Lecture T2 **DRAFT**

Fundamental Relations, Thermodynamic Potentials, and Chemical Potential

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These notes cover unit T2 of the thermodynamics sequence, in two parts. Part I asks which function of which variables to use when the surroundings, rather than the experimenter, fix a system's temperature or pressure, and derives the minimum principles that go with a reservoir. Part II examines the extensivity assumption that those results quietly use, and gives the chemical potential a physical reading. We assume the first and second laws, the entropy maximum principle for a composite system with internal constraints, and multivariable calculus. Notation and conventions are fixed in Section 1.1.

Contents

Part I Changing Variables and Reservoir Constraints

1 Which Variables Does the Laboratory Control?

A flask of liquid sits on a bench, open to the room. Two features of this utterly ordinary situation are worth noticing. The room fixes the temperature of the liquid, and the atmosphere fixes its pressure. Neither the energy of the liquid nor its volume is under our control; both settle to whatever values are consistent with the temperature and pressure imposed from outside. If we want to predict how much the liquid expands when the room warms, or how much heat it absorbs, we are asking about a system whose controlled variables are T and P.

The description built in the preceding lectures is organized around different variables. For a simple one-component fluid we have the fundamental relation in the entropy representation, $S(E, V, N)$, or equivalently in the energy representation, $E(S, V, N)$, whose differential is

$$dE = T\,dS - P\,dV + \mu\,dN. \tag{1}$$

Here T, P and μ are defined by the partial derivatives of E collected in Section 2. Equation (1) relates the differentials of state functions evaluated between neighbouring equilibrium states. It is not a statement about any particular process: $T\,dS$ becomes the heat $đQ$ only for a quasi-static change, and $-P\,dV$ becomes the work $đW$ only when the system's own pressure acts through the displacement. We keep that distinction throughout, because several of the results below are often misquoted as claims about heat and work.

The difficulty with using (1) for the flask is not that it is wrong but that its independent variables are the ones we cannot set. We do know how to handle the situation in principle. Treat flask and

room together as an isolated composite system, impose the constraint that their total energy is fixed, and maximize the total entropy, as in the equilibrium lecture. That procedure is correct, and we will use it below, but it forces us to carry the room's state through every calculation even though the only thing we ever want to know about the room is its temperature.

So we have two questions, one mathematical and one physical.

1. Can we re-express the fundamental relation in terms of T and P *without losing any of its content*? Simply substituting T for S will turn out to discard information, and we need to see why and what to do instead.

2. Can we find an equilibrium criterion that refers to the system alone, with the surroundings entering only through the fixed values of T and P?

The answer to the first is the Legendre transformation (Section 3), which produces the enthalpy, the Helmholtz free energy, the Gibbs free energy, and the grand potential (Section 4). The answer to the second is the family of minimum principles for those potentials, which we derive by putting a reservoir into the composite system and letting it be large (Section 5). Section 6 carries a monatomic ideal gas through the whole construction so that the abstract statements have a concrete referent.

1.1. Notation for This Unit

Table 1 fixes symbols, dimensions and conventions. We will keep every constrained derivative's subscript in place: in this subject the subscripts carry physics, and $\left(\frac{\partial E}{\partial V}\right)_{S,N}$ and $\left(\frac{\partial E}{\partial V}\right)_{T,N}$ are different quantities.

Symbol	Meaning	Units	Convention or note
E	internal energy	J	written U in many texts
S	entropy	$\mathrm{J\,K^{-1}}$	physical entropy, not S/k_B
T	thermodynamic temperature	K	assumed positive here
P	pressure	Pa	conjugate to V with a minus sign
N	particle number	—	particles, not moles; $R = N_A k_B$
μ	chemical potential	J	energy per particle
k_B	Boltzmann constant	$\mathrm{J\,K^{-1}}$	$\beta \equiv 1/(k_B T)$
s, v	entropy and volume per particle	$\mathrm{J\,K^{-1}}$, $\mathrm{m^3}$	$s = S/N$, $v = V/N$
C_V	heat capacity at fixed V, N	$\mathrm{J\,K^{-1}}$	$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$
Ω	grand potential	J	not a multiplicity in this unit

Table 1: Notation used in both parts of unit T2. Earlier lectures in this series wrote E for the energy of a body, and we keep that symbol for the internal energy rather than switching to U. Logarithms always take dimensionless arguments, which is why reference values such as v_0 and T_0 appear in Section 6.

2 Fundamental Relations and Equations of State

A *fundamental relation* is a single function that determines all equilibrium properties of the system. For a one-component fluid it is $E(S, V, N)$ or $S(E, V, N)$; the variables it takes are its *natural*

variables.

The Fundamental Relation and Its Derivatives

The equilibrium states of a simple fluid are described by $E(S, V, N)$, whose first derivatives define

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N}, \qquad P \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \qquad \mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V}.$$

Each of these three functions of (S, V, N) is an *equation of state*.

The distinction between the fundamental relation and an equation of state is easy to state and easy to forget. The fundamental relation determines the three equations of state by differentiation. A single equation of state does not determine the fundamental relation, because integrating one partial derivative leaves the dependence on the other variables undetermined. The ideal-gas law $PV = Nk_BT$, for example, says nothing about how the energy depends on volume at fixed temperature, and is satisfied by fluids with quite different thermal properties. In Section 6 we show that $PV = Nk_BT$ *together with* $E = \frac{3}{2}Nk_BT$ does recover the fundamental relation, up to one additive constant that classical thermodynamics cannot fix.

Passing between the two representations requires solving $E(S, V, N)$ for S, which is possible when E is strictly increasing in S at fixed V and N. That is the statement $T > 0$. Systems with a bounded energy spectrum violate it in part of their range, as the first lecture noted for negative-temperature states; those systems need the entropy representation and a separate argument. Everything below assumes $T > 0$ and, where stated, $C_V > 0$.

3 Changing the Controlled Variable

3.1. Why Substitution Is Not Enough

The naive route to a description in terms of temperature is to solve $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$ for S and substitute the result back into E. This produces a perfectly good function $E(T, V, N)$, but it is no longer a fundamental relation.

To see what has been lost, fix V and N and think of E as a function of the single variable S. Knowing E as a function of its own slope $T = dE/dS$ is knowing a first-order differential equation for the curve $E(S)$. Its solutions come in a one-parameter family: if $E(S)$ is a solution then so is $E(S - c)$ for any constant c, since shifting the curve sideways changes neither the set of slopes nor the energy at which each slope occurs. The map from curve to $E(T)$ therefore throws away the origin of the entropy axis. We check this explicitly for the ideal gas in Problem 1, where the lost constant reappears in the free energy as a term $-Ns_1T$.

There is a blunter symptom in the same example. For a monatomic ideal gas, $E(T, V, N) = \frac{3}{2}Nk_BT$ contains no volume dependence at all, so no amount of differentiating it will produce the pressure. The energy written in its natural variables, $E(S, V, N)$, gives the pressure immediately.

3.2. The Tangent-Line Construction

The repair is to record not just the slope of the curve but the family of tangent lines. A line is fixed by its slope and its intercept, and for a strictly convex curve each slope occurs exactly once, so the family of tangent lines contains the same information as the curve itself. The intercept of

the tangent line of slope T is

$$F = E - TS,$$

evaluated at the point where the slope is T (Figure 1). This quantity, expressed as a function of T, is the Legendre transform of E with respect to S.

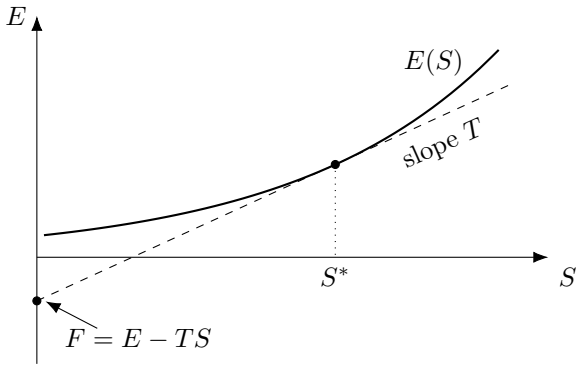


Figure 1: The Legendre transform at fixed V and N. The curve is the fundamental relation $E(S)$; the tangent at S^* has slope $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$ and intercept $F = E - TS$ on the $S = 0$ axis. Because E is strictly convex in S when $C_V > 0$, each slope belongs to one point of the curve, and the family of tangent lines carries the same information as the curve. The intercept is negative for the state drawn here; its sign has no particular significance.

Legendre Transformation

Let $f(x)$ be differentiable and strictly convex on the interval of interest, and let $p = df/dx$. Since $f'' > 0$, the relation $p(x)$ is invertible; write $x(p)$ for its inverse. The Legendre transform of f is

$$g(p) \equiv f\big(x(p)\big) - p\,x(p), \qquad \text{so that} \qquad dg = -x\,dp.$$

Strict convexity is the condition that makes the transform well defined, and applying the construction to g returns f. For a function of several variables the transform may be carried out in any subset of the slots, the untransformed variables coming along as parameters.

For $f = E$ and $x = S$ the convexity condition reads

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} = \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{C_V} > 0, \tag{2}$$

so a positive heat capacity at fixed volume is exactly what we need. Taking the differential of $F = E - TS$ and using (1),

$$dF = dE - T\,dS - S\,dT = -S\,dT - P\,dV + \mu\,dN. \tag{3}$$

The variable S has disappeared from the right-hand side and T has taken its place. The natural variables of F are (T, V, N), and we can read off $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ and $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$.

One structural point is worth recording now because T5 will need it. The transform inverts curvature in the slot it acts on: E is convex in S, while $\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} = -C_V/T < 0$ makes F concave in T. The stability conditions of a thermodynamic system are statements about exactly these curvatures.

4 The Four Potentials

The conjugate pairs in (1) are (S, T), $(V, -P)$ and (N, μ). The minus sign in the second pair is the reason the volume transform comes with a plus sign: exchanging V for its conjugate slope $-P$ means forming $E - (-P)V = E + PV$. Transforming one, two or three of the slots gives the potentials in Table 2.

Potential	Definition	Differential	Natural variables	Held fixed by
Energy E	—	$T\,dS - P\,dV + \mu\,dN$	S, V, N	isolation
Enthalpy H	$E + PV$	$T\,dS + V\,dP + \mu\,dN$	S, P, N	a pressure bath
Helmholtz F	$E - TS$	$-S\,dT - P\,dV + \mu\,dN$	T, V, N	a thermal bath
Gibbs G	$E - TS + PV$	$-S\,dT + V\,dP + \mu\,dN$	T, P, N	both baths
Grand Ω	$E - TS - \mu N$	$-S\,dT - P\,dV - N\,d\mu$	T, V, μ	a particle bath

Table 2: The potentials obtained by Legendre transformation of $E(S, V, N)$. Each differential is an identity between differentials of state functions, valid between neighbouring equilibrium states; none of them is a statement about heat or work along a process. The last column anticipates Section 5.

Each potential is useful because some experiment holds its natural variables fixed.

Enthalpy. Consider a system pressed on by a constant external pressure P_{ext} through a massless piston, doing no work other than that volume work. The work done on the system is $W_{\text{on}} = -P_{\text{ext}}\Delta V$ whether or not the process is quasi-static, so the first law gives $Q = \Delta E + P_{\text{ext}}\Delta V$. If the initial and final equilibrium states both have $P = P_{\text{ext}}$, the right-hand side is $\Delta(E + PV) = \Delta H$. The enthalpy change of such a process is the heat absorbed, which is why tabulated heats of reaction and of vaporization are enthalpy differences. Note what the statement needs: constant external pressure, endpoint pressures equal to it, and no other work.

Helmholtz and Gibbs free energies. These govern a system in a thermal bath at fixed volume, and in a thermal bath at fixed pressure. Their extremum properties are the subject of the next section, and they are the potentials the rest of the thermodynamics sequence uses most.

Grand potential. Ω is natural for a system that exchanges particles as well as energy with its surroundings, so that μ rather than N is imposed. We derive its variational statement in Part II, after the chemical potential has been given a physical reading, and the grand canonical ensemble of S2 is built directly on it.

There is one more transform to consider, and it fails in an instructive way. Transforming all three extensive slots gives $E - TS + PV - \mu N$, which vanishes identically for a system large enough to be treated as extensive. The reason is Euler's relation, which is the first result of Part II. A description purely in terms of (T, P, μ) is therefore impossible: those three intensive variables are not independent.

5 Reservoirs and the Minimum Principles

We now return to the flask. The equilibrium criterion we have is the entropy maximum principle for an isolated composite system. The criterion we want refers to the system alone. The bridge between them is the observation that a large enough surroundings enters the calculation only through its temperature and pressure.

Reservoir

A *reservoir* is a system whose intensive parameters do not change appreciably when it exchanges energy, volume or particles with the much smaller system of interest. For a thermal reservoir the relevant comparison is $C_A/C_R \ll 1$, where C_A and C_R are the heat capacities of system and reservoir. The reservoir is assumed to remain internally equilibrated throughout.

5.1. A Thermal Reservoir and the Helmholtz Criterion

Let system A have fixed volume V and particle number N, and let it exchange energy with a reservoir R at temperature T_R (Figure 2a). The composite is isolated, so $E_{\mathrm{tot}} = E_A + E_R$ is fixed. We also allow A to be held by some internal constraint, whose value we call X: a partition in a particular position, a chemical composition held out of equilibrium, a magnetic moment held at a prescribed value. The entropy of A is then $S_A(E_A, V, N; X)$, and the total entropy is

$$S_{\mathrm{tot}} = S_A(E_A, V, N; X) + S_R(E_{\mathrm{tot}} - E_A). \tag{4}$$

Because R is large, expand its entropy about $E_A = 0$:

$$S_R(E_{\mathrm{tot}} - E_A) = S_R(E_{\mathrm{tot}}) - \frac{E_A}{T_R} - \frac{E_A^2}{2T_R^2 C_R} + \cdots, \tag{5}$$

using $\partial S_R/\partial E_R = 1/T_R$ and $\partial^2 S_R/\partial E_R^2 = -1/(T_R^2 C_R)$. The ratio of the quadratic term to the linear one is $E_A/(2T_R C_R)$, which for E_A of order $C_A T_R$ is of order $C_A/(2C_R)$. This is the precise sense in which the reservoir is large: we drop the quadratic term, and every statement below inherits that approximation.

The first term in (5) is a constant. Dropping it and multiplying by the positive constant $-T_R$ turns maximizing S_{tot} into minimizing

$$\mathcal{A}(E_A, X) \equiv E_A - T_R\, S_A(E_A, V, N; X), \tag{6}$$

a function of the state of A alone, with the reservoir surviving only as the parameter T_R. This object is called the *availability*. It is not yet the Helmholtz free energy, because E_A is still a free variable and the system need not be at the reservoir temperature.

Minimize in two stages. First vary E_A at fixed X:

$$\left(\frac{\partial \mathcal{A}}{\partial E_A}\right)_X = 1 - \frac{T_R}{T_A} = 0 \quad \Longrightarrow \quad T_A = T_R, \tag{7}$$

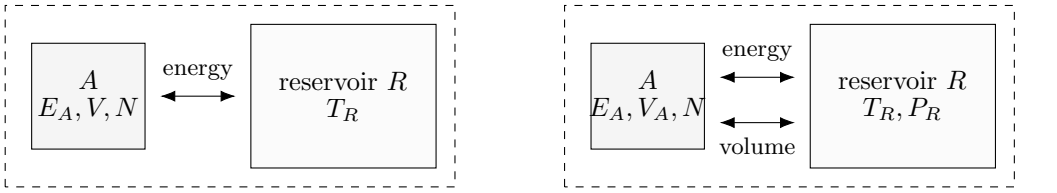
where T_A is the system's own temperature, $1/T_A = \left(\frac{\partial S_A}{\partial E_A}\right)_{V,N;X}$. This is a stationarity condition. It becomes a minimum when the second derivative is positive,

$$\left(\frac{\partial^2 \mathcal{A}}{\partial E_A^2}\right)_X = -T_R \left(\frac{\partial^2 S_A}{\partial E_A^2}\right)_{V,N;X} = \frac{T_R}{T_A^2\, C_{V,A}} > 0, \tag{8}$$

which holds if and only if $C_{V,A} > 0$. Concavity of S_A in E_A is what makes the stationary point a minimum of the availability; without it, the stationary point is not the equilibrium state. At the minimum, the availability takes the value

$$\mathcal{A}\big|_{T_A=T_R} = E_A - T_R S_A = F_A(T_R, V, N; X),$$

the Helmholtz free energy of the constrained state. The remaining minimization over X is therefore a minimization of F.



(a) energy exchange only: minimize F (b) energy and volume exchange: minimize G

Figure 2: The composite systems used in Section 5. The dashed boundary is isolated, so the total energy is fixed in both panels and the total volume is fixed in (b). The reservoir enters the criterion for A only through T_R and P_R.

5.2. Adding a Pressure Reservoir

Now let the wall between A and R also move, so that A exchanges volume as well as energy while the total volume $V_{\text{tot}} = V_A + V_R$ stays fixed (Figure 2b). Expanding the reservoir entropy in both arguments,

$$S_R(E_{\text{tot}} - E_A, V_{\text{tot}} - V_A) = S_R(E_{\text{tot}}, V_{\text{tot}}) - \frac{E_A}{T_R} - \frac{P_R V_A}{T_R} + \cdots,$$

where the neglected terms are quadratic and small in the same sense as before. Maximizing S_{tot} now means minimizing the availability

$$\mathcal{A}(E_A, V_A, X) = E_A + P_R V_A - T_R S_A(E_A, V_A, N; X). \tag{9}$$

Setting the first derivatives with respect to E_A and V_A to zero gives $T_A = T_R$ and then $P_A = P_R$; at that point the availability equals $G_A(T_R, P_R, N; X)$. Whether the stationary point is a minimum is now a statement about the full second-derivative matrix of S_A in (E_A, V_A), which requires $C_V > 0$ and $\kappa_T > 0$. T5 works out those conditions; here we state them as assumptions.

Minimum Principles and Their Conditions

Let a system exchange energy with a reservoir at temperature T_R, with its volume V and particle number N fixed, and let the reservoir be large in the sense $C_A/C_R \ll 1$. Among the constrained equilibrium states of the system at $T = T_R$, the unconstrained equilibrium state is the one of least $F(T_R, V, N)$, provided $C_V > 0$ so that the stationary point is a minimum. If the system instead exchanges both energy and volume with a reservoir at (T_R, P_R), at fixed N, the equilibrium state is the one of least $G(T_R, P_R, N)$, provided the thermal and mechanical stability conditions hold. Both statements are equivalent to maximizing the total entropy of the isolated composite, to first order in the ratio of system to reservoir size.

5.3. What the Minimum Principle Does Not Say

Three qualifications matter, and each of them is a place where the statement is commonly overextended.

The minimization runs over *constrained equilibrium states* of the system, not over arbitrary configurations and not over time. The principle selects which state is the equilibrium one; it says nothing about how long the system takes to get there, or by what route. A glass held for years in a state of higher free energy than the crystal is not a counterexample to the principle but an illustration that the constraint which keeps it there is slow to release.

The temperature appearing in F is the reservoir's. Before the two stages of the minimization are complete, the system need not have a well-defined temperature at all, which is why the availability (6) and not the free energy is the object that decreases.

The criterion presupposes the stability conditions used to convert a stationary point into a minimum. Where they fail, as they do inside the coexistence region of a fluid, the analysis has to be redone; that is the subject of T5 and T6.

5.4. A Bound on Work

The same reservoir gives a useful inequality, which T4 develops in detail. Let a system begin and end in equilibrium states at the reservoir temperature T_R, exchanging heat only with that reservoir. The second law applied to the isolated composite gives $\Delta S_A + \Delta S_R \geq 0$, and since the reservoir absorbs $-Q$ at temperature T_R we have $Q \leq T_R\,\Delta S_A$. Combining with $\Delta E = Q + W_{\mathrm{on}}$,

$$W_{\mathrm{on}} \;\geq\; \Delta E - T_R\,\Delta S_A \;=\; \Delta F, \tag{10}$$

with equality for a reversible process. The free energy change is the least work that must be done on the system, or, read the other way, $-\Delta F$ is the most work the system can deliver. At fixed T_R and P_R the same argument with the volume work separated out bounds the non-volume work by ΔG.

6 A Worked Fundamental Relation: the Monatomic Ideal Gas

It helps to see the whole construction carried out on a system where every step can be done explicitly. Take the two experimentally accessible equations of state of a dilute monatomic gas,

$$PV = Nk_BT, \qquad E = \tfrac{3}{2}Nk_BT, \tag{11}$$

and ask what fundamental relation they come from. In the entropy representation, (1) rearranges to $dS = (1/T)\,dE + (P/T)\,dV - (\mu/T)\,dN$, and (11) supplies the first two coefficients at fixed N:

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk_B}{2E}, \qquad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk_B}{V}.$$

Integrating at fixed N gives $S = Nk_B\left[\tfrac{3}{2}\ln(E/E_r) + \ln(V/V_r)\right] + f(N)$, where the reference values E_r and V_r keep the logarithms dimensionless and any change in them is absorbed into $f(N)$. That function is fixed by requiring that S be extensive, $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$, an assumption we examine critically in Part II. Writing $v = V/N$ and fixing the references as v_0 and T_0,

$$S(E,V,N) = Nk_B\left[\frac{3}{2}\ln\!\left(\frac{E}{\tfrac{3}{2}Nk_BT_0}\right) + \ln\!\left(\frac{v}{v_0}\right) + \frac{s_0}{k_B}\right]. \tag{12}$$

The single dimensionless constant s_0/k_B is not determined by (11). Classical thermodynamics cannot supply it; counting quantum states can, and S3 obtains the Sackur–Tetrode value.

Worked Example: the Monatomic Ideal Gas

Solving (12) for E gives the fundamental relation in the energy representation,

$$E(S,V,N) = \frac{3}{2}Nk_BT_0\left(\frac{v_0}{v}\right)^{2/3}\exp\left[\frac{2}{3}\left(\frac{S}{Nk_B}-\frac{s_0}{k_B}\right)\right].$$

Its derivatives return (11): $\left(\frac{\partial E}{\partial S}\right)_{V,N} = T$ reproduces $E = \frac{3}{2}Nk_BT$, and $-\left(\frac{\partial E}{\partial V}\right)_{S,N} = Nk_BT/V$ reproduces the ideal-gas law. Eliminating S in favour of T gives the Legendre transform

$$F(T,V,N) = Nk_BT\left[\frac{3}{2}-\frac{3}{2}\ln\left(\frac{T}{T_0}\right)-\ln\left(\frac{v}{v_0}\right)-\frac{s_0}{k_B}\right],$$

from which $-\left(\frac{\partial F}{\partial T}\right)_{V,N}$ returns (12) and $-\left(\frac{\partial F}{\partial V}\right)_{T,N} = Nk_BT/V$ returns the pressure.

Two things in this example are worth extracting. First, $F(T,V,N)$ and $E(S,V,N)$ carry exactly the same information, encoded differently; either one yields all three equations of state, while (11) on its own left s_0 free. Second, the failure of naive substitution is visible: replacing S by T inside E gives $E = \frac{3}{2}Nk_BT$, a function with no volume dependence whatever, from which the pressure cannot be recovered. The intercept of the tangent line, not the value of the function at the new argument, is what preserves the content.

Differentiating F with respect to N gives the chemical potential,

$$\mu(T,v) = k_BT\left[\frac{5}{2}-\frac{3}{2}\ln\left(\frac{T}{T_0}\right)-\ln\left(\frac{v}{v_0}\right)-\frac{s_0}{k_B}\right], \tag{13}$$

which we will need in Part II. Substituting $v = k_BT/P$ puts it in the compact form

$$\mu(T,P) = k_BT\ln\left(\frac{P}{P_*(T)}\right), \qquad P_*(T) \equiv \frac{k_BT}{v_0}\left(\frac{T}{T_0}\right)^{3/2} e^{\,s_0/k_B-5/2}, \tag{14}$$

where $P_*(T)$ depends only on the temperature and the reference constants. At fixed temperature the chemical potential of an ideal gas rises logarithmically with pressure. Part II uses this to answer which way particles move.

7 Optional: the Entropy Transforms

This section is not needed for the rest of the unit, but it is short and it removes an asymmetry that becomes important in statistical mechanics.

We transformed the energy. Nothing stops us from transforming the entropy instead. Starting from $S(E,V,N)$ and treating $1/T$ as the slope conjugate to E, the transform is the *Massieu function*

$$\Psi \equiv S - \frac{E}{T} = -\frac{F}{T}, \qquad d\Psi = -E\,d\left(\frac{1}{T}\right) + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN. \tag{15}$$

Transforming the volume slot as well gives the Planck function $\Phi \equiv S - E/T - PV/T = -G/T$, with $d\Phi = -E\,d(1/T) - V\,d(P/T) - (\mu/T)\,dN$; transforming the particle slot instead gives $S - E/T + \mu N/T = -\Omega/T$.

Units and normalization need care here. Ψ has the units of entropy, $\mathrm{J\,K^{-1}}$. The dimensionless version is $\Psi/k_B = S/k_B - \beta E$ with $\beta = 1/(k_B T)$, and the multiplier conjugate to E is $1/T$ when one maximizes the physical entropy S and β when one maximizes S/k_B; the two differ by the factor k_B and must not be identified. The point of the construction is that statistical mechanics computes the dimensionless objects directly: S2 will find $\Psi/k_B = \ln Z$ for the canonical distribution and $-\Omega/(k_B T) = \ln \Xi$ for the grand canonical one. Zia, Redish and McKay [2] argue that this dimensionless form is the more natural one for exhibiting the symmetry of the transforms. We stop here, because deriving those partition functions requires the ensembles themselves.

8 What We Have, and What Comes Next

We began with a flask whose temperature and pressure are set from outside and whose energy and volume are not. The Legendre transformation answered the mathematical half of the problem: the potentials H, F, G and Ω are re-encodings of the same fundamental relation, differing in which variables are independent, with the tangent-line intercept doing the work that naive substitution failed to do. Enlarging the composite system to include a reservoir answered the physical half: maximizing the total entropy is the same as minimizing an availability built from the system's own state and the reservoir's intensive parameters, which at the system's own equilibrium temperature is the appropriate free energy.

Along the way we twice leaned on an assumption without examining it. We used extensivity to fix the function $f(N)$ in (12), and we claimed without proof that the complete Legendre transform $E - TS + PV - \mu N$ vanishes identically. Neither is a consequence of the first and second laws. What does that assumption buy us, when is it false, and what exactly is the chemical potential that appears in every differential above but has so far been only a derivative? Those are the questions of Part II.

Part II Extensivity and the Chemical Potential

9 What Does Doubling the System Tell Us?

Slide an imaginary plane through a large uniform fluid, dividing it into two halves. Each half has half the energy, half the volume and half the particles of the whole; each has the same temperature, the same pressure and the same chemical potential. That two-sentence observation is the entire content of extensivity, and we have not yet used any of it.

It is worth being clear about how little we have assumed so far. The differential relation (1) holds for systems to which the scaling statement does not apply at all: a droplet whose surface energy is a sizeable fraction of its total, a star held together by its own gravity, a film whose thickness is a few molecules. What, then, does the scaling assumption buy?

It buys two things, and both are the subject of this part. The first is a closed expression for E itself rather than for its differential, which is Euler's relation of Section 11. The second is a constraint linking T, P and μ, which is the Gibbs–Duhem relation of Section 12; it says that the three equations of state of a one-component fluid are not independent, so that a description in terms of the three intensive variables alone carries no information. That last point closes the loose end left in Section 4, where the complete Legendre transform $E - TS + PV - \mu N$ was asserted to vanish.

Alongside this runs a second question. The chemical potential entered as $\left(\frac{\partial E}{\partial N}\right)_{S,V}$ and has stayed a derivative. Its name promises more: a temperature difference drives a flow of energy, and something called a potential ought to drive a flow of particles. Section 13 shows that it does, and Section 14 extends the statement to mixtures, where separate potentials govern separate species.

10 Additivity and Extensivity

Two statements are commonly run together, and it pays to keep them apart.

Additivity says that when a system is divided into macroscopic parts, its energy and entropy are the sums of those of the parts. This requires the interaction energy between parts to be negligible compared with the energy of the parts themselves, which in turn requires short-ranged forces and an interface whose energy is small compared with the bulk.

Extensivity says that E is a homogeneous function of degree one in its extensive arguments,

$$E(\lambda S, \lambda V, \lambda N) = \lambda\, E(S, V, N) \qquad \text{for all } \lambda > 0, \tag{16}$$

with T, P and μ correspondingly homogeneous of degree zero, that is, unchanged by the scaling. For a uniform system with short-ranged interactions the two statements amount to the same thing. They are not equivalent in general: systems with long-range interactions can be made extensive by rescaling their coupling strength with the number of particles and still fail to be additive, since the energy of the whole is not the sum of the energies of its macroscopic parts [4].

How good is the assumption for a laboratory sample? Write the energy as a bulk term plus a surface term, $E \simeq \varepsilon N + \sigma \mathcal{S}$, where the interfacial area of a compact sample scales as $\mathcal{S} \propto N^{2/3}$. The fractional surface correction then falls off as $N^{-1/3}$, which for $N \sim 10^{24}$ is of order 10^{-8}. Problem 4 puts numbers on the crossover for a water droplet and finds the surface term reaching one per cent of the bulk cohesive energy at a radius of about ten nanometres. For anything larger, extensivity is an excellent approximation; for anything smaller, the surface term *is* the physics.

Extensivity as a Model Assumption

Everything in Sections 11 to 14 assumes (16). The assumption models a single uniform phase with short-ranged interactions, in the thermodynamic limit, with surface contributions neglected, no external field imposing a spatial variation, and N large enough to be treated as a continuous variable. Every result below inherits these conditions, and we will say so again where the result is boxed.

The four ways the assumption fails are worth naming now, because each returns later in the sequence.

1. **Surfaces.** Droplets, bubbles, critical nuclei and thin films have surface terms comparable to bulk terms. T6 restores them as an explicit $\sigma\, d\mathcal{S}$ contribution and obtains the Laplace pressure and the nucleation barrier from it.

2. **Long-range interactions.** For gravitational and unscreened Coulomb systems the energy is not additive. The entropy need not be a concave function of energy, the microcanonical and canonical descriptions can disagree, and negative heat capacities are possible [4]. The equilibrium lecture met this already in the context of self-gravitating systems.

3. **External fields.** A column of gas in a gravitational field is not uniform, so there is no scaling to perform on the column as a whole. Section 13.4 shows the repair: apply the equilibrium conditions locally, to slabs small enough to be uniform. T10 builds the general local-equilibrium description on this idea.

4. **Discreteness.** N is an integer, and $\left(\frac{\partial E}{\partial N}\right)_{S,V}$ is really a difference over one particle. Treating it as a derivative needs N large, which is the same limit the rest of the assumption requires.

11 Euler's Relation

Differentiate (16) with respect to λ. The right-hand side gives $E(S,V,N)$. The left-hand side, by the chain rule, gives

$$S\left(\frac{\partial E}{\partial(\lambda S)}\right)+V\left(\frac{\partial E}{\partial(\lambda V)}\right)+N\left(\frac{\partial E}{\partial(\lambda N)}\right),$$

each derivative evaluated at the scaled arguments. Since the identity holds for every $\lambda>0$, we may set $\lambda=1$, where the three derivatives are T, $-P$ and μ.

Euler's Relation and Its Conditions

For a system satisfying the extensivity assumption of Section 10 — one uniform phase, short-ranged interactions, no external field, surface terms neglected, N continuous —

$$E = TS - PV + \mu N. \tag{17}$$

The differential relation (1) requires none of these conditions; the finite relation (17) requires all of them.

The distinction in the last sentence is the one most often lost. Nothing has been integrated here, and no process has been considered. The relation is a statement about how the fundamental relation behaves under a change of size, converted into an algebraic identity at fixed size.

Feeding (17) into the definitions of Section 4 collapses three of the potentials:

$$G = E - TS + PV = \mu N, \qquad \Omega = E - TS - \mu N = -PV, \qquad F = -PV + \mu N. \tag{18}$$

Two of these are worth pausing over. The first says that for a *single-component* system the chemical potential is the Gibbs free energy per particle, which is why μ is the natural variable of chemistry. The second says that the grand potential is nothing but $-PV$; combined with $d\Omega = -S\,dT - P\,dV - N\,d\mu$ it means that the single function $P(T,\mu)$ is a complete fundamental relation, which is the form statistical mechanics delivers most directly in the grand canonical ensemble of S2.

Finally, transforming all three extensive slots gives $E - TS + PV - \mu N = 0$ identically. The complete Legendre transform carries no information, so no fundamental relation can be written in terms of (T, P, μ) alone. The reason is that those three variables are not independent, which is the next result.

When surface energy is not negligible the scaling argument must include the area as a further extensive variable, and (17) acquires a term $\sigma\mathcal{S}$. T6 uses exactly that modification.

12 The Gibbs–Duhem Relation

Take the differential of Euler's relation, which is legitimate because (17) holds at every equilibrium state:

$$dE = T\,dS + S\,dT - P\,dV - V\,dP + \mu\,dN + N\,d\mu.$$

Subtracting (1) removes dE and the three terms it shares, leaving a relation among the differentials of the intensive variables alone.

$$S\,dT - V\,dP + N\,d\mu = 0. \tag{19}$$

Equation (19) inherits every condition attached to (17). Dividing by N puts it in its most useful form,

$$d\mu = -s\,dT + v\,dP, \tag{20}$$

with $s = S/N$ and $v = V/N$ the entropy and volume per particle. Read as a differential equation for μ, it says that the chemical potential is determined by the other two intensive variables once the equations of state $s(T,P)$ and $v(T,P)$ are known, up to a constant of integration that thermodynamics does not fix. The same statement holds for any one of the three: the equations of state of a one-component fluid are not independent.

Key Point

A single phase of a one-component fluid has two independently variable intensive parameters, not three. With r components the count is $r+1$. The constraint is (19), and it is a consequence of extensivity, not of the first or second law. The full bookkeeping for several coexisting phases is the Gibbs phase rule of T6.

As a check, take the monatomic ideal gas of Section 6, for which $v = k_B T/P$. At fixed temperature (20) reads $d\mu = k_B T\,dP/P$, so

$$\mu(T,P) = k_B T \ln\!\left(\frac{P}{P_*(T)}\right), \tag{21}$$

with the whole temperature dependence collected in the integration "constant" $P_*(T)$. This reproduces (14), obtained in Section 6 by differentiating the free energy with respect to N, where $P_*(T)$ came out explicitly. The two routes are independent, and they agree.

13 The Chemical Potential

13.1. One Quantity and Five Derivatives

Reading the differentials collected in Table 2 gives five expressions for the same number:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}. \tag{22}$$

These are different mathematical operations. Adding a particle at fixed entropy and volume is not the same experiment as adding one at fixed temperature and volume: the first requires heat to be removed as the particle is added, the second does not. What (22) says is that the five operations return the same number at the same equilibrium state, because each potential differs from E by terms that do not involve N.

Extensivity makes one of them special. Since T and P are intensive, $G(T,P,N)$ must be of the form $N\,g(T,P)$, so $\left(\frac{\partial G}{\partial N}\right)_{T,P} = g = G/N$, in agreement with (18). The same argument does *not* work for F, whose natural variables include the extensive V: writing $F(T,V,N) = Nf(T,v)$ with $v = V/N$ gives

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = f(T,v) - v\left(\frac{\partial f}{\partial v}\right)_T = \frac{F}{N} + Pv,$$

which differs from F/N by Pv, exactly as $G = F + PV$ requires. The chemical potential is the Gibbs free energy per particle; it is not the Helmholtz free energy per particle.

13.2. A Particle Reservoir and the Grand Potential

Section 5 derived minimum principles for a system exchanging energy, and energy and volume, with a reservoir. The remaining case completes the set. Let system A have fixed volume V and exchange both energy and particles with a reservoir R at temperature T_R and chemical potential μ_R, the composite being isolated so that E_{tot} and N_{tot} are fixed. Expanding the reservoir entropy to first order in the transferred quantities, exactly as before,

$$S_R(E_{\text{tot}} - E_A, N_{\text{tot}} - N_A) = S_R(E_{\text{tot}}, N_{\text{tot}}) - \frac{E_A}{T_R} + \frac{\mu_R N_A}{T_R} + \cdots,$$

where the signs follow from $\partial S_R/\partial E_R = 1/T_R$ and $\partial S_R/\partial N_R = -\mu_R/T_R$. Maximizing the total entropy is therefore the same as minimizing the availability

$$\mathcal{A}(E_A, N_A) = E_A - T_R S_A - \mu_R N_A. \tag{23}$$

Setting its first derivatives with respect to E_A and N_A to zero gives $T_A = T_R$ and then $\mu_A = \mu_R$, and at that point the availability equals $\Omega(T_R, V, \mu_R)$. As before, the stationary point is a minimum only if the relevant second-derivative matrix of S_A is negative definite, which adds the requirement that the particle-number fluctuations be stable; S2 will show that this condition is equivalent to a positive compressibility.

13.3. Which Way Do Particles Move?

Take two systems, 1 and 2, at the same temperature T, separated by a rigid wall that passes particles but not volume, with the pair isolated so that $N_1 + N_2$ is fixed. Using $dS = (1/T)dE + (P/T)dV - (\mu/T)dN$ for each, and $dN_2 = -dN_1$,

$$dS_{\text{tot}} = \frac{\mu_2 - \mu_1}{T}\, dN_1 \;\geq\; 0. \tag{24}$$

Particles cross into system 1 only if $\mu_2 > \mu_1$: matter moves from higher to lower chemical potential, just as energy moves from higher to lower temperature. That is what earns μ its name, and it is the sense in which Baierlein [3] calls the chemical potential a tendency to diffuse.

Three qualifications belong with (24). It assumes the two temperatures are already equal; if they are not, the energy and particle terms compete and the direction of particle flow is not fixed by the chemical potentials alone. It assumes each side stays internally equilibrated, since otherwise neither μ_1 nor μ_2 is defined. And it is a statement about the sign of the entropy change for a permitted transfer, so it identifies the direction of the spontaneous process and says nothing whatever about its rate; a membrane may impose that direction over microseconds or over years.

For two vessels of ideal gas at a common temperature, (21) makes μ increase with pressure, so gas flows from the vessel at higher pressure to the one at lower pressure. That the formalism reproduces the obvious answer is a check on the formalism, not news about gases. The next example is one where the obvious answer is wrong.

13.4. Equilibrium Is Not Uniformity

A column of gas in a gravitational field is denser at the bottom than at the top, and stays that way. If equilibrium meant a uniform density, or a uniform pressure, the atmosphere would be a standing violation of it.

Worked Example: an Isothermal Column

Take an ideal gas of particle mass m in a uniform field g, held at a single temperature T throughout, and divide it into horizontal slabs thin enough to be uniform. The energy of a slab at height z includes the potential energy $Nmgz$ of its particles, so adding a particle to it costs $\mu_{\text{int}}(T, P(z)) + mgz$, where μ_{int} is the chemical potential the gas would have in the absence of the field. Applying (24) to any two slabs, equilibrium requires the *total* chemical potential to be the same at every height (Figure 3),

$$\mu_{\text{int}}\big(T, P(z)\big) + mgz = \text{constant}.$$

With $\mu_{\text{int}} = k_B T \ln\big(P/P_*(T)\big)$ and P_* independent of height at fixed T, the constant quantity is $k_B T \ln\big(P(z)/P_*(T)\big) + mgz$, that is

$$P(z) = P(0)\, e^{-z/H}, \qquad H \equiv \frac{k_B T}{mg}.$$

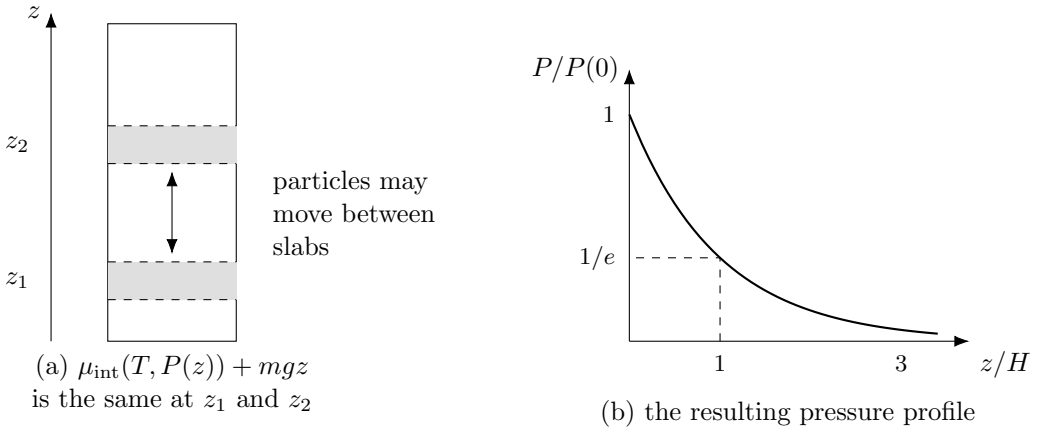
The same result follows from mechanical equilibrium alone: hydrostatic balance gives $dP/dz = -\rho g$ with $\rho = mP/(k_B T)$ for an ideal gas, and integrating returns the exponential. The two arguments are independent, one built from the chemical potential and one from force balance, and they agree.

For dry air, with a mean particle mass of 28.96 atomic mass units, and at $T = 290$ K, the scale height is $H \approx 8.5$ km, so the pressure falls by about 11% in the first kilometre. Two cautions on the numbers. The real atmosphere is neither isothermal nor, below the turbulent layers, in diffusive equilibrium at all, so this is an equilibrium model and not a fit; and the single scale height assumes a single particle mass, which Problem 5 takes apart.

Key Point

Equilibrium with respect to particle exchange means a uniform chemical potential, not a uniform density or pressure. Where an external field is present, the constant quantity is the chemical potential including the field's contribution.

The column also shows the third failure mode of Section 10 in action. The column as a whole is not uniform, so Euler's relation cannot be applied to it; it applies slab by slab, to regions small enough to count as homogeneous and large enough to contain many particles. That two-sided requirement is the local-equilibrium assumption, and T10 builds the thermodynamics of flowing systems on it.



(a) $\mu_{\text{int}}(T, P(z)) + mgz$ is the same at z_1 and z_2

(b) the resulting pressure profile

Figure 3: The isothermal column. In (a) the shaded slabs exchange particles freely; equilibrium equalizes the chemical potential including the gravitational term, not the pressure or the density. In (b) the resulting profile $P(z) = P(0)e^{-z/H}$, with $H = k_B T/mg$ equal to about 8.5 km for dry air at 290 K. The horizontal axis is in units of H.

14 Several Species

Nothing above used the fact that there was only one kind of particle. With species $i = 1, \ldots, r$ the fundamental relation becomes

$$dE = T\,dS - P\,dV + \sum_{i=1}^{r} \mu_i\,dN_i, \qquad \mu_i \equiv \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}}, \tag{25}$$

and the subscript on that derivative now has to say that the other species are held fixed as well. Scaling all the extensive variables together and repeating the argument of Section 11 gives

$$E = TS - PV + \sum_i \mu_i N_i, \qquad G = \sum_i \mu_i N_i, \qquad S\,dT - V\,dP + \sum_i N_i\,d\mu_i = 0. \tag{26}$$

The middle expression is worth a second look: μ_i is the derivative of G with respect to N_i at fixed T, P and the other populations, and it is not G/N_i. Only for a single component does the chemical potential become the Gibbs function per particle. The right-hand relation is the multicomponent Gibbs–Duhem relation, and counting its one constraint among the $r+2$ quantities T, P and $\{\mu_i\}$ gives the $r+1$ independently variable intensive parameters quoted earlier.

The immediate physical use is a wall that is selective. If a membrane passes species 1 and blocks the rest, then the argument of Section 13.3 applies to species 1 only, and equilibrium requires μ_1 to be equal on the two sides while the other chemical potentials, and the pressures, need not be. The pressure difference that develops across such a membrane is the osmotic pressure, which T8 obtains quantitatively. For a mixture of ideal gases, whose free energy is the sum of the free energies each species would have alone in the same volume at the same temperature, the single-species result carries over with the partial pressure $P_i = N_i k_B T/V$ in place of P,

$$\mu_i = k_B T \ln\!\left(\frac{P_i}{P_{*i}(T)}\right), \tag{27}$$

a statement about that model of a mixture rather than a general result. When the populations are not free to vary independently, as in a chemical reaction where $dN_i = \nu_i\, d\xi$ with fixed stoichiometric coefficients ν_i, the equilibrium condition becomes $\sum_i \nu_i \mu_i = 0$; T8 develops that line.

15 What We Have, and the Next Question

Table 3 collects the unit's results with the conditions each one carries, since a summary line separated from its assumptions is the most reliable way to generate a wrong statement later.

Result	Statement	Conditions
Potentials (Part I)	H, F, G, Ω from Legendre transforms of E	strict convexity in the transformed slot, e.g. $C_V > 0$ for $S \to T$
Minimum principles (Part I)	least F at fixed T_R, V, N; least G at fixed T_R, P_R, N	large reservoir; comparison among constrained equilibrium states; stability conditions for a minimum
Euler	$E = TS - PV + \mu N$	extensivity: uniform phase, short-ranged forces, no field, surfaces neglected, N continuous
Gibbs–Duhem	$S\,dT - V\,dP + N\,d\mu = 0$	the same conditions as Euler
Diffusive equilibrium	μ equal across a permeable wall; flow toward lower μ	equal temperatures; internally equilibrated sides; direction only, not rate

Table 3: Results of unit T2 with the assumptions they depend on. The conditions in the third column are part of each statement.

Every relation in this unit has been built from *first* derivatives of the potentials. Temperature, pressure and chemical potential are first derivatives of E; entropy and volume are first derivatives

of F and G; Euler and Gibbs–Duhem are algebraic identities among those same quantities.

The properties an experiment actually reports are not these. A calorimeter measures a heat capacity, $C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$; a dilatometer measures a thermal expansion coefficient; an acoustic measurement returns a compressibility. Each of these is a *second* derivative of a potential. Two questions follow immediately. Since mixed second partial derivatives commute, what relations must hold among such quantities, and can we use them to obtain something difficult to measure from something easy? And how many of the response functions of a simple fluid are genuinely independent? Those are the questions of T3.

Appendix A: Practice Problems

1. **What the transform remembers.** Let $E(S, V, N)$ be a fundamental relation, and define a second system by $\tilde{E}(S, V, N) = E(S - Ns_1, V, N)$ for a constant s_1, so the two differ only by a shift of the entropy scale. Show that both systems have the *same* energy when written as a function of (T, V, N), and that their Helmholtz free energies differ by $\tilde{F} - F = -Ns_1T$. Which measurement distinguishes them?

2. **Availability and entropy production.** A body with constant heat capacity C_V at initial temperature T_i is placed in thermal contact with a reservoir at T_R, at fixed V and N. Compute the entropy change of the body, the reservoir, and the composite. Show that the availability $\mathcal{A} = E - T_R S$ of the body decreases by exactly T_R times the total entropy produced. Verify that the total entropy change is non-negative for T_i either above or below T_R.

3. **Three equations of state and one constraint.** A one-component fluid obeys $PV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$. Use (20) to construct $\mu(T, P)$ from these, identifying clearly what the integration leaves undetermined. Then verify that the result agrees with the chemical potential obtained in Section 6 by differentiating $F(T, V, N)$ with respect to N, and explain in one sentence why a third, independent equation of state for μ could not have been supplied.

4. **When extensivity fails.** Model a spherical water droplet of radius R as a bulk term plus a surface term, taking the surface tension as $\sigma = 0.072\ \mathrm{N\,m^{-1}}$, the density as $10^3\ \mathrm{kg\,m^{-3}}$, the molar mass as $18.0\ \mathrm{g\,mol^{-1}}$, and the bulk cohesive energy per mole as the enthalpy of vaporization, $40.7\ \mathrm{kJ\,mol^{-1}}$. Find the radius at which the surface energy reaches one per cent of the bulk energy, and evaluate the ratio for $R = 1\,\mu\mathrm{m}$. Comment on what this implies for the use of Euler's relation in the laboratory.

5. **A two-component atmosphere.** An isothermal column contains two ideal gases of particle masses m_1 and m_2, free to move but not to interconvert. Show that in equilibrium each obeys its own barometric law with its own scale height $H_i = k_BT/m_ig$, and that the mixture therefore separates, the heavier species concentrating at the bottom. The observed lower atmosphere is instead almost uniformly mixed. Is that a failure of the calculation?

Solution Sketches

1. With $p = \partial\tilde{E}/\partial S = E'(S - Ns_1)$, inverting at fixed T gives $S = S^* + Ns_1$ where $E'(S^*) = T$. Hence $\tilde{E} = E(S^*)$, the same function of T as before, while $\tilde{F} = E(S^*) - T(S^* + Ns_1) = F - Ns_1T$. The two systems differ in entropy by Ns_1 at every temperature, so any determination of the absolute entropy separates them (T9), while $E(T, V, N)$ alone does not.

2. The body ends at T_R, so $\Delta S_{\mathrm{body}} = C_V \ln(T_R/T_i)$ and $Q = C_V(T_R - T_i)$ leaves the reservoir, giving $\Delta S_R = -C_V(T_R - T_i)/T_R$. Then

$$\Delta S_{\mathrm{tot}} = C_V \left[\ln \frac{T_R}{T_i} - \frac{T_R - T_i}{T_R} \right] = C_V \left[x - 1 - \ln x \right], \qquad x \equiv \frac{T_i}{T_R},$$

which is non-negative for all $x > 0$ and vanishes only at $x = 1$. Meanwhile $\Delta\mathcal{A} = C_V(T_R - T_i) - T_R C_V \ln(T_R/T_i) = -T_R \Delta S_{\mathrm{tot}} \le 0$, which is (6) seen from the other side.

3. From the two equations of state, $v = k_B T/P$ and, using the entropy per particle obtained in Section 6, $s = s(T, P)$. At fixed T, (20) gives $d\mu = k_B T\, dP/P$ and hence $\mu = k_B T \ln P + f(T)$; writing $f(T) = -k_B T \ln P_*(T)$ makes the logarithm dimensionless and reproduces (21). The integration determines μ only up to that one function of temperature, which the second relation $-\left(\frac{\partial \mu}{\partial T}\right)_P = s$ then fixes up to a single additive constant $\times T$; that residue is the same constant s_0 that classical thermodynamics could not supply in Section 6. A third independent equation of state is impossible because (19) constrains any two of T, P, μ to determine the third.

4. With n moles in the droplet, the bulk term is $n\,\Delta H_{\mathrm{vap}} = \frac{4}{3}\pi R^3 (\rho/M)\Delta H_{\mathrm{vap}}$ and the surface term is $4\pi R^2 \sigma$. Their ratio is $3\sigma M/(R\rho\,\Delta H_{\mathrm{vap}}) \approx 9.6 \times 10^{-11}\,\mathrm{m}/R$, which reaches 10^{-2} at $R \approx 10$ nm and is about 10^{-4} at $R = 1\,\mu$m. Samples of laboratory size are many orders of magnitude beyond the crossover, so Euler's relation may be used without apology; colloids, aerosols and critical nuclei may not.

5. Each species has its own conserved number, so the argument of Section 13.4 applies to each separately and $n_i(z) = n_i(0)\exp(-m_i g z/k_B T)$. The ratio n_2/n_1 then varies with height, and the heavier gas is concentrated below. This is a correct equilibrium result, and the lower atmosphere is not in that equilibrium: convective and turbulent stirring redistributes the components far faster than molecular diffusion can separate them, so the composition stays nearly uniform. Gravitational separation becomes visible only high enough that molecular diffusion wins. The calculation answers the question it was asked, which is what the equilibrium state would be, and the discrepancy is a reminder that thermodynamics does not supply the timescale on which a state is reached.

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