

Chapter 1 Thermodynamics, Fundamentals

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July 19, 2018

1.1

Examples of the two types of energy flow: boiling water with heat; evaporate water with a vacuum.

1.2

We assume E to be the energy, S to be the entropy and n to be the mole of the unit segment l_0 .

(i) The first equation gives that

$$S(E, L, n) = nl_0\gamma \exp\left(\frac{\theta E}{nl_0}\right) - nl_0\gamma \left[\frac{1}{2} \left(\frac{L}{nl_0}\right)^2 + \frac{nl_0}{L} - \frac{3}{2} \right] \quad (1)$$

Thus we find

$$S(\lambda E, \lambda L, \lambda n) = \lambda nl_0\gamma \exp\left(\frac{\theta \lambda E}{\lambda nl_0}\right) - \lambda nl_0\gamma \left[\frac{1}{2} \left(\frac{\lambda L}{\lambda nl_0}\right)^2 + \frac{\lambda nl_0}{\lambda L} - \frac{3}{2} \right] = \lambda S(E, L, n). \quad (2)$$

This means the entropy is an extensive quantity. However, the second equation does not give an extensive entropy S . Therefore the first equation is acceptable while the second one is not.

(ii)

$$\frac{f}{T} = \left(\frac{\partial S}{\partial L}\right)_{n,E} = nl_0\gamma \left(\frac{L}{n^2 l_0^2} - \frac{nl_0}{L^2}\right) \quad (3)$$

For conciseness, denote L/n by length per mole l . The tension is a function of T and l ,

$$f = \gamma T \left(\frac{l}{l_0} - \frac{l_0^2}{l^2}\right). \quad (4)$$

1.3

The variational theorem in the energy representation is

$$(\delta E)_{S, \mathbf{x}} \geq 0 \quad (5)$$

which indicates that S and \mathbf{x} are invariant during the virtual displacement.

$$E = E^{(1)} + E^{(2)}, \quad (6)$$

$$(\delta E)_{S, \mathbf{x}} = (\delta E^{(1)})_{S, \mathbf{x}} + (\delta E^{(2)})_{S, \mathbf{x}} = \left(\frac{\partial E^{(1)}}{\partial S^{(1)}}\right)_{S, \mathbf{x}} (\delta S^{(1)})_{S, \mathbf{x}} + \left(\frac{\partial E^{(2)}}{\partial S^{(2)}}\right)_{S, \mathbf{x}} (\delta S^{(2)})_{S, \mathbf{x}} \quad (7)$$

Also we have

$$S = S^{(1)} + S^{(2)} \quad (8)$$

$$(\delta S)_{S,\mathbf{X}} = (\delta S^{(1)})_{S,\mathbf{X}} + (\delta S^{(2)})_{S,\mathbf{X}} = 0, \quad (9)$$

and

$$\left(\frac{\partial E}{\partial S} \right)_{\mathbf{X}} = T. \quad (10)$$

Thus

$$(\delta E)_{S,\mathbf{X}} = T^{(1)}(\delta S^{(1)})_{S,\mathbf{X}} - T^{(2)}(\delta S^{(1)})_{S,\mathbf{X}}. \quad (11)$$

Therefore

$$(T^{(1)} - T^{(2)})(\delta S^{(1)})_{S,\mathbf{X}} \geq 0 \quad (12)$$

exists for all positive and negative $(\delta S^{(1)})_{S,\mathbf{X}}$. Thus $T^{(1)} = T^{(2)}$.

1.4

Because of the thermal equilibrium, the final temperature $T_f^{(1)} = T_f^{(2)}$. By definition,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{n,l} = \gamma \theta \exp \left(\frac{\theta E}{nl_0} \right) \quad (13)$$

Then

$$E = -\frac{nl_0}{\theta} \ln(\gamma \theta T). \quad (14)$$

Thus

$$E = E_1 + E_2 = -\frac{n^{(1)}l_0}{\theta} \ln(\gamma \theta T^{(1)}) - \frac{n^{(2)}l_0}{\theta} \ln(\gamma \theta T^{(2)}) = -\frac{n^{(1)}l_0}{\theta} \ln(\gamma \theta T_f) - \frac{n^{(2)}l_0}{\theta} \ln(\gamma \theta T_f) \quad (15)$$

Finally we obtain

$$\ln T_f = \frac{n^{(1)} \ln T^{(1)} + n^{(2)} \ln T^{(2)}}{n^{(1)} + n^{(2)}} \quad (16)$$

The final temperature is

$$T_f = \exp \left(\frac{n^{(1)} \ln T^{(1)} + n^{(2)} \ln T^{(2)}}{n^{(1)} + n^{(2)}} \right) \quad (17)$$

and the final energies for the two sub systems are

$$E_f^{(1)} = -\frac{n^{(1)}l_0}{\theta} \ln(\gamma \theta) \left(\frac{n^{(1)} \ln T^{(1)} + n^{(2)} \ln T^{(2)}}{n^{(1)} + n^{(2)}} \right) \quad (18)$$

$$E_f^{(2)} = -\frac{n^{(2)}l_0}{\theta} \ln(\gamma \theta) \left(\frac{n^{(1)} \ln T^{(1)} + n^{(2)} \ln T^{(2)}}{n^{(1)} + n^{(2)}} \right) \quad (19)$$

1.5

We suppose that all the walls and the pistons are adiabatic, and the total system is isolated from particle exchange with the environment. If we reversibly change p_A and/or p_B , we give mechanical work to the total system. And naturally after the change of the positions of the pistons, the system redistribute the particle numbers in the three cabins.

Instead of doing mechanical work, of course we can reversibly pump the particles to the desired concentration in the three cabins. While doing this, the pistons will move reversibly to their final places automatically, as if we only moved the pistons as described above. In this way, we associate the process of doing mechanical work with an equivalent process of changing the concentration of particles.

As another example, we can think of the reversible battery whose work is associated with the change of concentrations of the species.

1.6

Since the entropy S is a natural function of E, V, n ,

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dn \quad (20)$$

we propose two quantities

$$f = S - \frac{1}{T}E, \quad (21)$$

$$g = S - \frac{1}{T}E + \frac{\mu}{T}n. \quad (22)$$

Thus

$$df = Ed\left(\frac{1}{T}\right) + \frac{p}{T}dV - \frac{\mu}{T}dn, \quad (23)$$

$$dg = Ed\left(\frac{1}{T}\right) + \frac{p}{T}dV - nd\left(\frac{\mu}{T}\right) \quad (24)$$

Therefore we have natural functions of $f(1/T, V, n)$ and $g(1/T, V, \mu/T)$.

Note: We suspect that the symbol v in the question and in the context above in the textbook (eg. (p, v, n)) is a typo of V , because there is no prior definition of that.

1.7

(i) From

$$dH = TdS + Vdp + \mu dn \quad (25)$$

we have

$$dS = \frac{1}{T}dH - Vdp - \mu dn \quad (26)$$

which means S is a natural function of (H, p, n) . We can also find that

$$\left(\frac{\partial S}{\partial H}\right)_{p,n} = \frac{1}{T} > 0 \quad (27)$$

so that if we add an internal constraint to the system (H, p, n) without affect these three quantities, we have,

$$S(H, p, n) > S' = S(H, p, n; \text{internal constraint}). \quad (28)$$

There must be a system $(H', p, n; \text{internal constraint})$ that has the same entropy S ,

$$S(H, p, n) = S(H', p, n; \text{internal constraint}). \quad (29)$$

Thus

$$S(H', p, n; \text{internal constraint}) > S(H, p, n; \text{internal constraint}) \quad (30)$$

and notice that they are under the same condition p, n and the same internal constraint. Because of inequality (27), $H' > H$. That is,

$$H(S, p, n; \text{internal constraint}) > H(S, p, n) \quad (31)$$

Therefore

$$(\delta H)_{S,p,n} \geq 0, \quad (\Delta H)_{S,p,n} > 0. \quad (32)$$

(ii) Under the condition of constant (T, V, n) , if we add some internal constraint to the system, we have to introduce work into the system, and it could be reversible. Thus

$$(\Delta S)_{T,V,n} = \frac{(\Delta E)_{T,V,n} - W_{i.c.}}{T} < \frac{(\Delta E)_{T,V,n}}{T} \quad (33)$$

Obviously,

$$[\Delta(E - TS)]_{T,V,n} > 0 \quad (34)$$

That is,

$$(\Delta A)_{T,V,n} > 0 \quad (35)$$

(iii) Under the condition of constant (T, p, n) , similarly, we can introduce work associated with the internal constraint into the system reversibly. Thus

$$(\Delta S)_{T,p,n} = \frac{(\Delta H)_{T,p,n} - W_{i.c.}}{T} < \frac{(\Delta H)_{T,p,n}}{T} \quad (36)$$

$$[\Delta(H - TS)]_{T,p,n} > 0 \quad (37)$$

$$(\Delta G)_{T,p,n} > 0 \quad (38)$$

1.8

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{p,n} \quad (39)$$

$$\begin{aligned} \left(\frac{\partial C_p}{\partial p} \right)_{T,n} &= T \left[\frac{\partial}{\partial p} \left(\frac{\partial S}{\partial T} \right)_{p,n} \right]_{T,n} \\ &= T \left[\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial p} \right)_{T,n} \right]_{p,n} \end{aligned} \quad (40)$$

From

$$dG = -SdT + Vdp + \mu dn \quad (41)$$

we get the relation

$$\left(\frac{\partial S}{\partial p} \right)_{T,n} = - \left(\frac{\partial V}{\partial T} \right)_{p,n} . \quad (42)$$

Thus

$$\left(\frac{\partial C_p}{\partial p} \right)_{T,n} = -T \left[\frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T} \right)_{p,n} \right]_{p,n} = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_{p,n} . \quad (43)$$

1.9

Since $z = z(x, y)$,

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (44)$$

or written as

$$\left(\frac{\partial z}{\partial x} \right)_y dx = dz - \left(\frac{\partial z}{\partial y} \right)_x dy \quad (45)$$

Because $z = z(x, y)$, we also have $x = x(y, z)$. Therefore

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad (46)$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left[\left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \right] = dz - \left(\frac{\partial z}{\partial y}\right)_x dy \quad (47)$$

$$\therefore \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1, \quad (48)$$

$$\therefore \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z dy + dz = dz - \left(\frac{\partial z}{\partial y}\right)_x dy \quad (49)$$

Therefore

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x. \quad (50)$$

1.10

For a homogeneous function of order n $f(x_1, \dots, x_n)$,

$$f(\lambda x_1, \dots, \lambda x_n) = \lambda^n f(x_1, \dots, x_n), \quad (51)$$

$$\left(\frac{\partial f(\lambda x_1, \dots, \lambda x_n)}{\partial \lambda}\right)_{x_1, \dots, x_n} = n\lambda^{n-1} f(x_1, \dots, x_n), \quad (52)$$

On the other hand,

$$\begin{aligned} \left(\frac{\partial f(\lambda x_1, \dots, \lambda x_n)}{\partial \lambda}\right)_{x_1, \dots, x_n} &= \sum_{i=1}^n \left(\frac{\partial f(\lambda x_1, \dots, \lambda x_n)}{\partial(\lambda x_i)}\right)_{\lambda x_j, j \neq i} \left(\frac{\partial \lambda x_i}{\partial \lambda}\right)_{x_i} \\ &= \sum_{i=1}^n \left(\frac{\partial f(\lambda x_1, \dots, \lambda x_n)}{\partial(\lambda x_i)}\right)_{\lambda x_j, j \neq i} x_i \end{aligned} \quad (53)$$

Set $\lambda = 1$,

$$nf(x_1, \dots, x_n) = \sum_{i=1}^n \left(\frac{\partial f(x_1, \dots, x_n)}{\partial x_i}\right)_{x_j, j \neq i} x_i. \quad (54)$$

1.11

X and Y are extensive, so they are first-order homogeneous functions. For a derived function X/Y ,

$$\left(\frac{X}{Y}\right)(\lambda \mathbf{x}) \equiv \frac{X(\lambda \mathbf{x})}{Y(\lambda \mathbf{x})} = \frac{\lambda X(\mathbf{x})}{\lambda Y(\mathbf{x})} = \frac{X(\mathbf{x})}{Y(\mathbf{x})} = \left(\frac{X}{Y}\right)(\mathbf{x}). \quad (55)$$

Thus X/Y is intensive.

For $\partial X/\partial Y$, λ regarded as a constant,

$$\left(\frac{\partial X}{\partial Y}\right)(\lambda \mathbf{x}) \equiv \frac{\partial X(\lambda \mathbf{x})}{\partial Y(\lambda \mathbf{x})} = \frac{\partial[\lambda X(\mathbf{x})]}{\partial[\lambda Y(\mathbf{x})]} = \frac{\lambda \partial X(\mathbf{x})}{\lambda \partial Y(\mathbf{x})} = \left(\frac{\partial X}{\partial Y}\right)(\mathbf{x}). \quad (56)$$

Thus $\partial X/\partial Y$ is intensive.

1.12

Because E is extensive, from

$$dE = TdS + fdL + \mu dn \quad (57)$$

we get

$$E = TS + fL + \mu n. \quad (58)$$

Thus

$$0 = SdT + Ldf + nd\mu. \quad (59)$$

1.13

(i) Given

$$E = \frac{\theta S^2 L}{n^2}, \quad (60)$$

we adopt the equation (57),

$$\mu = \left(\frac{\partial E}{\partial n} \right)_{S,L} = -\frac{2\theta S^2 L}{n^3}. \quad (61)$$

$$T = \left(\frac{\partial E}{\partial S} \right)_{L,n} = \frac{2\theta SL}{n^2}, \quad (62)$$

$$S = \frac{n^2 T}{2\theta L}. \quad (63)$$

Thus

$$\mu = -\frac{nT^2}{2\theta L} = \mu(T, L/n). \quad (64)$$

(ii)

$$f = \left(\frac{\partial E}{\partial L} \right)_{S,n} = \frac{\theta S^2}{n^2} = \frac{n^2 T^2}{4\theta L^2} = f(T, L/n). \quad (65)$$

$$d\mu = -\frac{nT}{\theta L} dT + \frac{n^2 T^2}{2\theta L^2} d(L/n), \quad (66)$$

$$df = \frac{n^2 T}{2\theta L^2} dT - \frac{n^3 T^2}{2\theta L^3} d(L/n) \quad (67)$$

Therefore

$$SdT + Ldf + nd\mu = \frac{n^2 T}{2\theta L} dT + \frac{n^2 T}{2\theta L} dT - \frac{n^3 T^2}{2\theta L^2} d(L/n) - \frac{n^2 T}{\theta L} dT + \frac{n^3 T^2}{2\theta L^2} d(L/n) = 0. \quad (68)$$

1.14

Since

$$G = \mu n \quad (69)$$

and

$$dG = -SdT + Vdp, \quad (70)$$

we can have

$$d\mu = -sdT + vdp. \quad (71)$$

Because

$$dp = \left(\frac{\partial p}{\partial v} \right)_T dv + \left(\frac{\partial p}{\partial T} \right)_v dT, \quad (72)$$

$$d\mu = -sdT + v \left(\frac{\partial p}{\partial v} \right)_T dv + v \left(\frac{\partial p}{\partial T} \right)_v dT. \quad (73)$$

Thus

$$\left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial p}{\partial v} \right)_T. \quad (74)$$

1.15

(i) The construction has been shown in question 1.6, equation (23), (24).

(ii) First considering $E = E(\beta, V, n)$,

$$(dE)_V = \left(\frac{\partial E}{\partial \beta} \right)_{n,V} (d\beta)_V + \left(\frac{\partial E}{\partial n} \right)_{\beta,V} (dn)_V. \quad (75)$$

Then, because it is legitimate to consider $\mu = \mu(T, V, n)$, we can consider $n = n(\beta, \beta\mu, V)$ as well. This gives

$$(dn)_V = \left(\frac{\partial n}{\partial \beta} \right)_{\beta\mu,V} (d\beta)_V + \left(\frac{\partial n}{\partial \beta\mu} \right)_{\beta,V} (d\beta\mu)_V. \quad (76)$$

Combine equation (75) and (76),

$$(dE)_V = \left(\frac{\partial E}{\partial \beta} \right)_{n,V} (d\beta)_V + \left(\frac{\partial E}{\partial n} \right)_{\beta,V} \left(\frac{\partial n}{\partial \beta} \right)_{\beta\mu,V} (d\beta)_V + \left(\frac{\partial E}{\partial n} \right)_{\beta,V} \left(\frac{\partial n}{\partial \beta\mu} \right)_{\beta,V} (d\beta\mu)_V. \quad (77)$$

Thus

$$\left(\frac{\partial E}{\partial \beta} \right)_{\beta\mu,V} = \left(\frac{\partial E}{\partial \beta} \right)_{n,V} + \left(\frac{\partial E}{\partial n} \right)_{\beta,V} \left(\frac{\partial n}{\partial \beta} \right)_{\beta\mu,V}. \quad (78)$$

Using

$$\left(\frac{\partial n}{\partial \beta} \right)_{\beta\mu,V} = - \left(\frac{\partial n}{\partial \beta\mu} \right)_{\beta,V} \left(\frac{\partial \beta\mu}{\partial \beta} \right)_{n,V} \quad (79)$$

we finally get

$$\left(\frac{\partial E}{\partial \beta} \right)_{\beta\mu,V} = \left(\frac{\partial E}{\partial \beta} \right)_{n,V} - \left(\frac{\partial E}{\partial n} \right)_{\beta,V} \left(\frac{\partial n}{\partial \beta\mu} \right)_{\beta,V} \left(\frac{\partial \beta\mu}{\partial \beta} \right)_{n,V}. \quad (80)$$

1.16

Analog to the common definition of the heat capacity,

$$c_l = T \left(\frac{\partial s}{\partial T} \right)_l \quad (81)$$

$$\left(\frac{\partial c_l}{\partial l} \right)_T = T \left[\frac{\partial}{\partial l} \left(\frac{\partial s}{\partial T} \right)_l \right]_T = T \left[\frac{\partial}{\partial T} \left(\frac{\partial s}{\partial l} \right)_T \right]_l. \quad (82)$$

Because $dA = -SdT + fdL + \mu dn$ from question 1.12,

$$\left(\frac{\partial s}{\partial l} \right)_T = \left(\frac{\partial S}{\partial L} \right)_{T,n} = - \left(\frac{\partial f}{\partial T} \right)_{L,n} = -\frac{l}{\theta}. \quad (83)$$

Obviously

$$\left(\frac{\partial c_l}{\partial l} \right)_T = T \left[\frac{\partial}{\partial T} \left(-\frac{l}{\theta} \right) \right]_l = 0. \quad (84)$$

1.17

We have to design a reversible process that has the same initial and final states as that of the process described in the question. The temperature holds constant, while f and l vary according to $l = \theta f/T$ instead of a sudden change. Thus

$$(dS)_{n,T} = \left(\frac{\partial S}{\partial f} \right)_{n,T} df \quad (85)$$

Because $dG = -SdT - Ldf + \mu dn$,

$$\left(\frac{\partial S}{\partial f} \right)_{n,T} = \left(\frac{\partial L}{\partial T} \right)_{n,f} = n \left(\frac{\partial l}{\partial T} \right)_f = -\frac{n\theta f}{T^2} \quad (86)$$

$$\Delta S_{n,T} = \int_f^{f+\Delta f} \left(-\frac{n\theta f}{T^2} \right) df = -\frac{n\theta}{2T^2} [2f\Delta f + (\Delta f)^2]. \quad (87)$$

1.18

Assume $\theta_i, i = 1, 2, \dots, n$ are non-zero real constants. On the one hand,

$$\left(\frac{\partial f(\lambda^{\theta_1} x_1, \dots, \lambda^{\theta_n} x_n)}{\partial \lambda} \right)_{x_1, \dots, x_n} = f(x_1, \dots, x_n), \quad (88)$$

while on the other hand,

$$\left(\frac{\partial f(\lambda^{\theta_1} x_1, \dots, \lambda^{\theta_n} x_n)}{\partial \lambda} \right)_{x_1, \dots, x_n} = \sum_{i=1}^n \left(\frac{\partial f(\lambda^{\theta_1} x_1, \dots, \lambda^{\theta_n} x_n)}{\partial \lambda^{\theta_i} x_i} \right)_{\lambda^{\theta_j} x_j, j \neq i} \theta_i \lambda^{\theta_i - 1} x_i. \quad (89)$$

Set $\lambda = 1$,

$$\sum_{i=1}^n \left(\frac{\partial f(x_1, \dots, x_n)}{\partial x_i} \right)_{x_j, j \neq i} \theta_i x_i = f(x_1, \dots, x_n). \quad (90)$$