

2 Chapter 2: Conservation of Energy

2.1 Functions of the State

Thermodynamic state completely defined by certain independent variables, eg. E, V , mole number $n_1 \dots n_c$, eg. $T, V, n_1 \dots n_c$

Functions expressed in terms of these variables called *functions of the state*.

Eg. Ideal Gas

$$S = Nk_B \left[\frac{5}{2} - \frac{3}{2} \ln(3\pi\hbar^3/m) \right] + Nk_B \ln(E^{3/2}V/N^{5/2}), \quad N = \text{number of particles, } m = \text{mass}$$

Give two examples of functions of the state for different systems. Eg. Einstein solid, gas of photons, etc.

2.2 Conservation of Energy - Closed Systems

The first principle of thermodynamics.

Energy – function of the state.

Change of energy only due to flow from, or into, exterior;

$$dE = d_e E, \quad d_i E = 0 \quad (1)$$

Energy supplied by exterior is sum of heat flow dQ and mechanical work $dW = -pdV$ (if pressure is normal to surface).

$$dE = dQ - pdV \quad (2)$$

Consider system undergoing internal change characterized by ξ .

E is a function of the state so can be expressed in terms of variables V, T , mole number $n_1 \dots n_c$.

Mole numbers can be expressed in terms of ξ . Therefore $E = E(V, T, \xi)$

Total differential of E ;

$$dE = \left(\frac{\partial E}{\partial V} \right)_{T\xi} dV + \left(\frac{\partial E}{\partial T} \right)_{V\xi} dT + \left(\frac{\partial E}{\partial \xi} \right)_{TV} d\xi \quad (3)$$

Using eqn. (2)

$$dQ = C_{V\xi} dT + l_{T\xi} dV - r_{TV} d\xi \quad (4)$$

where

$$C_{V\xi} = \left(\frac{\partial E}{\partial T} \right)_{V\xi}, \quad l_{T\xi} - p = \left(\frac{\partial E}{\partial V} \right)_{T\xi}, \quad -r_{TV} = \left(\frac{\partial E}{\partial \xi} \right)_{TV} \quad (5)$$

$C_{V\xi}$ - heat capacity, $l_{T\xi}$ - heat effect of compression, r_{TV} - heat of reaction (positive for an exothermic reaction).

2.3 Enthalpy

$$H \equiv E + pV \quad (6)$$

$$dH = dE + pdV + Vdp$$

Principle of conservation of energy

$$dH = dQ + Vdp \quad (7)$$

In terms of the enthalpy

$$dQ = C_{p\xi}dT + h_{T\xi}dp - r_{Tp}d\xi \quad (8)$$

where

$$C_{p\xi} = \left(\frac{\partial H}{\partial T} \right)_{p\xi}, \quad h_{T\xi} + V = \left(\frac{\partial H}{\partial p} \right)_{T\xi}, \quad -r_{Tp} = \left(\frac{\partial H}{\partial \xi} \right)_{Tp} \quad (9)$$

Using the variables $n_1 \dots n_c$ instead of ξ

$$dQ = C_{p,n_1 \dots n_c}dT + h_{T,n_1 \dots n_c}dp + \sum_{\gamma} h_{\gamma}dn_{\gamma} \quad (10)$$

h_{γ} is the specific enthalpy (per mole) of component γ

$$h_{\gamma} = \left(\frac{\partial H}{\partial n_{\gamma}} \right)_{pTn'_{\gamma}} \quad (11)$$

n'_{γ} denotes all mole number $n_1 \dots n_c$ with the exception of n_{γ} .

The specific enthalpy of component γ *per unit mass*

$$h_{\gamma}^+ = \left(\frac{\partial H}{\partial m_{\gamma}} \right)_{pTm'_{\gamma}} = \frac{1}{M_{\gamma}}h_{\gamma} \quad (12)$$

2.4 Open Systems

In conservation of energy, must take into account exchange of matter with exterior (incoming or outgoing matter can carry internal energy). Instead of eqn. (2)

$$dE = d\phi - pdV \quad (13)$$

ϕ is resultant flow of energy due to heat transfer and exchange of matter $d\phi = dQ + dE_m$.

Enthalpy

$$dH = d\phi + Vdp \quad (14)$$

Note that the enthalpy, like energy or entropy, is defined apart from an arbitrary additive constant

$$H' = H + \alpha \quad (15)$$

Note that for a homogeneous system, H , and therefore also H' is proportional to the mass of the system. Thus α is proportional to m and no longer a constant for *open* systems.

$$H' = H + \beta m \quad (16)$$

Follows that the change of enthalpy or energy in an open system is defined apart from the term βdm . Also applies to $d\phi$.

2.5 Example

Consider system formed of two subsystems (I and II). Each subsystem is open but the whole system is closed. For each subsystem,

$$dH^I = d^I\phi + V^I dp^I, \quad dH^{II} = d^{II}\phi + V^{II} dp^{II} \quad (17)$$

Assuming $p^I = p^{II} = p$, change of total enthalpy

$$dH = d^I\phi + d^{II}\phi + V dp \quad (18)$$

where $V = V^I + V^{II}$. Since system is closed, must obey usual formulation of the first law;

$$dH = dQ + V dp \quad (19)$$

hence

$$dQ = d^I\phi + d^{II}\phi \quad (20)$$

Now,

$$d^I\phi = d_e^I Q + d_i^I\phi \quad d^{II}\phi = d_e^{II} Q + d_i^{II}\phi \quad (21)$$

but

$$dQ = d_e^I Q + d_e^{II} Q \quad (22)$$

therefore

$$d_i^I\phi + d_i^{II}\phi = 0 \quad (23)$$

Energy flow received by subsystem I from subsystem II is equal and of opposite sign to that received by phase II from phase I.

For closed subsystems this gives

$$d_i^I Q + d_i^{II} Q = 0 \quad (24)$$

Expresses conservation of energy for the system.