being the extensive & T the intensive variable. By definition, extensive variables are proportional to the size (i.e., V or N) of the system. Thus, if we change the size of the system by a factor of λ , every extensive variable will be changed by the same factor λ , and vice versa.

From the 1st law for reversible processes [see (2.23)],

$$dU = T dS + \mathbf{Y} \cdot d\mathbf{X} + \sum_j \mu_j' dN_j \quad (2.55a)$$

we see that

$$U = U(S, \mathbf{X}, \{N_j\}) \quad (2.55b)$$

is a state function whose independent variables are all extensive. Thus, U is itself extensive.

Inverting (2.55a), we get

$$S = S(U, \mathbf{X}, \{N_j\})$$

Changing the size of the system by a factor λ then gives

$$S(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\}) = \lambda S(U, \mathbf{X}, \{N_j\}) \quad (2.55)$$

For an irreversible process that produces a heat change $\bar{d}Q$, the resultant entropy change is still given by (2.55a) as

$$T dS = dU - \mathbf{Y} \cdot d\mathbf{X} - \sum_j \mu_j' dN_j \quad (2.55c)$$

where $(dU, d\mathbf{X}, \{dN_j\})$ denotes the changes between the initial and final (equilibrium) states of the process. However, by the 2nd law,

$$\bar{d}Q \leq T dS = dU - \mathbf{Y} \cdot d\mathbf{X} - \sum_j \mu_j' dN_j \quad (2.56)$$

where we have included the equal sign that applies only to reversible processes.

Caution: (2.56) is not the same as Reichl's (2.56).

Combining (2.56) with the 1st law

$$dU = \bar{d}Q - \bar{d}W$$

we see that

$$\begin{aligned} \bar{d}W &= \bar{d}Q - dU \\ &\leq -\mathbf{Y} \cdot d\mathbf{X} - \sum_J \mu_j' dN_j \end{aligned}$$

Setting

$$(\bar{d}W)_{\text{rev}} = -\mathbf{Y} \cdot d\mathbf{X} - \sum_J \mu_j' dN_j \quad (2.56a)$$

we have

$$\bar{d}W \leq (\bar{d}W)_{\text{rev}} \quad (2.56b)$$

Thus, for irreversible processes, both $\bar{d}Q$ & $\bar{d}W$ are less than the respective values for reversible processes connecting the same initial & final states. However, their difference, dU , remains the same for all processes.

Reminder: $\bar{d}Q$ & $\bar{d}W$ themselves can be either positive or negative.

From (2.55c), we have, for reversible changes,

$$\begin{aligned} dS &= \frac{1}{T} dU - \frac{1}{T} \mathbf{Y} \cdot d\mathbf{X} - \frac{1}{T} \sum_J \mu_j' dN_j \\ &= \left(\frac{\partial S}{\partial U} \right)_{\mathbf{X}, \{N_j\}} dU + \left(\frac{\partial S}{\partial \mathbf{X}} \right)_{U, \{N_j\}} \cdot d\mathbf{X} + \sum_J \left(\frac{\partial S}{\partial N_j} \right)_{U, \mathbf{X}, \{N_{k \neq j}\}} dN_j \end{aligned}$$

Equating the coefficients of the (independent) differentials, we have

$$\left(\frac{\partial S}{\partial U} \right)_{\mathbf{X}, \{N_j\}} = \frac{1}{T} \quad (2.58)$$

$$\left(\frac{\partial S}{\partial \mathbf{X}} \right)_{U, \{N_j\}} = -\frac{1}{T} \mathbf{Y} \quad \text{or} \quad \left(\frac{\partial S}{\partial X_k} \right)_{U, \{X_{i \neq k}\}, \{N_j\}} = -\frac{1}{T} Y_k \quad (2.59)$$

$$\left(\frac{\partial S}{\partial N_j} \right)_{U, \mathbf{X}, \{N_{k \neq j}\}} = -\frac{1}{T} \mu_j' \quad (2.60)$$

With $S = S(U, \mathbf{X}, \{N_j\})$ understood, $\frac{d}{d\lambda}$ (2.55) gives

$$\begin{aligned} \frac{d}{d\lambda} (\lambda S) &= \frac{dS(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\})}{d\lambda} \\ &= \frac{d(\lambda U)}{d\lambda} \frac{\partial S(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\})}{\partial(\lambda U)} + \frac{d(\lambda \mathbf{X})}{d\lambda} \cdot \frac{\partial S(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\})}{\partial(\lambda \mathbf{X})} \\ &\quad + \sum_J \frac{d(\lambda N_j)}{d\lambda} \frac{\partial S(\lambda U, \lambda \mathbf{X}, \{\lambda N_k\})}{\partial(\lambda N_j)} \end{aligned} \quad (2.60a)$$

Now,

$$\left. \frac{\partial S(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\})}{\partial(\lambda U)} = \frac{\partial S(U, \mathbf{X}, \{N_j\})}{\partial U} \right|_{(U, \mathbf{X}, \{N_j\}) \rightarrow \lambda(U, \mathbf{X}, \{N_j\})}$$

$$\begin{aligned}
&= \frac{1}{T(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\})} \quad [(2.58) \text{ used. }] \\
&= \frac{1}{T(U, \mathbf{X}, \{N_j\})} = \frac{1}{T} \quad (2.60b)
\end{aligned}$$

where

$$T(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\}) = T(U, \mathbf{X}, \{N_j\})$$

because T is an intensive variable so that it is unaffected by any change in the size of the system.

Similarly, we have

$$\frac{\partial S(\lambda U, \lambda \mathbf{X}, \{\lambda N_j\})}{\partial (\lambda \mathbf{X})} = \left(\frac{\partial S}{\partial \mathbf{X}} \right)_{U, \{N_j\}} = -\frac{1}{T} \mathbf{Y} \quad [(2.59) \text{ used. }] \quad (2.60c)$$

$$\frac{\partial S(\lambda U, \lambda \mathbf{X}, \{\lambda N_k\})}{\partial (\lambda N_j)} = \left(\frac{\partial S}{\partial N_j} \right)_{U, \mathbf{X}, \{N_{k \neq j}\}} = -\frac{1}{T} \mu_j' \quad [(2.60) \text{ used. }] \quad (2.60d)$$

Putting (2.60b-d) into (2.60a) gives

$$\frac{d}{d\lambda} (\lambda S) = \frac{1}{T} \frac{d(\lambda U)}{d\lambda} - \frac{1}{T} \mathbf{Y} \cdot \frac{d(\lambda \mathbf{X})}{d\lambda} - \frac{1}{T} \sum_j \mu_j' \frac{d(\lambda N_j)}{d\lambda}$$

Since $(S, U, \mathbf{X}, \{N_j\})$ are all independent of λ , we have

$$S = \frac{1}{T} U - \frac{1}{T} \mathbf{Y} \cdot \mathbf{X} - \frac{1}{T} \sum_j \mu_j' N_j$$

or

$$TS = U - \mathbf{Y} \cdot \mathbf{X} - \sum_j \mu_j' N_j \quad (2.61)$$

which is known as the **fundamental equation of thermodynamics**, or the **Euler's equation**.

Now, $d(2.61) - (2.55c)$ gives

$$S dT + \mathbf{X} \cdot d\mathbf{Y} + \sum_j N_j d\mu_j' = 0 \quad (2.62)$$

often called the **Gibbs-Duhem equation**.

Note that (2.62) involves only differentials of intensive variables with extensive variables as coefficients.

Since dividing an extensive variable X with a quantity \mathcal{D} that denotes the size of the system turns it into an intensive variable $\mathbf{x} = X/\mathcal{D}$, we can turn (2.62) into an equation of purely intensive variables,

$$\mathfrak{s} dT + \mathbf{x} \cdot d\mathbf{Y} + \sum_j \eta_j d\mu_j' = 0 \quad (2.63a)$$

Some common choices of \mathcal{D} are

$$\mathcal{D} = V \quad \rightarrow \quad \mathbf{x} = \frac{X}{V} = X \text{ per unit volume} = \text{density of } X$$

$$\mathcal{D} = M \quad \rightarrow \quad \mathbf{x} = \frac{X}{M} = X \text{ per unit mass} = \text{specific } X$$

$$\mathcal{D} = N \quad \rightarrow \quad \mathbf{x} = \frac{X}{N} = X \text{ per particle}$$

$$\mathcal{D} = n \quad \rightarrow \quad \mathbf{x} = \frac{X}{n} = X \text{ per mole} = \text{molar } X$$

$$\frac{\eta_j}{n} = \text{molar fraction of type } j \text{ molecules}$$

Dividing the fundamental equation (2.61) by \mathcal{D} gives

$$T s = u - \mathbf{Y} \cdot \mathbf{x} - \sum_j \mu_j' n_j \quad (2.63b)$$

$d(2.63) - (2.63a)$ then gives

$$T ds = du - \mathbf{Y} \cdot d\mathbf{x} - \sum_j \mu_j' dn_j \quad (2.64a)$$

As an example, let $\mathcal{D} = n$ so that

$$\sum_j n_j = \frac{1}{n} \sum_j n_j = 1$$

As an example, consider $\mathcal{D} = n$ for a system of a single molecular species. (2.63a, b) & (2.64a) reduce to

$$s dT + \mathbf{x} \cdot d\mathbf{Y} + d\mu = 0 \quad [\text{Gibbs-Duhem equation.}] \quad (2.65)$$

$$T s = u - \mathbf{Y} \cdot \mathbf{x} - \mu \quad [\text{Fundamental equation.}] \quad (2.63)$$

$$T ds = du - \mathbf{Y} \cdot d\mathbf{x} \quad [\text{1st law.}] \quad (2.64)$$

where s, u, \mathbf{x} are molar quantities.

Since the partial derivatives in (2.58-60) are between extensive variables, their values are unchanged if replaced by their intensive counterparts. Hence,

$$\left(\frac{\partial s}{\partial u} \right)_{\mathbf{x}, \{n_j\}} = \frac{1}{T} \quad \left(\frac{\partial s}{\partial \mathbf{x}} \right)_{u, \{n_j\}} = -\frac{1}{T} \mathbf{Y} \quad \left(\frac{\partial s}{\partial n_j} \right)_{u, \mathbf{x}, \{n_{k \neq j}\}} = -\frac{1}{T} \mu_j' \quad (2.65a)$$

Ex.2.3.

The entropy of n moles of a monatomic ideal gas is given by the **Sackur-Tetrode equation**,

$$S = nR \left\{ \frac{5}{2} + \ln \left[\frac{V}{V_0} \frac{n_0}{n} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} \quad (1a)$$

where V_0, n_0, T_0 are constants. The equation of state is the ideal gas law

$$PV = nRT \quad (1b)$$

- Compute the internal energy U .
- Compute the chemical potential μ .
- Find the fundamental equation and show that it is a 1st order homogeneous function of the extensive variables.

Answer (a)

It is more convenient to work with molar quantities so that (1a-b) simplify to

$$s = R \left\{ \frac{5}{2} + \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} \quad (1c)$$

$$Pv = RT \quad (1d)$$

The 1st law (2.64) becomes

$$T ds = du + P dv \quad (1e)$$

The phase space is the 4-D space with coordinates (s, T, P, v) . Owing to the equation of state (1d), all system points are restricted to a 3-D manifold \mathcal{M} that is the solution to (1d). For a given initial state, the 1st law (1e) restricts its evolution to a 2-D submanifold of \mathcal{M} that contains the initial system point. Thus, there are only two independent variables among (s, T, P, v) .

Choosing the independent variables to be (T, v) , we have

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

so that (1e) becomes

$$\begin{aligned} du &= T ds - P dv \\ &= T \left(\frac{\partial s}{\partial T} \right)_v dT + \left[T \left(\frac{\partial s}{\partial v} \right)_T - P \right] dv \end{aligned} \quad (1f)$$

Borrowing the results from the next section, we have

$$\left(\frac{\partial s}{\partial v} \right)_T = - \left(\frac{\partial}{\partial v} \left(\frac{\partial f}{\partial T} \right) \right)_T = - \left(\frac{\partial}{\partial T} \left(\frac{\partial f}{\partial v} \right)_T \right)_v = \left(\frac{\partial P}{\partial T} \right)_v \quad (1g)$$

where f is the **molar Helmholtz free energy** defined by its differential as

$$df = -s dT - P dv$$

From the equation of motion (1d), we have

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v} = \frac{P}{T} \quad (1h)$$

so that (1f) becomes

$$du = T \left(\frac{\partial s}{\partial T} \right)_v dT \quad (1i)$$

Experiments give the molar heat capacity at constant volume of a monatomic ideal gas as

$$c_v \equiv \frac{1}{n} \left(\frac{dQ}{dT} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v = \frac{3}{2} R$$

so that (1i) becomes

$$du = \frac{3}{2} R dT$$

which can be integrated to give

$$u = u_0 + \frac{3}{2} R (T - T_0) \quad (1j)$$

where T_0 is some reference temperature and

$$u_0 = u \Big|_{T=T_0}$$

The internal energy of an ideal gas is therefore

$$U = n u = U_0 + \frac{3}{2} n R (T - T_0) \quad (1k)$$

where

$$U_0 = n u_0 = U \Big|_{T=T_0}$$

On the other hand, the equipartition theorem in statistical mechanics (see later) gives

$$U = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (1m)$$

which corresponds to setting

$$U_0 = \frac{3}{2} n R T_0 \quad (1n)$$

Answer (b)

Using (1d) to replace v & v_0 in (1c) gives

$$\begin{aligned} s &= R \left\{ \frac{5}{2} + \ln \left[\frac{T P_0}{P T_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} \\ &= R \left\{ \frac{5}{2} + \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] \right\} \end{aligned} \quad (2a)$$

where

$$P_0 v_0 = R T_0$$

From the Gibbs-Duhem equation [see (2.65)]

$$s dT - v dP + d\mu = 0$$

we get

$$\begin{aligned} \left(\frac{\partial \mu}{\partial T} \right)_P &= -s \\ &= -R \left\{ \frac{5}{2} + \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] \right\} \quad [(2a) \text{ used. }] \end{aligned} \quad (2b)$$

and

$$\begin{aligned} \left(\frac{\partial \mu}{\partial P} \right)_T &= v \\ &= \frac{R T}{P} \quad [(1d) \text{ used. }] \end{aligned} \quad (2c)$$

Integrating (2c) gives

$$\begin{aligned} \mu &= \int dP \frac{R T}{P} + f(T) \\ &= R T \ln P + f(T) \end{aligned} \quad (2d)$$

where the integration “constant” $f(T)$ is an arbitrary function of T .

$\left(\frac{\partial (2d)}{\partial T} \right)_P$ gives

$$\left(\frac{\partial \mu}{\partial T} \right)_P = R \ln P + \frac{df(T)}{dT}$$

which, when compared with (2b), gives

$$\frac{df(T)}{dT} = -R \left\{ \frac{5}{2} + \ln \left[P_0 \left(\frac{T}{T_0} \right)^{5/2} \right] \right\} \quad (2e)$$

Using

$$\int \ln T dT = -T + T \ln T$$

we integrate (2e) to get

$$f(T) = -R \left\{ \frac{5}{2} + \ln \left[P_0 \left(\frac{1}{T_0} \right)^{5/2} \right] \right\} T - \frac{5}{2} R (-T + T \ln T) + \text{const}$$

$$= -RT \ln \left[P_0 \left(\frac{T}{T_0} \right)^{5/2} \right] + \text{const}$$

Putting this into (2d) gives

$$\mu = -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_0 \quad (2)$$

where

$$\mu_0 = \mu \Big|_{(P,T,v)=(P_0,T_0,v_0)}$$

Answer (c)

Using (1m-n), we can write (1a) as

$$\begin{aligned} S &= nR \left\{ \frac{5}{2} + \ln \left[\frac{V}{V_0} \frac{n_0}{n} \left(\frac{n_0 U}{n U_0} \right)^{3/2} \right] \right\} \\ &= nR \left\{ \frac{5}{2} + \ln \left[\frac{V}{V_0} \left(\frac{n_0}{n} \right)^{5/2} \left(\frac{U}{U_0} \right)^{3/2} \right] \right\} \end{aligned} \quad (3)$$

which is the fundamental equation for an ideal gas written in term of only extensive variables (S, n, V, U).

By definition, changing the size of the system by a factor λ changes every extensive variable by the same factor λ , i.e.,

$$(S, n, V, U) \rightarrow (\lambda S, \lambda n, \lambda V, \lambda U) \quad (3a)$$

Applying (3a) to (3) then gives

$$\begin{aligned} \text{LHS of (3)} &\rightarrow \lambda S \\ \text{RHS of (3)} &\rightarrow \lambda n R \left\{ \frac{5}{2} + \ln \left[\frac{\lambda V}{V_0} \left(\frac{n_0}{\lambda n} \right)^{5/2} \left(\frac{\lambda U}{U_0} \right)^{3/2} \right] \right\} \\ &= \lambda n R \left\{ \frac{5}{2} + \ln \left[\frac{V}{V_0} \frac{n_0}{n} \left(\frac{U}{U_0} \right)^{3/2} \right] \right\} \\ &= \lambda S \\ &= \text{LHS of (3)} \end{aligned}$$

Thus, (3) is a 1st order homogeneous equation in the extensive variables (S, n, V, U).

Comment: (3) does not hold if $U(T)$ is given by the more general thermodynamic result (1k). This is one of many signs that S cannot be properly understood without the help of statistical mechanics.