Exact differentials [tln14]

Total differential of a function $F(x_1, x_2)$: $dF = \frac{\partial F}{\partial x_1}dx_1 + \frac{\partial F}{\partial x_2}dx_2$.

The differential $dF = c_1(x_1, x_2)dx_1 + c_2(x_1, x_2)dx_2$ is exact if dF is the total differential of a function $F(x_1, x_2)$.

Condition: $\frac{\partial^2 F}{\partial x_1 \partial x_2} = \frac{\partial^2 F}{\partial x_2 \partial x_1} \;\Rightarrow\; \frac{\partial c_1}{\partial x_2} = \frac{\partial c_2}{\partial x_1}$.

Consequences: $\int_{(a_1,a_2)}^{(b_1,b_2)} dF = F(b_1, b_2) - F(a_1, a_2), \qquad \oint dF = 0.$

Internal energy U

U is a state variable. $\oint dU = 0$ for reversible cyclic processes.

$dU = \delta Q + \delta W + \delta Z = TdS + YdX + \mu dN$ is an exact differential.

$\delta Q = TdS$: heat transfer
$\delta W = YdX$: work performance $(-pdV + HdM + \ldots)$
$\delta Z = \mu dN$: matter transfer

Entropy S

Carnot cycle: $\frac{|\Delta Q_L|}{\Delta Q_H} = \frac{T_L}{T_H} \;\Rightarrow\; \frac{\Delta Q_L}{T_L} + \frac{\Delta Q_H}{T_H} = 0.$

Any reversible cyclic process is equivalent to an array of Carnot cycles running in parallel.

$\Rightarrow \oint \frac{\delta Q}{T} \equiv \oint dS = 0$ for reversible cyclic processes.

S is a state variable.

Irreversible process:

$$\eta = 1 - \frac{|\Delta Q_L|}{\Delta Q_H} < 1 - \frac{T_L}{T_H} \;\Rightarrow\; \frac{|\Delta Q_L|}{\Delta Q_H} > \frac{T_L}{T_H} \;\Rightarrow\; \frac{\Delta Q_L}{T_L} + \frac{\Delta Q_H}{T_H} < 0.$$

More general cyclic process: $\oint \frac{\delta Q}{T} < 0, \;\; \oint dS = 0 \;\Rightarrow\; dS > \frac{\delta Q}{T}$.

Irreversible process in isolated system: $\delta Q = 0 \;\Rightarrow\; dS > 0$.