

# Laws of Thermodynamics

## First law

The first law is a statement about conservation of energy. If we let  $U$  denote the internal energy of a system, we state that we can decompose this energy change as *heat*,  $Q$  and *work*,  $W$ .

$$\Delta U = Q \pm W.$$

Note that we use  $\pm$  to denote the work, this is because we can define the work both *on* the system or *by* the system, both conventions are used regularly and so care should be taken. The heat is usually defined as the heat *entering* the system.

If the number of particles in a system is constant the instantaneous work done by the system will be

$$dW = PdV,$$

so we have

$$dU = dQ - PdV.$$

## Second law

The second law states that the entropy of an isolated system always will increase. Mathematically we can state it as

$$\Delta S \geq T\Delta Q,$$

at least for a constant temperature. For a reversible process, this becomes an equality

$$\Delta S = T\Delta Q \quad (\text{reversible process})$$

This implies that a reversible process is a process that produces no entropy, it is thus a system continuously changing through equilibria states and will therefore often be infinitely slow. A reversible process is thus usually an abstraction, and not a real quality of a process. Processes can however, be close to reversible.

Combining the first and second law gives us the important inequality

$$T\Delta S \geq \Delta U + P\Delta V.$$

For an infinitesimal quantity, this will always be true

$$T dS = dU + P dV.$$

## Maxwell relations

From the first law we have

$$dU = T dS - P dV. \quad (1)$$

Should therefore express  $U$  as a function of  $S$  and  $V$ ,  $U = U(S, V)$ , can then look at the total derivative of  $U$

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV. \quad (2)$$

Comparing and gives

$$T = \left( \frac{\partial U}{\partial S} \right)_V, \quad P = - \left( \frac{\partial U}{\partial V} \right)_S.$$

Generally

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}.$$

So we get

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V.$$

## General state variables

Let us say we have three state variables,  $X$ ,  $Y$ ,  $Z$ , and we have an equation of state  $Z(X, Y)$ . We see that  $Z$  is not a free variable, but is given by  $X$  and  $Y$ . Of course, we could have said that  $X$  is not the free variable, because it can be given by  $X(Y, Z)$ , i.e., the equation of state can be solved for any of the three state variables.

The total derivatives of all equation of states become

$$\begin{aligned} dZ &= \left( \frac{\partial Z}{\partial X} \right)_Y dX + \left( \frac{\partial Z}{\partial Y} \right)_X dY, \\ dX &= \left( \frac{\partial X}{\partial Y} \right)_Z dY + \left( \frac{\partial X}{\partial Z} \right)_Y dZ, \\ dY &= \left( \frac{\partial Y}{\partial X} \right)_Z dX + \left( \frac{\partial Y}{\partial Z} \right)_X dZ. \end{aligned}$$

Inserting  $dY$  into  $dX$  gives

$$\left[ \left( \frac{\partial X}{\partial Y} \right)_Z \left( \frac{\partial Y}{\partial X} \right)_Z - 1 \right] dX + \left[ \left( \frac{\partial X}{\partial Y} \right)_Z \left( \frac{\partial Y}{\partial Z} \right)_X + \left( \frac{\partial X}{\partial Z} \right)_Y \right] dZ = 0.$$

The differentials are of course independant, so we get

$$\left( \frac{\partial X}{\partial Y} \right)_Z = \left( \frac{\partial Y}{\partial X} \right)_Z^{-1},$$

and

$$\left( \frac{\partial X}{\partial Y} \right)_Z \left( \frac{\partial Y}{\partial Z} \right)_X \left( \frac{\partial Z}{\partial X} \right)_Y = -1.$$

We can now let another state variable be given by  $X$  and  $Y$

$$dU = \left( \frac{\partial U}{\partial X} \right)_Y dX + \left( \frac{\partial U}{\partial Y} \right)_X dY.$$

Dividing by  $dX$  and holding the equation constant at  $Z$  gives

$$\left( \frac{\partial U}{\partial X} \right)_Z = \left( \frac{\partial U}{\partial X} \right)_Y + \left( \frac{\partial U}{\partial Y} \right)_X \left( \frac{\partial Y}{\partial X} \right)_Z$$

## Specific Heat

When we add a small amount of heat to a system, the temperature will rise by some small amount, this is the definition of the specific heat of that system. For a given state variable  $X$  it is defined as

$$C_X = \lim_{\Delta T \rightarrow 0} \left( \frac{\Delta Q}{\Delta T} \right)_X = T \left( \frac{\partial S}{\partial T} \right)_X.$$

Starting at the first law we have

$$TdS = dU + P dV,$$

inserting the complete derivative for  $dU$  gives

$$TdS = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + P dV,$$

If we look at the specific heat for a constant volume, we get

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V.$$

If we instead keep the pressure constant, we get

$$C_P = C_V + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial T} \right)_P.$$

This can also be formulated as

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P.$$

Where  $H$  is the *enthalpy*:

$$H = U + PV.$$

## Equation of State

For most systems all state variables are not independent, but will depend on each other. If we can explicitly give a state variable in terms of the other state variables, that is an equation of state. An example could be the relation

$$P(T, V).$$

The equation of state give important information about how matter will behave under different physical conditions and so is very material dependant.

## Ideal gas law

The ideal gas law is an equation of state

$$P = \frac{NkT}{V}, \quad P = kT\rho.$$

## Van der Waals Equation of State

The ideal gas presupposes no interaction between the particles. The van der Waals equation of state tries to include some interaction in a basic and approximate manner

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}.$$

Here  $a$  and  $b$  are parameters describing the particles,  $b$  reflects the particles having some volume and  $a$  models the attraction between the particles.

## Constants

Boltzmann's constant	$k = 1.381 \times 10^{-23} \text{JK}^{-1}$
Avogadro's Number	$N_A = 6.023 \times 10^{23} \text{mol}^{-1}$
$k \cdot N_A$	$R = 8.314 \text{JK}^{-1} \text{mol}^{-1}$