

ENTROPY AND HEAT

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The thermodynamic identity for an infinitesimal process is

$$dU = TdS - PdV \quad (1)$$

This relation bears a resemblance to heat plus work relation for the change in internal energy:

$$dU = Q + W \quad (2)$$

In a quasistatic process, where a gas is being compressed slowly enough that the pressure has a chance to equalize throughout the volume of the gas at each stage, the work done in compressing the gas is $-PdV$ (this is positive, as the volume decreases in compression so $dV < 0$). In that case, then

$$W = -PdV \quad (3)$$

$$Q = TdS \quad (4)$$

and the change in entropy can be calculated as

$$dS = \frac{Q}{T} \quad (5)$$

which agrees with the original definition of entropy.

As an example, suppose we have a litre of air at room temperature (300 K) and atmospheric pressure (10^5 N m^{-2}), and we heat it at constant pressure until it doubles in volume. From the ideal gas law, if P is constant and V doubles, then T must also double. The entropy change is therefore

$$\Delta S = C_P \int_{T_i}^{T_f} \frac{dT}{T} \quad (6)$$

$$= C_P \ln \frac{T_f}{T_i} = C_P \ln 2 \quad (7)$$

where C_P is the heat capacity at constant pressure. From the appendix to Schroeder's book, $C_P \approx 29 \text{ J K}^{-1}$ for one mole of air (the values for

nitrogen and oxygen are both around 29). The number of moles of air in one litre is

$$n = \frac{PV}{RT} \quad (8)$$

$$= \frac{10^5 \times 10^{-3}}{(8.314)(300)} \quad (9)$$

$$= 0.04 \text{ mol} \quad (10)$$

The change in entropy is therefore

$$\Delta S = (0.04)(29) \ln 2 = 0.81 \text{ J K}^{-1} \quad (11)$$

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