

Entropy

It is the most important thermodynamic property, which serves as measure of the unavailability or degradation of energy. A thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system. The entropy of a system is affected only by the nature of the matter under consideration and the state in which it exists. And it is not affected by the external position of the body or its motion relative to other bodies.

- The entropy of the system is increased by the addition of heat through any mechanism or from source.
- The increase in entropy accompanying the addition of a given amount of heat to a system with lowering the temperature at which the heat is added. And it leads to a greater degradation of energy than at a higher temperature.
- In addition, in order to complete the definition of entropy, the nature of the process should also be specified. The change in entropy (a state function) is dependent only on the initial and final states and not on the path.
- The amount of heat transferred to measure the increase in entropy through the term (Q / T) is the degradation of higher forms of energy into heat, which is possible only in a reversible process. Therefore be measured as (Q_R / T) , where Q_R is the heat transferred when the process is occurring reversibly.

Equation for a Carnot engine may be written:

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

If the heat quantities refer to working fluid in the engine (rather than to the heat reservoirs), the numerical value of Q_H is positive and that of Q_C is negative. The equivalent equation written without absolute-value signs is therefore

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

Or
$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

Each Carnot cycle has its own pair of isotherms T_H and T_C and associated heat quantities Q_H and Q_C . When the adiabatic curves are so closely spaced that the isothermal steps are infinitesimal, the heat quantities become dQ_H and dQ_C , and equation above for each Carnot cycle is written:

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$$

In this equation T_H and T_C , absolute temperatures of the working fluid of the Carnot engines, are also the temperatures traversed by the working fluid of the arbitrary cycle. Summation of all quantities dQ/T for the Carnot engines leads to the integral:

$$\oint \frac{dQ_{\text{rev}}}{T} = 0$$

where the circle in the integral sign signifies integration over the arbitrary cycle, and the subscript "rev" indicates that the cycle is reversible. Thus the quantities Q_{rev}/T sum to zero for the arbitrary cycle, exhibiting the characteristic of a property. The property is called entropy, and its differential changes are:

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

Where : S^t the total (rather than molar) entropy of the system. Alternatively,

$$\boxed{dQ_{rev} = T dS^t}$$

If a process is reversible and adiabatic, $dQ_{rev} = 0$; $dS^t = 0$. Thus the entropy of a system is constant during a reversible adiabatic process, and the process is said to be isentropic.

The change in entropy of any system undergoing a finite reversible process is:

$$\Delta S^t = \int \frac{dQ_{rev}}{T}$$

Integration is not carried out for the irreversible path. Since entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.

***The mathematical statement of the second law is that every process proceeds in such a direction the total entropy changes ΔS^t associated with it is always positive, the process is possible.**

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

This mathematical statement of the second law affirms 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.

Entropy Changes of an Ideal Gas:

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

$$dU = dQ_{\text{rev}} - P dV$$

Differentiation of the defining equation for enthalpy, $H = U + P V$, yields:

$$dH = dU + P dV + V dP$$

Eliminating dU gives:

$$dH = dQ_{\text{rev}} - P dV + P dV + V dP$$

$$dQ_{\text{rev}} = dH - V dP$$

or For an ideal gas, $dH = C_p^{ig} \cdot dT$ and $V = RT/P$. With these substitutions and then division by T ,

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

$$dS = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P}$$

this becomes:

$$\frac{dS}{R} = \frac{C_p^{ig}}{R} \frac{dT}{T} - d \ln P$$

Where : S is the molar entropy of an ideal gas. Integration from an initial state at conditions T_0 and P_0 to a final state at conditions T and P gives:

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

Although derived for a mechanically reversible process, this equation relates properties only, and is independent of the process causing the change of state. It is therefore a general equation for the calculation of entropy changes of an ideal gas.

$$\langle C_P^{ig} \rangle_S = \frac{\int_{T_0}^T C_P^{ig} dT/T}{\ln(T/T_0)}$$

$$\int_{T_0}^T C_P^{ig} \frac{dT}{T} = \langle C_P^{ig} \rangle_S \ln \frac{T}{T_0}$$

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

This form of the equation for entropy changes of an ideal gas may be useful when iterative calculations are required.

It can be calculate the C_p^{ig} from the equation below and depending on the APPENDIX C and D

$$(C_p^{ig})_S/R = A + B \cdot T_{lm} + T_{am} \cdot T_{lm} \left[C + \frac{D}{(T_1 \cdot T_2)^2} \right]$$

$$T_{am} = \frac{T_1 + T_2}{2}$$

$$T_{lm} = \frac{T_2 - T_1}{\ln(T_2 - T_1)}$$

example of the C_p values for ideal gas from Appendix CTable C.1 Heat Capacities of Gases in the Ideal-Gas State[†]Constants in equation $C_p^{ig}/R = A + BT + CT^2 + DT^{-2}$ T (kelvins) from 298.15 to T_{max}

Chemical species	T_{max}	C_p^{ig}/R	A	$10^3 B$	$10^6 C$	$10^{-5} D$
Paraffins:						
Methane	CH ₄	1500	4.217	1.702	9.081	-2.164
Ethane	C ₂ H ₆	1500	6.369	1.131	19.225	-5.561
Propane	C ₃ H ₈	1500	9.001	1.213	28.785	-8.824
n-Butane	C ₄ H ₁₀	1500	11.928	1.935	36.915	-11.402
iso-Butane	C ₄ H ₁₀	1500	11.901	1.677	37.853	-11.945
n-Pentane	C ₅ H ₁₂	1500	14.731	2.464	45.351	-14.111
n-Hexane	C ₆ H ₁₄	1500	17.550	3.025	53.722	-16.791
n-Heptane	C ₇ H ₁₆	1500	20.361	3.570	62.127	-19.486
n-Octane	C ₈ H ₁₈	1500	23.174	4.108	70.567	-22.208
1-Alkenes:						
Ethylene	C ₂ H ₄	1500	5.325	1.424	14.394	-4.392
Propylene	C ₃ H ₆	1500	7.792	1.637	22.706	-6.915
1-Butene	C ₄ H ₈	1500	10.520	1.967	31.630	-9.873
1-Pentene	C ₅ H ₁₀	1500	13.437	2.691	39.753	-12.447
1-Hexene	C ₆ H ₁₂	1500	16.240	3.220	48.189	-15.157
1-Heptene	C ₇ H ₁₄	1500	19.053	3.768	56.588	-17.847
1-Octene	C ₈ H ₁₆	1500	21.868	4.324	64.960	-20.521
Miscellaneous organics:						
Acetaldehyde	C ₂ H ₄ O	1000	6.506	1.693	17.978	-6.158
Acetylene	C ₂ H ₂	1500	5.253	6.132	1.952
Benzene	C ₆ H ₆	1500	10.259	-0.206	39.064	-13.301
1,3-Butadiene	C ₄ H ₆	1500	10.720	2.734	26.786	-8.882
Cyclohexane	C ₆ H ₁₂	1500	13.121	-3.876	63.249	-20.928
Ethanol	C ₂ H ₆ O	1500	8.948	3.518	20.001	-6.002
Ethylbenzene	C ₈ H ₁₀	1500	15.993	1.124	55.380	-18.476
Ethylene oxide	C ₂ H ₄ O	1000	5.784	-0.385	23.463	-9.296
Formaldehyde	CH ₂ O	1500	4.191	2.264	7.022	-1.877
Methanol	CH ₄ O	1500	5.547	2.211	12.216	-3.450
Styrene	C ₈ H ₈	1500	15.534	2.050	50.192	-16.662
Toluene	C ₇ H ₈	1500	12.922	0.290	47.052	-15.716
Miscellaneous inorganics:						
Air		2000	3.509	3.355	0.575
Ammonia	NH ₃	1800	4.269	3.578	3.020
Bromine	Br ₂	3000	4.337	4.493	0.056
Carbon monoxide	CO	2500	3.507	3.376	0.557
Carbon dioxide	CO ₂	2000	4.467	5.457	1.045
Carbon disulfide	CS ₂	1800	5.532	6.311	0.805
Chlorine	Cl ₂	3000	4.082	4.442	0.089
Hydrogen	H ₂	3000	3.468	3.249	0.422
Hydrogen sulfide	H ₂ S	2300	4.114	3.931	1.490
Hydrogen chloride	HCl	2000	3.512	3.156	0.623
Hydrogen cyanide	HCN	2500	4.326	4.736	1.359
Nitrogen	N ₂	2000	3.502	3.280	0.593
Nitrous oxide	N ₂ O	2000	4.646	5.328	1.214
Nitric oxide	NO	2000	3.590	3.387	0.629
Nitrogen dioxide	NO ₂	2000	4.447	4.982	1.195
Dinitrogen tetroxide	N ₂ O ₄	2000	9.198	11.660	2.257
Oxygen	O ₂	2000	3.535	3.639	0.506
Sulfur dioxide	SO ₂	2000	4.796	5.699	0.801
Sulfur trioxide	SO ₃	2000	6.094	8.060	1.056
Water	H ₂ O	2000	4.038	3.470	1.450

[†] Selected from H. M. Spencer, *Ind. Eng. Chem.*, vol. 40, pp. 2152-2154, 1948; K. K. Kelley, *U.S. Bur. Mines Bull.* 584, 1960; L. B. Pankratz, *U.S. Bur. Mines Bull.* 672, 1982.

Liquid Entropy:

Consider unit mass of a liquid which will ultimately be raised to unit mass of vapor at constant pressure. For the unit mass of liquid,

$$dQ = C_{pL} \cdot dT$$

where: C_{pL} is specific heat capacity of the liquid at constant pressure. Dividing eq. throughout by T, then,

$$dQ/T = C_{pL} \cdot dT/T$$

Since

$$dS = dQ/T$$

$$dS = C_{pL} \cdot dT/T$$

Integrating this equation from initial state to final state:

$$\Delta S = [S_2 - S_1] = C_{pL} \cdot \ln (T_2/T_1)$$

Example A 40 kg steel casting ($C_p = 0.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$) at temperature of 723.15 K (450C) is quenched in 150 kg of oil ($C_p = 2.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$) at 298.15 K (25 C). If there is no heat losses what is the change in the entropy of (a) the casting (b) the oil (c) both considered together.

Solution: the final temperature T_2 of the oil and the steel casting is founded by the energy balance. Since the change in energy of the oil and steel casting together must be zero

$$(40)(0.5)(T - 723.15) + (150)(2.5)(T - 298.15) = 0$$

Solution yields $T = 319.67 \text{ K}$ (46.52 C)

a) Change in the entropy of the casting

$$\Delta S = \int \frac{dQ}{T} = m \int \frac{C_p dt}{T} = m C_p \ln \frac{T_2}{T_1}$$
$$(40)(0.5) \ln \frac{319.67}{723.15} = -16.33 \text{ kJ K}^{-1}$$

b) Change entropy for the oil

$$\Delta S = (150)(2.5) \ln \frac{319.67}{298.15} = 26.13 \text{ kJ K}^{-1}$$

c) Total entropy change

$$\Delta S_{total} = -16.33 + 26.13 = 9.80 \text{ kJ K}^{-1}$$
