

Topic: Chemical Engineering Thermodynamics

1.1 Entropy

Synthesising information from different sources

- **Using information from all excerpts, write a paragraph of not more than 170 words discussing entropy.**

Remember that you need to:

- **Use information from all sources.**
- **Cite your sources appropriately.**
- **Use your own words! You must not plagiarise!**

Excerpt 1

The second law of thermodynamics is a statement about the tendency of a system to change spontaneously because of entropy. It says that for any change in the thermodynamic state of an isolated system, the entropy change is greater than or equal to zero.

The entropy change is zero only for a reversible process. This makes sense because reversibility means that equilibrium is maintained throughout a process. To do that continuously seems possible only if the number of configurations available to the system is not changing. In a reversible isothermal expansion of a gas, there is a nonzero entropy change for the gas because it gains heat from the reservoir that maintains the temperature; however, the heat loss is a diminishment of the entropy of the reservoir equal and opposite to the entropy increase of the gas. On the other hand, an irreversible process, such as adiabatic free expansion, occurs spontaneously *in the direction of increasing total entropy*. Given this, one may take as a definition of equilibrium that it is the state of a system when it can no longer undergo any spontaneous processes.

For an engine that turns heat into mechanical work, the second law of thermodynamics is an important concern. Heat must be exchanged irreversibly. This requires a temperature differential, and it means that entropy is increased as the engine cycles. Consequently, entropy is sometimes associated with a capacity to do work. A system that has changed spontaneously to maximize entropy loses the capacity to do work. Consider again the two gas chambers connected by a valve. If the valve were replaced by a piston, there would be a capacity to do work under the initial conditions of the system. Gas in one chamber could move the piston in the direction of the evacuated chamber. However, by allowing for free expansion of the gas (opening the valve), there is no longer the same capacity to do work. This is true even though the energy of the system has not changed (*1, p. 66*).

Excerpt 2

The measure of disorder used in thermodynamics is called the *entropy, S*. Initially, we can take entropy to be a synonym for the extent of disorder, but shortly we shall see that it can be defined precisely and quantitatively, measured, and then applied to chemical reactions. At this point, all we need to know is that when matter and energy become disordered, the entropy increases. That being so, we can combine the two remarks above into a single statement known as the Second Law of thermodynamics:

The entropy of an isolated system tends to increase.

The 'isolated system' may consist of a system in which we have a special interest (a beaker containing reagents) and that system's surroundings: the two components jointly form a little 'universe' in the thermodynamic sense.

To make progress and turn the Second Law into a quantitatively useful statement, we need to define entropy precisely. We shall use the following definition of a *change* in entropy for a system maintained at constant temperature:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

That is, the change in entropy of a substance is equal to the energy transferred as heat to it *reversibly* divided by the temperature at which the transfer takes place. This definition can be

justified thermodynamically, but we shall confine ourselves to showing that it is plausible and then show how to use it to obtain numerical values for a range of processes.

There are three points we need to understand about the definition in the above eqn: the significance of the term 'reversible', why heat (not work) appears in the numerator, and why temperature appears in the denominator (2, p. 85).

Excerpt 3

The classical approach to the second law is based on a *macroscopic* viewpoint of properties independent of any knowledge of the structure of matter or behavior of molecules. It arose from study of the *heat engine*, a device or machine that produces work from heat in a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically returns to its original state. In such a power plant the cycle (in simple form) consists of the following steps:

1. Liquid water at approximately ambient temperature is pumped into a boiler.
2. Heat from a fuel (heat of combustion of a fossil fuel or heat from a nuclear reaction) is transferred in the boiler to the water, converting it to steam at high temperature and pressure.
3. Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine.
4. Exhaust steam from the turbine is condensed by the transfer of heat to cooling water, thus completing the cycle...

A Carnot engine operates between two heat reservoirs in such a way that all heat absorbed is absorbed at the constant temperature of the hot reservoir and all heat rejected is rejected at the constant temperature of the cold reservoir. Any reversible engine operating between two heat reservoirs is a Carnot engine; an engine operating on a different cycle must necessarily transfer heat across finite temperature differences and therefore cannot be reversible (3, pp. 141-42).

Excerpt 4

The interpretation of entropy as disorder has prevailed in the literature for over 100 years. It is true that many spontaneous processes may be viewed as proceeding from an ordered to a disordered state. However, there are two difficulties with this interpretation. First, the concept of order is not well-defined, and in many processes it is difficult, if not impossible, to decide which of the two states of the system is more or less ordered. Some specific examples are provided in refs 4 and 6. Note however that the term disorder here is used in its colloquial sense. There are some specific systems for which an "order parameter" may be defined, but this is not the type of order discussed in describing entropy. Second, there are cases in which an increase in disorder is clearly observed, yet the entropy change can be either zero or negative, therefore, invalidating the interpretation of entropy in terms of order and disorder. In spite of these difficulties, the order-disorder interpretation still lingers in the literature (4, p. 594).

References

1. Davis, W. D; Dykstra, C. E. *Physical Chemistry: A Modern Introduction*; CRC Press: NW, 2012.
2. Atkins, P.; de Paula, J. *Elements of Physical Chemistry*, (5th ed.); Oxford University Press: New York, 2009.
3. Smith, J. M.; van Ness, H. C. *Introduction to Chemical Engineering Thermodynamics*, (3rd ed.); McGraw-Hill: New York, 1975.
4. Arie, B.-N. Entropy: Order of Information. *J. Chem. Educ.*, **88**(5), pp 594–596, 2011.