

QUANTITIES AND VARIABLES  
IN THERMODYNAMICS

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Thermodynamics has a very large number of variables, spanning both Latin and Greek characters, which can often become confusing. Herein I will lay out each variable, it's units, and a brief definition of it's function. Note: Equations marked with a star denote a DeHoff equation, such equations do not hold across phase changes, but are very useful in the DeHoff method. This excludes  $W^*$ , which is the path dependent non-mechanical work, which is often neglected in practice. Some basic quantities are not defined herein, but are required for all given definitions: temperature, pressure, energy, and volume.

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# 1 Variables

## 1. Internal Energy

Symbol: U, E [Units: Energy]

Equations:

- $dU = \delta Q + \delta W + \delta W^*$
- $dU = TdS - PdV + \delta W^*$
- $*dU = (C_P - PV\alpha_V)dT - V(T\alpha_V - P\beta_T)dP$

Internal energy is used to characterize a system as it moved between two states. It includes the kinetic energy and potential energy of a system or object, and also includes the energy held in the chemical bonds of the material in question. This is useful if one need to convert kinetic or potential energy into heat (q, TdS) or a change in volume (dV) under a given pressure. A negative value indicates that some work or heat is leaving the system, while a positive implies that work or heat is entering the system.

## 2. Enthalpy

Symbol: H [Units: Energy]

Equations:

- $H \equiv U + PV$
- $dH = TdS - PdV$
- $*dH = C_P dT - V\alpha_V dP$

Enthalpy relates the energy stored in mass or objects. This can be used to track energy coming into a system by the first law, or to quantify the heat of reaction given a chemical reaction. The most frequently given values are enthalpy of formation for a given compound, which is defined as zero for pure and elemental compounds (like diatomic oxygen, or graphitic carbon).

## 3. Entropy

Symbol: S [Units: Energy]

Equations:

- $dS \geq \frac{\delta Q}{T}$
- $dS = \frac{dH}{T} \quad (dP = 0)$
- $*dS = \frac{C_P}{T} dT - V\alpha_V dP$

Entropy can be described as the energy of disorder, and always increases. Similarly to enthalpy, entropy can be tracked through phase and temperature changes, to relate the energy of a system. Most calculations involving entropy must be assumed to be completely reversible, in order to make the above inequality an exact equality.

#### 4. Gibbs Energy

Symbol:  $G$  [Units: Energy]

Equations:

- $G \equiv H - TS$
- $dG = VdP - SdT$
- $\Delta G = \Delta G^\circ + RT \ln(J_a)$

Gibbs energy relates the amount of non-mechanical work a system is capable of doing at constant temperature and pressure. For a reaction,  $\Delta G$  is the quantity of interest. If it is positive, the reaction will only run in the direction opposite of how it is written, if it is zero you have equilibrium, and if it is negative, the reaction will occur spontaneously. The third equation is the one applied to a reaction at a given temperature, for a given reaction quotient.

#### 5. Helmholtz Energy

Symbol:  $F$  [Units: Energy]

Equations:

- $F = U - TS$
- $dF = -SdT - PdV$
- $*dF = -(S - PV\alpha_V)dT + PV\beta_T dP$

Helmholtz energy quantifies the amount of mechanical work one is able to extract from a system.

#### 6. Electromotive Force

Symbol:  $\mathcal{E}$  [Units: Volts]

Equations:

- $\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{zF} \ln(J_a)$

The electromotive force is the voltage provided by an electrochemical reaction. The similarity to Gibbs energy is not coincidental, as electrochemistry is treated simply as an extension of thermochemistry.

#### 7. Heat Capacity

Symbol:  $C_p$  [Units: Energy Mass<sup>-1</sup> Temperature<sup>-1</sup>] (constant pressure)

Symbol:  $C_v$  [Units: Energy Mass<sup>-1</sup> Temperature<sup>-1</sup>] (constant volume)

Equations:

- $C_p = \left(\frac{\partial H}{\partial T}\right)_P$
- $C_v = \left(\frac{\partial U}{\partial T}\right)_V$

The heat capacity terms express how much energy it takes to change the temperature of a given amount of material. This becomes useful in the DeHoff method, as well as in first law problems where the temperature of a specific material is of interest (a boiler, cooler, furnace, etc.).

#### 8. Coefficient of Thermal Expansion

Symbol:  $\alpha_v$  [Units: Temperature<sup>-1</sup>]

Equations:

- $\frac{1}{v} \left( \frac{\partial V}{\partial T} \right)_P$

The coefficient of thermal expansion relates how volume changes as temperature changes at constant pressure. Similarly,  $\alpha_l$  denotes the linear analogue. This value is useful in practical applications as well as the DeHoff method.

#### 9. Coefficient of Compressibility

Symbol:  $\beta_t$  [Units: Pressure<sup>-1</sup>]

Equations:

- $\beta_t = -\frac{1}{v} \left( \frac{\partial V}{\partial P} \right)_T$

The coefficient of compressibility relates how volume changes as pressure changes at constant temperature. This value is useful in practical applications as well as the DeHoff method.

#### 10. Chemical Potential

Symbol:  $\mu_i$  [Units: Energy Mass<sup>-1</sup>]

Equations:

- $\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}}$

The chemical potential relates how a thermodynamic parameter changes when one changes the number of moles of species  $i$  present, but holds all other relevant quantities, including moles of other species, constant.

#### 11. Activity and Related Symbols

**Activity of  $i$**  [Units: None]

Symbol:  $a_i$  Equations:

- $a_i = \frac{P_i}{P_i^0}$
- $a_i = X_i \gamma_i$

The activity of a component in a system relates it's relative presence. The first formula given has the vapor pressure present, divided by the partial pressure at standard state. If working from the Raoultian standard state (most common, assume unless otherwise indicated),  $P_i^0$  is the vapor pressure of pure  $i$  at the temperature of interest.

**Mole Fraction of  $i$**  [Units: None]

Symbol:  $X_i$

- $$X_i = \frac{n_i}{n_i + \sum n_{other}}$$

The mole fraction of a given element is useful in calculating its activity, as well as for tackling problems involving solutions and mixtures.

**Activity Coefficient of  $i$**  [Units: None]

Symbol:  $\gamma_i$

- $$a_i = \gamma_i X_i$$

The activity coefficient accounts for non-ideal behavior in mixtures. A value less than one causes what is referred to as "negative behavior", while a value greater than one causes "positive behavior". These imply a great willingness to mix to reach lower energy (negative) and a repulsion that prevents mixing (positive). If  $\gamma_i = 1$  then the solution is ideal, and the activity of a component is exactly the mole fraction of that component.

**Henry's Law Value of  $i$**  [Units: None]

Symbol:  $\gamma_i^\circ$

The Henry's Law value is the value that  $\gamma$  approaches as the fraction component  $i$  approaches zero. If one were to plot activity of  $i$  against mole fraction of  $i$ , it would, for negative behavior, look like a tilted "S". The linear portion near the bottom is referred to as the Henry's Law region, and if one were to extend the line all the way to a mole fraction  $i$  of 1, the height would be  $\gamma_i^\circ$ . This line is the Henry's Law line, and is important in the context of changing standard states.

## 2 Notes on Notation

The numerous variables are often presented with myriad super scripts, subscripts, over-lines, and underlines. Each of these effectively modifies the exact meaning of the variable. While I will present these examples in terms of Gibbs energy, most are applied to the energy terms in thermodynamics (U, S, H, G, F).

### Intensive

Denoted by: Underline,  $\underline{G}$

Meaning: When one wishes to express a thermodynamic relation without a mass term (moles, kilograms, etc.) one can make the terms intensive by underlining them. This simplifies expressions like the ideal gas law. Expressed with extensive variables (the opposite of intensive), it looks like this:  $PV = nRT$ . Changing to intensive:  $\underline{P}\underline{V} = RT$ . The term representing  $n$  moles was moved to the other side,  $\frac{P}{n} = \underline{P}$ . It only makes sense to undertake this change with variables that realistically are proportional to mass, generally volume and the energy variables. Note that one can make the quotient of two such variables intensive without issue nor change, as it would divide out. Both heat capacity variables are innately per mass (intensive), and as such are never underlined. If entropy or enthalpy are found in terms of heat capacity, they too are intensive.

### Standard State

Denoted by: Superscript zero,  $G^0$

Meaning: Standard state values come up most often during chemical reactions as a baseline from which to evaluate how a reaction will occur at non-standard conditions. It is important to remember that the superscript zero does **not** mean standard state when applied to  $\gamma$ . This modifier is most often applied to energy terms, but also  $\mathcal{E}$ , the electromotive force of an electrochemical cell, with much the same interpretation.

### Partial Molar Quantity

Denoted by: Over-line,  $\overline{G}_i$

Meaning: Partial molar quantities relate the variable in terms of a single species or component. This comes up most often in the context of mixtures, mixing processes, and alloys. In addition, a superscript *rel* ( $\overline{G}_i^{rel}$ ) means relative partial molar quantity, meaning it is referenced from standard state (which ever one you happen to be working in, but again, most often Raoultian). Partial molar quantities can be expressed as (using internal energy as an example):

$$\overline{U}_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}}$$

Note that volume and entropy are held constant, as they are the variables internal energy is a direct function of, however a partial molar quantity is ideally with everything held constant save for the change in moles of the species in question. In a mixture, to find the total value, simply multiply each partial molar quantity by the number of moles of the appropriate species.

### Path Dependant Change or Differential

Denoted by: Lowercase delta or "del",  $\delta Q$

Meaning: Unlike most of the other modifiers, this applies only to heat and work terms in the context of the first law, as they are not state variables. A state variable is one that does not depend on how the material in question reached the state it is in, such as entropy, enthalpy, internal energy, volume, temperature, and so forth. Only by imposing conditions can we convert these path dependent variables into more workable state variables. For example, by imposing the restriction that the process is entirely reversible, we can state that  $\delta Q = TdS$ . It is this freedom that allows us to frequently neglect  $\delta W^*$ , the non-mechanical work of a system by simply imposing the restriction that we take a path with none.