CEN 202 THERMODYNAMICS

CHAPTER 5: THE SECOND LAW OF THERMODYNAMICS

TEXT BOOK: : J. M. SMITH, H. C. VAN NESS, M. M. ABBOTT, M. T. SWIHART. "INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS", EIGHTH EDITION. 2018

ENTROPY

Entropy is an intrinsic property for systems at internal equilibrium. Differential changes in this property are given by the equation:

$$dS^t = \frac{dQ_{rev}}{T} \tag{1}$$

S^t : is the system (rather than the molar) entropy

THE SECOND LAW OF THERMODYNAMICS

The entropy change of any **system** and its **surroundings**, considered together, and resulting from any real process, is positive, approaching zero when the process approaches reversibility. Mathematically,

$$\Delta S_{total} \geq 0 \tag{2}$$

The second law confirms that every process proceeds in such a direction that **the total entropy change** associated with it **is positive**, the limiting value of zero being attained only **by a reversible process**. No process is possible for which **the total entropy** decreases.

The second law relates to:

- heat flows from hot to cold,
- limits to the conversion of heat to work by any device.

Application of the Second Law to Simple Heat Transfer

The equation for the entropy change of a heat reservoir follows from Eq. (1).
Because T is constant, integration gives:

$$\Delta S = \frac{Q}{T}$$

Q (heat) is transferred to or from a reservoir at temperature T

Q_H and Q_C have opposite signs:
Therefore, $\mathbf{Q_H = -Q_C}$, and the entropy changes of the reservoirs at $\mathbf{T_H}$ and at $\mathbf{T_C}$ are:

$$\Delta S_H^t = \frac{Q_H}{T_H} = \frac{-Q_C}{T_H} \quad \textbf{and} \quad \Delta S_C^t = \frac{Q_C}{T_C}$$

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From these two entropy changes:

$$\Delta S_{total} = \Delta S_H^t + \Delta S_C^t = \frac{-Q_C}{T_H} + \frac{Q_C}{T_C} = Q_C\left(\frac{T_H - T_C}{T_H T_C}\right)$$

Because the heat-transfer process is irreversible, Eq. (2) requires a positive value for ΔS_{total}, and therefore

$$Q_C\ (T_H - T_C) > 0$$

With the temperature difference positive, Q_C must also be positive, which means that heat flows into the reservoir at T_C, i.e., **from the higher to the lower temperature.**

As result:

No process is possible which consists solely of the transfer of heat from one temperature level to a higher one.

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Application of the Second Law to Heat Engines

Heat can be converted into work: heat engines

With respect to the engine, from the first law as given by Eq. $\Delta U = Q + W$ becomes:

$$\Delta U = Q + W = Q_H + Q_C + W$$

Because the engine inevitably operates in cycles, its properties over a cycle do not change.

Therefore, $\Delta U = 0$, and $W = -Q_H - Q_C$.

The entropy change of the surroundings equals the sum of the entropy changes of the reservoirs. Because the entropy change of the engine over a cycle is zero, the total entropy change is that of the heat reservoirs. Therefore

$$\Delta S_{total} = -\frac{Q_H}{T_H} - \frac{Q_C}{T_C}$$

Combining this equation with the equation for W to eliminate Q_H yields:

$$W = T_H \Delta S_{total} + Q_C \left(\frac{T_H - T_C}{T_C}\right)$$

If the engine is totally ineffective, W = 0; → $\Delta S_{total} = -Q_C \left(\frac{T_H - T_C}{T_H T_C}\right)$

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Application of the Second Law to Heat Engines

If the process is reversible in all respects, then $\Delta S_{total} = 0$, and the equation reduces to:

$$W = Q_C\left(\frac{T_H}{T_C} - 1\right)$$

A heat engine operating as described in a completely reversible manner is very special and is called a **Carnot engine (an ideal engine),** described by N. L. S. Carnot in 1824.

"It is impossible to construct an engine that, operating in a cycle, produces no effect (in system and surroundings) other than the extraction of heat from a reservoir and the performance of an equivalent amount of work".

Combining this equation with $\mathbf{W = -Q_H - Q_C}$ to eliminate first **W** and then $\mathbf{Q_C}$ leads to **Carnot's equations:**

$$-\frac{Q_C}{T_C} = \frac{Q_H}{T_H}$$

$$\frac{W}{Q_H} = \frac{T_C}{T_H} - 1 \rightarrow W = Q_H\left(\frac{T_C}{T_H} - 1\right)$$

the thermal efficiency of a Carnot engine: $\eta_{Carnot} = 1 - \frac{T_C}{T_H}$

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HEAT PUMPS

HEAT PUMP

Because a **Carnot engine is reversible**, it may be operated in **reverse**; the Carnot cycle is then traversed **in the opposite direction**, and it becomes a reversible **HEAT PUMP** operating between the same temperature levels and with the same quantities Q_H, Q_C, and W as for the engine but reversed in direction (see the figure).

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ENTROPY CHANGES FOR THE IDEAL-GAS STATE

For one mole or a unit mass of fluid undergoing a mechanically reversible process in a closed system, the first law:

$$dU = dQ_{rev} - PdV$$

For the ideal-gas state, **$dH^{ig} = C_P^{ig}\, dT$** and **$V^{ig} = RT/P$**. As results of substitutions and division by T,

$$\frac{dQ_{rev}}{T} = C_P^{ig}\frac{dT}{T} - R\frac{dP}{P}$$

$$dS^{ig} = C_P^{ig}\frac{dT}{T} - R\frac{dP}{P} \quad \text{or} \quad \frac{dS^{ig}}{R} = \frac{C_P^{ig}}{R}\frac{dT}{T} - d\ln P$$

where S^{ig} is the molar entropy for the ideal-gas state. Integration from an initial state at conditions T_0 and P_0 to a final state at conditions T and P gives:

$$\frac{\Delta S^{ig}}{R} = \int_{T_0}^{T}\frac{C_P^{ig}}{R}\frac{dT}{T} - \ln\frac{P}{P_0}$$

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