## 2 1. INTRODUCTION TO THERMODYNAMICS AND REACTION KINETICS

**1.1.1. Temperature.** We have seen that both energy and entropy are additive quantities and that entropy is maximized. Consider a system consisting of two connected bodies such that  $E = E_1 + E_2$ . In order for the entropy  $S = S_1(E_1) + S_2(E_2)$  to be extremal,

$$0 = \frac{\mathrm{d}S}{\mathrm{d}E} = \frac{\mathrm{d}S}{\mathrm{d}E_1} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} + \frac{\mathrm{d}S_2}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}E_1} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} - \frac{\mathrm{d}S_2}{\mathrm{d}E_2}$$
(1.3)

must hold. The two derivatives of entropy for energy must be equal for both bodies to be in equilibrium. To measure how far they are from that, one defines

$$\frac{\mathrm{d}S}{\mathrm{d}E} =: \frac{1}{T} \tag{1.4}$$

and denotes with T the *temperature* of the system. It is clear that if the two bodies are in equilibrium  $T_1$  must equal  $T_2$ .

By dividing a body into small, reorderable test volumes we can exploit the additivity of energy and entropy to conclude that for a body at rest, the constants in the definition of entropy (1.1) only depend on the volume of this body but not on its particular shape. Thus, the state of a system is completely described by two state variables. Consequently, we should add to definition (1.4) that V must be kept fixed while taking the derivative. It is common to denote this by adding a subscript after the derivative:

$$\left(\frac{\mathrm{d}S}{\mathrm{d}E}\right)_V = \frac{1}{T}.\tag{1.5}$$

**1.1.2. Pressure.** If an amount of a gas is enclosed in a solid box of volume V, it asserts force on the walls. *Pascal's law* states that this force is orthogonal to the area and amounts to

$$p = -\left(\frac{\partial E}{\partial V}\right)_S.$$
(1.6)

p is called the *pressure* of the system.

**1.1.3.** Enthalpy and heat capacity. The energy of a body can change due to the application of physical work when changing its volume and due to direct exchange of energy with connected bodies. The latter part of the energy is called *heat* and denoted by Q. Using (1.6) and (1.4) we find that

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}E}{\mathrm{d}t} + p\frac{\mathrm{d}V}{\mathrm{d}t} = \left(T\frac{\mathrm{d}S}{\mathrm{d}t} - p\frac{\mathrm{d}V}{\mathrm{d}t}\right) + p\frac{\mathrm{d}V}{\mathrm{d}t} = T\frac{\mathrm{d}S}{\mathrm{d}t}.$$
(1.7)

The heat amount required to change a body's temperature by one degree is defined as

$$C = T \frac{\partial S}{\partial T},\tag{1.8}$$

where one again adds the subscripts V or p to denote which quantity is kept constant while taking the derivative. By small  $c_p$  and  $c_v$  one typically denotes the *specific heat capacities*, which are the capital Cs divided by the number of molecules in the system.