

Thermodynamics: a Review. The output of an equilibrium statistical physics (ESP) calculation is the input to thermodynamic calculations. Here are two examples from ESP

1. The ideal gas described in the **microcanonical ensemble**:

$$S(E, V, N) = Nk_B \ln \left(\frac{V}{N} \left[\frac{4\pi m E}{3h^2 N} \right]^{\frac{3}{2}} \right) + \frac{3}{2} Nk_B. \quad (1)$$

2. The ideal gas described in the **canonical ensemble**:

$$F(T, V, N) = -Nk_B T \ln \left(\left[\frac{mk_B T}{2\pi\hbar^2} \right]^{\frac{3}{2}} \frac{V}{N} \right). \quad (2)$$

These two equations are examples of *fundamental relations*, they are a **system specific** input into thermodynamics.

In his textbook *Thermodynamics* H.B. Callen states "If the Fundamental Relation of a particular system is known, all conceivable thermodynamic information about the system is ascertainable therefrom." Callen continues. "The importance of the foregoing statement cannot be overemphasized. The information contained in a fundamental relation is all-inclusive it is equivalent to all conceivable numerical data, to all charts, and to all imaginable types of descriptions of thermodynamic properties. If the fundamental relation of a system is known, every thermodynamic attribute is completely and precisely determined." You make use of fundamental relations by employing thermodynamics.

The essential equations of thermodynamics are a set of relationships among the variables of macroscopic description, T, V, N, P, S, \dots , that are independent of system specific details.

Things like

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T}, \quad (3)$$

where $\alpha = (\partial V/\partial T)_P$ and $\kappa_T = -(\partial P/\partial V)_T$.

To turn the fundamental relations into something useful one generally calculates the equations of state (EOS). These come from the equations of thermodynamics which exhibit the differential form of S , E , F , H and G .

1. Entropy, S . When in principle (E, V, N) are the independent variables (that means you are supposed to know these)

$$S = S(E, V, N), \quad (4)$$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN, \quad (5)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{VN}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{EN}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{EV}, \quad (6)$$

where the last line is the 3 equations of state.

2. Energy, E . When in principle (S, V, N) are the independent variables (that means you are supposed to know these)

$$E = E(S, V, N), \quad (7)$$

$$dE = TdS - PdV + \mu dN, \quad (8)$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{VN}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{SN}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{SV}, \quad (9)$$

where the last line is the 3 equations of state.

3. Helmholtz free energy, F . When in principle (T, V, N) are the independent variables (that means you are supposed to know these)

$$F = E - TS, \quad (10)$$

$$F = F(T, V, N), \quad (11)$$

$$dF = -SdT - PdV + \mu dN, \quad (12)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{VN}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{TN}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{TV}, \quad (13)$$

where the last line is the 3 equations of state.

4. Enthalpy, H . When in principle (E, P, N) are the independent variables (that means you are supposed to know these)

$$H = E + PV, \quad (14)$$

$$H = H(E, P, N), \quad (15)$$

$$dH = TdS + VdP + \mu dN, \quad (16)$$

$$T = \left(\frac{\partial H}{\partial S} \right)_{PN}, \quad V = \left(\frac{\partial H}{\partial P} \right)_{EN}, \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{EP}, \quad (17)$$

where the last line is the 3 equations of state.

5. Gibbs free energy, G . When in principle (T, P, N) are the independent variables (that means you are supposed to know these)

$$G = E - TS + PV, \quad (18)$$

$$G = G(T, P, N), \quad (19)$$

$$dG = -SdT + VdP + \mu dN, \quad (20)$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_{PN}, \quad V = \left(\frac{\partial G}{\partial P} \right)_{TN}, \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{TP}, \quad (21)$$

where the last line is the 3 equations of state.

There is a large number of defined derivatives that are usually something you might measure, e.g. the specific heats, the thermal expansion, change in volume with respect to pressure, etc.

There are inputs from ESP only for $S(E, V, N)$ and for $F(T, V, N)$. [An exception is certain problems in which the grand canonical ensemble is used. For this case there is no conveniently defined thermodynamic function.] Suppose you needed $H(E, P, N)$. What to do? Build it up from things you know. Use $H = E + PV$ and attempt to express V as a function of (E, P, N) , i.e., $H = E + PV(E, P, N)$. Here is a system specific example of how to proceed.

From Eqs. (6)

$$\frac{1}{T} = \frac{3Nk_B}{2E}, \quad \frac{P}{T} = \frac{Nk_B}{V} \quad (22)$$

thus

$$V = \frac{2E}{3P} \quad (23)$$

and

$$H = E + PV(E, P, N) = \frac{5}{3}E. \quad (24)$$

Suppose you wanted to confirm Eq. (3) for the ideal gas by calculating everything, i.e., $\alpha = (\partial V/\partial T)_P$, $\kappa_T = -(\partial P/\partial V)_T$, $C_P = T(\partial S/\partial T)_P$ and $C_V = (\partial E/\partial T)_V$. To work out

these derivatives it would seem you need dE , dS , dV , dT , dP . From the first two EOS in the (T, V, N) description (skip the last as N is not changing in anything you want to calculate). Before starting it is simplifying to *string* the *log* out as here.

$$F = -Nk_B T \left(\ln V - \ln N + \frac{3}{2} \ln T + C \right) \quad (25)$$

Calculate S , $E = F + TS$ and P and then form dS , dE and dP . Find

$$dS = Nk_B \left(\frac{dV}{V} - \frac{dN}{N} + \frac{3}{2} \frac{dT}{T} \right), \quad (26)$$

$$dE = \frac{3}{2} Nk_B (NdT + TdN), \quad (27)$$

$$dP = Nk_B \left(\frac{dT}{V} - \frac{TdV}{V^2} + \frac{3}{2} \frac{TdN}{V} \right). \quad (28)$$

Here $dN = 0$ always. To form C_P put $dP = 0$ and feed the result into dS , divide by dT . Etc.