

Fundamental laws and rules in thermodynamics

name	closed systems	open systems
first law	$dU^t + dE_k^t + dE_p^t = \delta Q + \delta W$	$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_S$
second law	$dS^t = \frac{\delta Q_{rev}}{T} ; \Delta S_{universe} \geq 0$	$\frac{d(mS)_{cv}}{dt} + \Delta [Sm]_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0$
third law	$S = 0$ for all perfect crystalline substances at absolute zero	
Gibbs phase rule	$F = 2 - \pi + N$	

Fundamental definitions and relations in thermodynamics

$dW = -PdV^t$	$C_V \equiv \left(\frac{dU}{dT} \right)_V$	$\kappa \equiv -\frac{1}{V} \left(\frac{dV}{dP} \right)_T$	$\Delta S_{reservoir}^t = Q/T$	$\Delta H_{latent} = T \Delta V \frac{dP^{sat}}{dT}$
$Z \equiv \frac{PV}{RT}$	$C_P \equiv \left(\frac{dH}{dT} \right)_P$	$\beta \equiv \frac{1}{V} \left(\frac{dV}{dT} \right)_P$	$S^t = k_B \ln \Omega$	$\Delta S_{latent} = \frac{\Delta H_{latent}}{T}$

Fundamental thermodynamic functions for closed systems

name	definition	differential form	natural variables	conditions at equilibrium
internal energy		$dU = TdS - PdV$	$U(S, V)$	minimized at constant S and V
enthalpy	$H \equiv U + PV$	$dH = d(U + PV)$ $= dU + PdV + VdP$ $= TdS + VdP$	$H(S, P)$	minimized at constant S and P
Helmholtz free energy	$A \equiv U - TS$	$dA = d(U - TS)$ $= dU - TdS - SdT$ $= -SdT - PdV$	$A(T, V)$	minimized at constant T and V
Gibbs free energy	$G \equiv U + PV - TS$ $= A + PV$ $= H - TS$	$dG = d(H - TS)$ $= dH - TdS - SdT$ $= -SdT + VdP$	$G(T, P)$	minimized at constant T and P

Material property relations for specific substances

ideal gas, constant heat capacity	ideal gas, variable heat capacity	nonideal substances, with cubic equation of state
$P = \frac{RT}{V}$ $U = U(T)$ only $\frac{C_V}{R} = \frac{3}{2}, \frac{C_P}{R} = \frac{5}{2}$ (monatomic) $\frac{C_V}{R} = \frac{5}{2}, \frac{C_P}{R} = \frac{7}{2}$ (diatomic)	$P = \frac{RT}{V}$ $U = U(T)$ only $\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$ $C_V = C_P - R$	$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$ $U = U(T, V)$ $\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$ $C_V = C_P - T \left(\frac{dP}{dT} \right)_V \left(\frac{dV}{dT} \right)_P$

Explanation of differential forms

Let's examine the internal energy, U , whose differential form is $dU = TdS - PdV$. This notation tells us several things:

- Consider U to be a function of the two intensive state variables S and V . According to the Gibbs phase rule, these are two pieces of information we can use to completely specify U for a single component system. For multicomponent systems, we need these two pieces of information plus the system composition (e.g., the mole fractions of all species).
- We can think of $U(S, V)$ as a function that will return for us the internal energy for any specified state. Notice that U is just a mathematical function with two independent variables.
- The partial derivatives of U are related to other thermodynamic properties: $(dU/dS)_V = T$ and $(dU/dV)_S = -P$. Here, the subscripts indicate what is constant during the derivative.
- In general, we don't have to pick S and V as the independent variables. For example, we could pick T and P , for $U(T, P)$. However, in this case, the partial derivatives of U will not both be related simply to other properties, like the temperature and pressure as before. Instead, they will be related to combinations of properties, or derivatives of properties, like the heat capacity. For this reason, we say that S and V are **natural variables** of U .
- The second law of thermodynamics can be reformulated to show that U always tends towards a **minimum** at equilibrium for systems held at constant S and V . This is mathematically equivalent to saying that S tends toward a maximum at constant U and V , i.e., for an isolated system.

Similar arguments extend towards the other thermodynamics functions:

- The natural variables of the enthalpy H are S and P , with $(dH/dS)_P = T$ and $(dH/dP)_S = V$. H tends toward a minimum for systems that are held at constant S and P .
- The natural variables of the Helmholtz free energy A are T and V , with $(dA/dT)_V = -S$ and $(dA/dV)_T = -P$. A tends towards a minimum for systems held at constant T and V .
- The natural variables of the Gibbs free energy G are T and P , with $(dG/dT)_P = -S$ and $(dG/dP)_T = V$. G tends towards a minimum for systems held at constant T and P . Because so many processes are performed at constant temperature and pressure (e.g., chemical reactions), the Gibbs free energy is an extremely important quantity that indicates to what state a system will evolve (e.g., in which direction and to what extent a reaction will proceed).

Maxwell relations

For any well-behaved mathematical function of two variables, the cross second derivative doesn't depend on the order of the independent variables. In other words, for a function $f(x, y)$:

$$\frac{d}{dy} \left[\left(\frac{df}{dx} \right)_y \right]_x = \frac{d^2 f}{dy dx} = \frac{d^2 f}{dx dy} = \frac{d}{dx} \left[\left(\frac{df}{dy} \right)_x \right]_y$$

We can apply this logic to each of the four fundamental thermodynamic functions. Consider $U(S, V)$:

$$\frac{d}{dV} \left[\left(\frac{dU}{dS} \right)_V \right]_S = \frac{d}{dS} \left[\left(\frac{dU}{dV} \right)_S \right]_V$$

Substituting for the inner partial derivatives, based on the differential form of U :

$$\frac{d}{dV} [T]_S = \frac{d}{dS} [-P]_V$$

Simplifying:

$$\left(\frac{dT}{dV} \right)_S = - \left(\frac{dP}{dS} \right)_V$$

This equation establishes a relationship between derivatives of thermodynamic variables. This is called a Maxwell relation, named after James Maxwell, an early founder of thermodynamics. This is a fundamental relationship, and it is *never violated* for systems at equilibrium. Therefore, one cannot set independently the derivatives on the left and right hand side.

Since there are four thermodynamic potentials, there are four Maxwell relations. The remaining three are derived in an analogous manner to the approach before. These relations are extremely useful in thermodynamics because they enable us to relate derivatives involving quantities that are not directly measurable, like the entropy, to ones that are, like the pressure, molar volume, and temperature. The table below summarizes the four relations.

Maxwell relations for closed systems

thermodynamic function	derivation	Maxwell relation
internal energy	$\frac{d}{dV} \left[\left(\frac{dU}{dS} \right)_V \right]_S = \frac{d}{dS} \left[\left(\frac{dU}{dV} \right)_S \right]_V$	$\left(\frac{dT}{dV} \right)_S = - \left(\frac{dP}{dS} \right)_V$
enthalpy	$\frac{d}{dP} \left[\left(\frac{dH}{dS} \right)_P \right]_S = \frac{d}{dS} \left[\left(\frac{dH}{dP} \right)_S \right]_P$	$\left(\frac{dT}{dP} \right)_S = \left(\frac{dV}{dS} \right)_P$
Helmholtz free energy	$\frac{d}{dV} \left[\left(\frac{dA}{dT} \right)_V \right]_T = \frac{d}{dT} \left[\left(\frac{dA}{dV} \right)_T \right]_V$	$\left(\frac{dS}{dV} \right)_T = \left(\frac{dP}{dT} \right)_V$
Gibbs free energy	$\frac{d}{dP} \left[\left(\frac{dG}{dT} \right)_P \right]_T = \frac{d}{dT} \left[\left(\frac{dG}{dP} \right)_T \right]_P$	$\left(\frac{dS}{dP} \right)_T = - \left(\frac{dV}{dT} \right)_P$