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Classical Mechanics and Thermodynamics - Garrod
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1   Garrod #5.2: Entropy of Substance - Equation of State.

One mole of a substance satisfies the equations of state

$$T = \lambda \varepsilon^{2/3} v^{-1/2} \text{ and } pv = \frac{3}{2}\varepsilon \ , \tag{1}$$

where λ is a constant. Determine $s(\varepsilon, v)$ within an arbitrary constant.

From Garrod equations 5.6 and 5.11, we find

$$\frac{\partial s}{\partial v} = \gamma = \beta p = \frac{1}{k_B \lambda} \varepsilon^{-2/3} v^{1/2} \left(\frac{3\varepsilon}{2v} \right) = \frac{3}{2k_B \lambda} \varepsilon^{1/3} v^{-1/2} \ , \tag{2}$$

where γ is the free expansion coefficient and k_B is the Boltzmann constant. If we take the energy density to be independent of the volume per particle (volume density), we can integrate this expression with respect to v and find

$$\int \frac{\partial s}{\partial v} \mathrm{d}v = \frac{3}{2k_B \lambda} \varepsilon^{1/3} \int v^{-1/2} \mathrm{d}v \tag{3}$$

$$s(\varepsilon, v) = \frac{3}{k_B \lambda} \varepsilon^{1/3} v^{1/2} + F(\varepsilon) \ , \tag{4}$$

where $F(\varepsilon)$ is an arbitrary function of energy density only, picked up from integrating the partial derivative. We must now enforce the relation of entropy and temperature,

$$\frac{\partial s}{\partial \varepsilon} = \frac{3}{k_B \lambda} v^{1/2} \left(\frac{1}{3} \varepsilon^{-2/3} \right) + \frac{\mathrm{d}F(\varepsilon)}{\mathrm{d}\varepsilon} = \beta = \frac{1}{k_B T} \ . \tag{5}$$

From the first equation of state we see

$$\frac{1}{k_B \lambda} v^{1/2} \varepsilon^{-2/3} + \frac{\mathrm{d}F(\varepsilon)}{\mathrm{d}\varepsilon} = \frac{1}{k_B} \left(\lambda \varepsilon^{2/3} v^{-1/2} \right)^{-1} \ , \tag{6}$$

which requires $\mathrm{d}F/\mathrm{d}\varepsilon = 0$. Now we see that $F \neq F(\varepsilon)$, so we may replace it with a constant. We now have a complete description of the entropy of this substance,

$$s(\varepsilon, v) = \frac{3}{k_B \lambda} \varepsilon^{1/3} v^{1/2} + f \ , \tag{7}$$

where f is some arbitrary constant.

2   Garrod #5.3: Gibbs Phase Rule.

Consider a substance containing K different types of particles. For example, $K = 3$ for a water, sugar, and salt solution. Let the spatial densities of the particles be called $n_1, \ldots, n_K$. For a single phase of the substance, we can independently vary the K densities and the temperature, but all other physical quantities are then determined by those $K + 1$ parameters. Thus, for a single phase, we have $K + 1$ free variables. For an equilibrium state of the substance containing two phases in contact (a two-phase state), one has the $2K + 1$ variables $n_1^{(1)}, \ldots, n_K^{(1)}, n_1^{(2)}, \ldots, n_K^{(2)}$, and β, but these are restricted by $K + 1$ equilibrium conditions, $\alpha_1^{(1)} = \alpha_1^{(2)}, \ldots, \alpha_K^{(1)} = \alpha_K^{(2)}$, and $p^{(1)} = p^{(2)}$. This leaves only K free variables. Show that, for a state containing P phases in equilibrium, the number of free variables is $F = K - P + 2$. This is the Gibbs phase rule. Notice that it says that the triple point of a simple substance has no free variables - there is a unique temperature and pressure at which three phases of a simple substance can be in equilibrium.

We notice that each equilibrium condition imposes an equation that describes the relationship between a variable in each state. In this case, each phase has K densities $(n_1, \ldots, n_K)$, and a temperature (β). Therefore there is one equation for each pair of densities (*e.g.*, $n_i^{(1)}$, $n_i^{(2)}$), so in a two-phase state this contributes K variables and $2K$ conditions (equations) per phase. For the last variable β, we get the final equation for the pressure of each phase $(p^{(1)} = p^{(2)})$ which must be determined by the corresponding β, and we get the total

$$V = K + 1 \quad \text{and} \quad C = 2K + 1 \ , \tag{8}$$

where V is the total number of variables and C is the total number of equilibrium conditions. For a system of V variables and C equations, we know there are $F = V - C$ arbitrary (free) variables.

We can extend this to P phases in equilibrium. In each phase there are still K variables for the densities, and the state has variable β, so we see

$$V = PK + 1 \ . \tag{9}$$

Let us examine the equilibrium conditions for the phases in contact. The affinity a_k for each number density n_k, must be the same in each phase:

$$(\alpha_1^{(1)} = \alpha_1^{(2)}), \quad (\alpha_1^{(1)} = \alpha_1^{(3)}), \quad \ldots, (\alpha_1^{(1)} = \alpha_1^{(P)}) \tag{10}$$

$$(\alpha_1^{(2)} = \alpha_1^{(3)}), \quad \ldots, (\alpha_1^{(2)} = \alpha_1^{(P)}) \tag{11}$$

$$\ldots \tag{12}$$

$$(\alpha_1^{(P-1)} = \alpha_1^{(P)}) \ , \tag{13}$$

but this is really only $P - 1$ equations because by ensuring $(\alpha_1^{(1)} = \alpha_1^{(2)})$ and $(\alpha_1^{(2)} = \alpha_1^{(3)})$, we automatically ensure $(\alpha_1^{(1)} = \alpha_1^{(3)})$, and so on. Each phase has $K + 1$ parameters that are subject to conditions (α_i and p), and there are $P - 1$ phases, so we see the total number of conditions is

$$C = (K + 1)(P - 1) = KP + P - K - 1 \ . \tag{14}$$

We now see that for a state of P phases with K different types of particles in each phase, the total number of free parameters is

$$F = (PK + 1) - (KP + P - K - 1) = K - P + 2 \ . \tag{15}$$

3 Garrod #5.9: Ideal Gas Adiabatic and Isothermal Curves.

Many ideal gases satisfy equations of state of the form $pV = Nk_BT$ and $E = KNk_BT$. (For monatomic gases, $K = \frac{3}{2}$, for diatomic gases with only rotational kinetic energy, $K = \frac{5}{2}$, and, for diatomic gases in which rotational and vibrational degrees of freedom can be treated classically, $K = \frac{7}{2}$.)

3.1 Adiabatic Curves.

For such an ideal gas, show that, along an adiabatic curve,

$$pV^{(K+1)/K} = \text{const.} \quad \text{and} \quad VE^K = \text{const.} \tag{16}$$

Let us begin by finding a condition that is satisfied by an adiabatic process. Consider the total differential of the entropy $S(N, E, V)$, for a system with a fixed number of particles:

$$dS = \beta dE + \gamma dV , \tag{17}$$

where α, β are defined in Garrod equation 5.6. From the definition of mechanical pressure p (in units such that $k_b = 1$) we see

$$dS = \beta(dE + pdV) \quad \Rightarrow \quad TdS = dE + pdV , \tag{18}$$

where TdS is simply the change in heat dQ. In an adiabatic process, no heat is exchanged so $dQ = 0$, so the condition

$$dE = -pdV , \tag{19}$$

must be satisfied by an adiabatic process.

From the equations of state of the ideal gas, we see

$$dE = KNdT = Kd(pV) = K(pdV + Vdp) , \tag{20}$$

using the differential chain rule. We can now equate Equations 19 and 20,

$$0 = K(pdV + Vdp) + pdV \tag{21}$$

$$-KVdp = (K+1)pdV , \tag{22}$$

and after gathering differentials with their variables, we see

$$\frac{K+1}{K}\frac{dV}{V} = -\frac{dp}{p} . \tag{23}$$

We can integrate both sides to find

$$\frac{K+1}{K}\log V = -\log p + C , \tag{24}$$

where C' is a constant of integration. Upon exponentiation of this expression, we get

$$V^{(K+1)/K} = e^C\frac{1}{p} \quad \Rightarrow \quad pV^{(K+1)/K} = \text{const.} \tag{25}$$

Similarly, we can substitute the equation of state involving pressure into Equation 19, to get the expression

$$\mathrm{d}E = -\left(\frac{NT}{V}\right)\mathrm{d}V = -\left(\frac{E/K}{V}\right)\mathrm{d}V \ , \tag{26}$$

from the first equation of state. Combining differentials with the corresponding variable and integrating gets us

$$K\frac{\mathrm{d}E}{E} = -\frac{\mathrm{d}V}{V} \tag{27}$$

$$\log(VE^K) = D \ , \tag{28}$$

after exponentiation we receive the desired result

$$VE^K = \mathrm{const.} \tag{29}$$

3.2   Isothermal Curve Comparison.

Also show that, in the $E - V$ plane, the adiabatic curves are steeper than the isotherms.

Consider an adiabatic decrease in volume ($\mathrm{d}S = 0$). The fundamental thermodynamic relation (Garrod equation 5.19)

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V \ , \tag{30}$$

tells us the work done by the system must go completely into raising the internal energy of the gas, because the entropy must remain unchanged. Now consider the same change of volume, but done isothermally. In this case the work done by the system can go into heat or the internal energy of the gas. Therefore a change in volume has a larger effect on energy in an adiabatic process than an isothermal one. In the $E - V$ plane, this represents adiabatic curves having a steeper[1] slope than isothermal curves.

Mathematically, we can see this by examining Equation 30 in the adiabatic case:

$$\mathrm{d}E = -p\mathrm{d}V \ , \tag{31}$$

which if we take p to be independent of V, we see

$$\left(\frac{\partial E}{\partial V}\right)\bigg|_T = -p \ , \tag{32}$$

which corresponds to the slope of an adiabatic curve in the $E - V$ plane. Alternatively, for an isothermal process, we have

$$\left(\frac{\partial E}{\partial V}\right)\bigg|_T = -p + T\left(\frac{\partial S}{\partial V}\right)_T \ , \tag{33}$$

where the second term is a positive definite quantity. When all remaining parameters are held equal, the change in entropy must have the same sign as the change in volume (*i.e.*, when the volume containing a gas is increased while the temperature is held constant, the entropy must increase, similarly for decreasing the volume, the entropy must decrease). Additionally, temperature is a non-negative quantity, therefore the slope of an isothermal curve (Equation 33) is always less negative than the slope of an adiabatic curve (Equation 32) - therefore an adiabat is always steeper than an

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[1]Steeper will be taken to mean having a more negative slope.

isotherm. This is a general result[2], and must be true for a gas obeying the equations of state given in the problem.

For the ideal gas satisfying the given equations of state, we see that on an adiabatic curve

$$E \propto V^{-1/k} \quad \Rightarrow \quad \frac{\partial E}{\partial V} \propto V^{-(K+1)/K} \propto p, \tag{34}$$

as expected. Similarly, on an isothermal curve, from the equation of state we see

$$\frac{E}{K} = pV = NT \ , \tag{35}$$

which implies, since T is constant, that all equivalent expressions are also constant. Additionally, for an isothermal process we have $V \propto p$, so $E \propto$ const., yielding

$$\left. \frac{\partial E}{\partial V} \right|_T = 0 \tag{36}$$

so we can see an adiabatic curve is always steeper than an isothermal one. The slope of an adiabat is nonzero, and therefore is steeper (regardless of sign) than an isotherm.

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[2]Garrod. Section 5.14, Point 4. Additionally, figure 5.11.

4 Garrod #5.12: Stefan-Boltzmann Law.

In the nineteenth century, using Maxwell's equations, it was possible to show that the pressure exerted on the walls of an evacuated container by the electromagnetic radiation inside was related to the energy density of the radiation by the formula $p = \frac{1}{3}E/V$. The entropy function of that "system" of electromagnetic radiation would be a function $S(E, V)$. Assuming that the energy density is related to the temperature by an equation of the form $E/V = AT^\lambda$, where A and λ are constants, show that λ must be equal to 4. This result was first derived by Ludwig Boltzmann after being guessed at, from an analysis of experimental data, by Josef Stefan.

Let us begin by defining the energy density, $\varepsilon = E/V$, so that the pressure of electromagnetic radiation is given by

$$p = \frac{\varepsilon}{3} \ . \tag{37}$$

Additionally, we can use the fundamental thermodynamic relation (Garrod equation 5.19) to write

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V \quad \Rightarrow \quad \frac{\mathrm{d}E}{\mathrm{d}V} = T\frac{\mathrm{d}S}{\mathrm{d}V} - p \ , \tag{38}$$

which if we take T to be a constant, becomes

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - \frac{\varepsilon}{3} \ , \tag{39}$$

after substituting in Equation 37. We can continue using the energy density to write

$$\varepsilon\left(\frac{\partial V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - \frac{\varepsilon}{3} \ , \tag{40}$$

if we assume the energy density is only a function of temperature (assume $\varepsilon = AT^\lambda$ from problem description). Furthermore, using the Maxwell Relation[3]

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \ , \tag{41}$$

we see Equation 40 becomes

$$\varepsilon = T\left(\frac{\partial p}{\partial T}\right)_V - \frac{\varepsilon}{3} = \frac{T}{3}\left(\frac{\partial \varepsilon}{\partial T}\right)_V - \frac{\varepsilon}{3} \ , \tag{42}$$

after substituting in Equation 37 again. Solving for the partial derivative we see

$$\left(\frac{\partial \varepsilon}{\partial T}\right)_V = \frac{4}{T}\varepsilon \quad \Rightarrow \quad \frac{\mathrm{d}\varepsilon}{\varepsilon} = 4\frac{\mathrm{d}T}{T} \ . \tag{43}$$

Upon integration we see $\log \varepsilon = \log(T^4) + A'$, and exponentiation reveals the desired result,

$$\varepsilon = AT^4 \ , \tag{44}$$

which proves the Stefan-Boltzmann Law, $\lambda = 4$.

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[3]Garrod Equation 6.59.

5 Garrod #5.21: Osmotic Pressure.

Consider a container separated into two parts by means of a rigid partition that can pass water molecules but not glucose molecules. On one side is pure water but on the other is a dilute solution of glucose. Using the Gibbs-Duhem equation and Garrod equation 5.78 for α_g, show that, at equilibrium, the pressure in the solution will exceed that in the pure water by an amount (called the osmotic pressure) $\Delta p = n_g kT$. Notice that this is exactly what would be obtained by treating the glucose molecules as an ideal gas, although a derivation of the result using that picture would be very questionable.

The Gibbs-Duhem equation, Garrod equation 5.42, can be written

$$0 = N\mathrm{d}(-\beta\mu) + E\mathrm{d}\beta + V\mathrm{d}(\beta p) \ , \tag{45}$$

using $\alpha = -\beta\mu$ and $\gamma = \beta p$. Expanding the differentials and gathering terms, we get

$$(E - N\mu + pV)\mathrm{d}\beta + V\beta\mathrm{d}p - N\beta\mathrm{d}\mu = 0 \ , \tag{46}$$

but if we are considering a system in equilibrium, we assume the temperature is constant, $\mathrm{d}\beta = 0$, so we have

$$\mathrm{d}p = \frac{N\beta}{V\beta}\mathrm{d}\mu = n\mathrm{d}\left(\frac{\alpha}{-\beta}\right) = -\frac{n}{\beta}\mathrm{d}\alpha \ , \tag{47}$$

where $n \equiv N/V$ is the particle density. Consider the two-region container described in the problem only containing water on both sides. At equilibrium, the water pressure p_w is equal on both sides of the barrier. If we now add a small number of glucose molecules (to keep the system dilute) to one region, the pressure will be

$$p_w + \Delta p \ , \tag{48}$$

where Δp is the pressure added by the glucose molecules. The added pressure is

$$\Delta p = \int \mathrm{d}p = \int -\frac{n}{\beta}\mathrm{d}\alpha_g = \int_0^{n_g} -\frac{n}{\beta}\left(-\frac{\mathrm{d}n}{n}\right) \ , \tag{49}$$

using the affinity for a dilute solution given by Garrod equation 5.78. After carrying out the integration and writing $\beta^{-1} = kT$, where k is the Boltzmann constant, we obtain the result

$$\Delta p = n_g kT \ , \tag{50}$$

which is the osmotic pressure.