

Chapter 1

ThermoS26-03

1.1 Exact Differentials in Thermodynamics

Recall, we wrote, as a shorthand,

$$d\tilde{U} = T_U dS - P_U dV + \sum_{i=1}^r \mu_{U,i} dN_i. \quad (1.1.1)$$

This has the form

$$F_1 dx_1 + F_2 dx_2 + \cdots + F_n dx_n = \vec{F} \cdot d\vec{x}, \quad (1.1.2)$$

where

$$F_1 = T_U, \quad F_2 = -P_U, \quad \dots \quad (1.1.3)$$

We say that $\vec{F} \cdot d\vec{x}$ is an **exact differential** iff \vec{F} is conservative.

Clearly

$$d\tilde{U} = \nabla \tilde{U} \cdot d\vec{r} \quad (\vec{r} \in \Sigma_S) \quad (1.1.4)$$

is an exact differential, because $\nabla \tilde{U}$ is conservative, trivially. Thus, the integral

$$\int_{\vec{Y}} d\tilde{U} = \int_{\vec{Y}} \nabla \tilde{U} \cdot d\vec{r} \quad (1.1.5)$$

is path independent. If $\vec{Y} : [a, b] \rightarrow \Sigma_S$ is the path in question, with

$$\vec{Y}(a) = \vec{r}_a, \quad \vec{Y}(b) = \vec{r}_b, \quad (1.1.6)$$

then

$$\int_{\vec{Y}} d\tilde{U} = \int_{\vec{Y}} \nabla \tilde{U} \cdot d\vec{r} = \tilde{U}(\vec{r}_b) - \tilde{U}(\vec{r}_a). \quad (1.1.7)$$

We can use any path we want in state space Σ_S .

The same is true for

$$d\tilde{S} = \frac{1}{T_S} dU + \frac{P_S}{T_S} dV - \sum_{i=1}^r \frac{\mu_{S;i}}{T_S} dN_i, \quad (1.1.8)$$

that is

$$d\tilde{S} = \nabla \tilde{S} \cdot d\vec{r} \quad (\vec{r} \in \Sigma_U) \quad (1.1.9)$$

is an exact differential.

1.2 Heat Flow

We examine the approach to thermal equilibrium using a diathermal wall. Suppose the substance is unary, $r = 1$. It must be that the variables

$$V^\alpha, V^\beta, N^\alpha, N^\beta$$

are fixed, but energy can be exchanged in the process. Suppose the variable γ parameterizes the process.

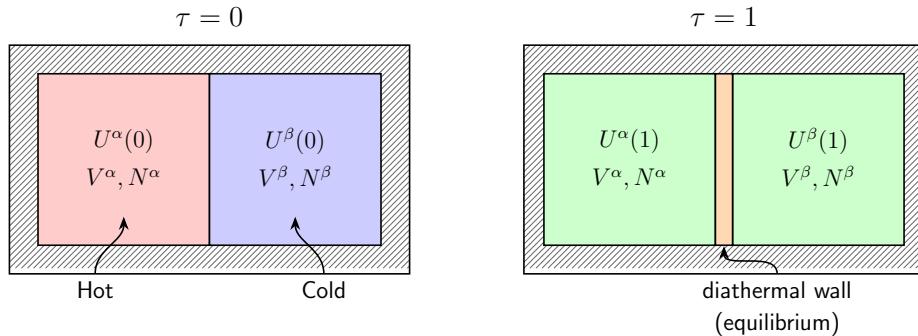


Figure 1.1: Initial and equilibrium configurations for $\gamma = 0$ and $\gamma = 1$. At $\gamma = 0$ the insulating wall is replaced with a diathermal wall; left hot subsystem has $U^\alpha(0), V^\alpha, N^\alpha$ and right cold subsystem has $U^\beta(0), V^\beta, N^\beta$. At $\gamma = 1$ a diathermal wall separates subsystems with $U^\alpha(1), V^\alpha, N^\alpha$ and $U^\beta(1), V^\beta, N^\beta$ in equilibrium.

The initial and equilibrium states satisfy

$$\begin{aligned} S(0) &= \tilde{S}^\alpha(U^\alpha(0), V^\alpha, N^\alpha) + \tilde{S}^\beta(U^\beta(0), V^\beta, N^\beta) \\ &\leq \tilde{S}^\alpha(U^\alpha(1), V^\alpha, N^\alpha) + \tilde{S}^\beta(U^\beta(1), V^\beta, N^\beta) = S(1). \end{aligned}$$

We require that

$$U^\alpha(\gamma) + U^\beta(\gamma) = U_0.$$

The entropy is at a maximum at equilibrium. Suppose that, as indicated by Figure 1.1,

$$\tilde{T}^\alpha(U^\alpha(0), V^\alpha, N^\alpha) > \tilde{T}^\beta(U^\beta(0), V^\beta, N^\beta)$$

while at equilibrium

$$\tilde{T}^\alpha(U^\alpha(1), V^\alpha, N^\alpha) = \tilde{T}^\beta(U^\beta(1), V^\beta, N^\beta).$$

We will show that

$$U^\alpha(0) > U^\alpha(1) \quad (\text{energy is lost in } \alpha)$$

and

$$U^\beta(0) < U^\beta(1) \quad (\text{energy is gain in } \beta).$$

To see this, compute

$$\begin{aligned} \frac{dS}{d\gamma} &= \frac{\partial \tilde{S}^\alpha}{\partial U^\alpha} \frac{\partial U^\alpha}{\partial \gamma} + \frac{\partial \tilde{S}^\beta}{\partial U^\beta} \frac{\partial U^\beta}{\partial \gamma} \\ &= \frac{1}{\tilde{T}_S^\alpha(\gamma)} \frac{\partial U^\alpha}{\partial \gamma} + \frac{1}{\tilde{T}_S^\beta(\gamma)} \frac{\partial U^\beta}{\partial \gamma} \\ &= \left(\frac{1}{\tilde{T}_S^\alpha(\gamma)} - \frac{1}{\tilde{T}_S^\beta(\gamma)} \right) \frac{\partial U^\alpha}{\partial \gamma}, \end{aligned} \tag{3.1}$$

where

$$\tilde{T}_S^q(\gamma) := T_S^q(U^q(\gamma)), \quad q = \alpha, \beta.$$

We know that

$$S(0) \leq \tilde{S}(1).$$

We also know that

$$\tilde{T}_S^\alpha(0) > \tilde{T}_S^\beta(0) \quad \text{and} \quad \tilde{T}_S^\alpha(1) = \tilde{T}_S^\beta(1).$$

Set

$$R(\gamma) := \frac{1}{\tilde{T}_S^\alpha(\gamma)} - \frac{1}{\tilde{T}_S^\beta(\gamma)}, \quad 0 \leq \gamma \leq 1.$$

We know that $R(0) < 0$ and $R(1) = 0$.

The red curve in Figure 1.2 is not possible; if it were, equilibrium would be reached earlier at $\gamma = \gamma^*$. Thus

$$R(\gamma) < 0 \quad \forall \gamma \in [0, 1).$$

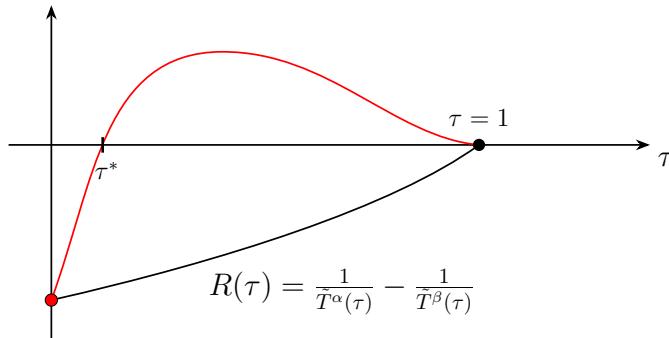


Figure 1.2: Plot of $R(\gamma)$ on $[0, 1]$. The red curve is impossible; if it occurred, equilibrium would be reached earlier at $\gamma = \gamma^*$. The valid curve remains negative with $R(1) = 0$.

Integrating (3.1), we get

$$0 \leq \tilde{S}(1) - \tilde{S}(0) = \int_0^1 R(\gamma) \frac{dU^\alpha}{d\gamma} d\gamma. \quad (3.2)$$

For $U^\alpha(\gamma)$ we have two options:

$$\text{Case (1)} \quad U^\alpha(0) > U^\alpha(1), \quad \text{Case (2)} \quad U^\alpha(0) \leq U^\alpha(1).$$

We are free to pick a parameterization however we want. Let us take a simple linear path

$$\frac{dU^\alpha}{d\gamma} = U^\alpha(1) - U^\alpha(0) =: C^\alpha.$$

Then Case (1) implies $C^\alpha < 0$, while Case (2) implies $C^\alpha \geq 0$. The integral in (3.2) is

$$0 \leq \tilde{S}(1) - \tilde{S}(0) = C^\alpha \int_0^1 R(\gamma) d\gamma.$$

Therefore the only possible choice is Case (1). Thus

$$U^\alpha(0) > U^\alpha(1) \quad (U^\beta(0) < U^\beta(1)).$$

This is consistent with our intuition about temperature. If $\tilde{T}^\alpha(0) > \tilde{T}^\beta(0)$ heat energy flows from subsystem α to subsystem β .

Heat Transfer Principle: Heat energy always flows from hotter to colder system. This is equivalent to the second law of thermodynamics.

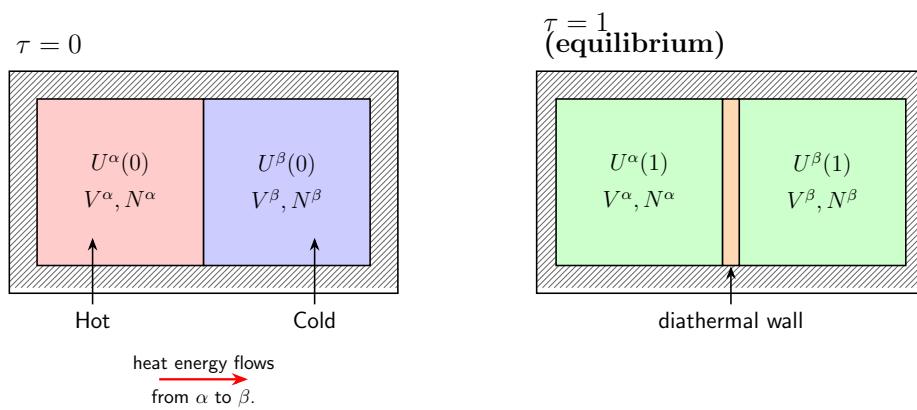


Figure 1.3: Energy transfer for $\gamma = 0$ (hot to cold through replaced wall) and $\gamma = 1$ (equilibrium with diathermal wall) showing flow from subsystem α to subsystem β .