

## 21.1: Entropy Increases With Increasing Temperature

### Learning Objectives

- Define entropy and its relation to energy flow.

### Entropy versus temperature

We can put together the first and the second law for a reversible process with no other work than volume ( $PV$ ) work and obtain:

$$dU = \delta q_{rev} + \delta w_{rev}$$

Entropy is the dispersal of energy and is related to heat:

$$\delta q_{rev} = TdS$$

Work is related to the change in volume:

$$\delta w_{rev} = -PdV$$

Plugging these into our expression for  $dU$  for reversible changes:

$$dU = TdS - PdV$$

We no longer have any path functions in the expression, as  $U$ ,  $S$  and  $V$  are **all state functions**. This means this expression must be an exact differential. We can generalize the expression to hold for irreversible processes, but then the expression becomes an inequality:

$$dU \leq TdS - PdV$$

This equality expresses  $U$  as a function of two variables, entropy and volume:  $U(S, V)$ .  $S$  and  $V$  are the **natural variables** of  $U$ .

### Entropy and heat capacity

At constant volume,  $dU$  becomes:

$$dU = TdS$$

Recall that internal energy is related to constant volume heat capacity,  $C_V$ :

$$C_V = \left( \frac{dU}{dT} \right)_V$$

Combining these two expressions, we obtain:

$$dS = \frac{C_V}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

If we know how  $C_V$  changes with temperature, we can calculate the change in entropy,  $\Delta S$ . Since heat capacity is always a positive value, entropy must increase as the temperature increases. There is nothing to stop us from expressing  $U$  in **other** variables, e.g.  $T$  and  $V$ . In fact, we can derive some interesting relationships if we do.

### ✓ Example 21.1.1

- Write  $U$  as a function of  $T$  and  $V$ .
- Write  $U$  as a function of its natural variables.
- Rearrange (2) to find an expression for  $dS$ .
- Substitute (1) into (3) and rearrange. This is the definition of  $C_V$ .

5. Write out  $S$  as a function of  $T$  and  $V$ .

We can also derive an expression for the change in entropy as a function of constant pressure heat capacity,  $C_P$ . To start, we need to change from internal energy,  $U$ , to enthalpy,  $H$ :

$$\begin{aligned}H &= U + PV \\dH &= dU + d(PV) \\&= dU + PdV + VdP\end{aligned}$$

For reversible processes:

$$\begin{aligned}dH &= dU + PdV + VdP \\&= TdS - PdV + PdV + VdP \\&= TdS + VdP\end{aligned}$$

The natural variables of the enthalpy are  $S$  and  $P$  (not:  $V$ ). A similar derivation as above shows that the temperature change of entropy is related to the constant pressure heat capacity:

$$dH = TdS + VdP$$

At constant pressure:

$$dH = TdS + VdP$$

Recall that:

$$C_P = \frac{dH}{dT}$$

Combining, we obtain:

$$dS = \frac{C_P}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

This means that if we know the heat capacities as a function of temperature we can calculate how the entropy changes with temperature. Usually it is easier to obtain data under constant  $P$  conditions than for constant  $V$ , so that the route with  $C_p$  is the more common one.

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