

# Engineering Thermodynamics

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## 1 Basic Definition

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### 1.1 能量转换装置

- 热能动力装置:
    - 蒸汽动力装置(Vapor Power Systems): 工质: Steam/Water
    - 燃气动力装置(Gas Power Systems): 工质: 燃气
      - 内燃机
      - 燃气轮机
      - 喷气发动机
  - 制冷和热泵装置 (Refridgeration and Heat Pump Systems): 工质: 制冷剂
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### 1.2 热力系

物质交换:

- 闭口系 (closed system): 控制质量 (C.M.) ——与外界无物质交换
- 开口系 (open system): 控制体积 (C.V.) ——与外界有物质交换

能量交换:

- 简单热力系: 与外界只交换热量和一种形式的准静功
  - (简单压缩系 (simple compressive system): 准静功为可逆体积变化功)
  - 绝热系 (adiabatic system): 与外界无热量交换
  - 孤立系 (isolated system): 与外界无能量交换也无物质交换
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### 1.3 热力状态与基本状态参数

- Thermodynamic State
    - steady state: 状态参数不随时间变化
    - equilibrium state: 所有参数达到平衡, 即不再变化
  - State Properties
    - extensive property:  $M, V, U, E, H, S$
    - intensive property:  $T, p$ , 广延量的比参数 ( $v, u, h, s$ )
    - Basic Properties:  $T, p, v$
  - Process

irreversibility:

    - reversible:(quasi-steady & non-dissipative) (准稳态及无耗散)
    - irreversible

thermodynamic:

    - quasi-steady 准静态
    - isothermal 等温
    - adiabatic 绝热
    - isentropic 等熵
  - Process para
    - $Q, W$
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## 1.4 Zeroth law of thermodynamics

“It’s a matter of experience that when two objects are in thermal equilibrium with a third object, they are in thermal equilibrium with one another.”

## 1.5 Temperature Scales

- Kelvin scale
- Rankine scale

$$T(^{\circ}R) = 1.8T(K)$$

- Celsius scale

$$T(^{\circ}C) = T(K) - 273.15$$

- Fahrenheit scale

$$T(^{\circ}F) = T(^{\circ}R) - 459.67 = 1.8T(^{\circ}C) + 32$$

开尔文温标	摄氏度	华氏度
$0K$	$-273.15^{\circ}C$	$-459.67^{\circ}F$
$273.15K$	$0^{\circ}C$	$32^{\circ}F$
$373.15K$	$100^{\circ}C$	$212^{\circ}F$

## 2 Energy and the First law of Thermodynamics

### 2.1 Energy

- Internal energy:  $U$
  - Kinetic energy:  $E_k$
  - Potential energy:  $E_p$
- Total energy:

$$E = U + E_k + E_p$$
$$\Delta E = \Delta U + \Delta E_k + \Delta E_p$$

### 2.2 Work

- 输出功 Output work (对外输出总功量):  $W'$
- 净输出功:  $W_{net}$ 、轴功 (叶轮机械净输出功):  $W_s$
- 膨胀功/压缩功/体积功 Expansion or Compression work:

$$W = p\Delta V$$
$$\delta W = pdV$$
$$\delta w = pdv$$

- 推动功/推挤功:  
流体进出系统系统所对流体做出的推动功量

$$W_p = pV$$

- 流动功 Flow work/energy(State property):

$$W_f = \sum_i W_{p,i} = \Delta(pV)$$
$$\delta W_f = V dp + p dV$$
$$\delta w_f = v dp + p dv$$

- 技术功 Technical work:

$$\begin{aligned}W_t &= \Delta E_k + \Delta E_p + W_{net} \\ \delta W_t &= \delta W - \delta W_f = -V dp \\ \delta w_t &= -v dp\end{aligned}$$

Relation:

$$\begin{aligned}W' &= W_{net} + W_f \\ W_t &= \Delta E_k + \Delta E_p + W_{net} \\ W &= W_t + W_f\end{aligned}$$

## 2.3 Heat

Conduction:

$$\dot{Q} = -\kappa A \frac{dT}{dx}$$

Radiation:

$$\dot{Q} = \varepsilon \sigma A T^4$$

Convection:

$$\dot{Q} = h A \Delta T$$

## 2.4 The first law of Thermodynamics

“During an interaction, energy can change from one form to another but the total amount of energy remains constant.”

general form:

$$\begin{aligned}\Delta E &= Q - W \\ \Delta E_k + \Delta E_p + \Delta U &= Q - W\end{aligned}$$

differential form:

$$dE = \delta Q - \delta W'$$

time rate form:

$$\frac{dE}{dt} = \dot{Q} - \dot{W}'$$

## CLOSED SYSTEMS(C.M.)

1. differential form:

闭口系热一定律基本表达式:

$$dU = \delta Q - \delta W \quad (1)$$

$$du = dq - p dv \quad (2)$$

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## OPEN SYSTEMS(C.V.)

### 1. differential form:

热一定律:

$$dE = \delta Q - \delta W'$$

输出总功量转化为净功量和流动功:

$$\delta W' = \delta W_{net} + d(pV)$$

技术功、焓的定义:

$$\begin{aligned}\delta W_t &= \delta W_{net} + dE_k + dE_p \\ dH &= dU + d(pV)\end{aligned}$$

开口系-热力学第一定律基本表达式:

$$dH = \delta Q - \delta W_t \quad (1.1)$$

$$dU = \delta Q - \delta W \quad (1.2)$$

$$\begin{aligned}dh &= du + vdp + pdv \\ dh &= dq + vdp\end{aligned} \quad (2.1)$$

$$du = dq - pdv \quad (2.2)$$

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### 2. time rate & integral form:

热一定律:

$$\begin{aligned}\frac{dE}{dt} &= \dot{Q} - \dot{W}' \\ e &= u + \frac{V^2}{2} + gz \\ E &= \int_{CV} e dm = \int_{CV} e \rho d\mathcal{V}\end{aligned} \quad (1)$$

differential form:

$$dE_{CV} = \delta Q - \delta W + d(ms)$$

Steady Flow:

$$0 = \delta Q - \delta W + mds$$

积分形式(Reynolds Transport Theorem)

$$\frac{d}{dt}(E_{sys}) = \dot{Q} - \dot{W}' = \frac{d}{dt}(\int_{CV} e \rho d\mathcal{V}) + \int_{CS} e \rho V_n dA$$

输出总功量转化为净功量和流动功:

$$\dot{W}' = \dot{W}_{net} + \int_{CS} p V_n dA$$

焓的定义：

$$h = u + pv$$

$$\int_{CS} h \rho V_n dA = \int_{CS} (u + \frac{p}{\rho}) \rho V_n dA$$

连续介质力学形式：

$$\dot{Q} - \dot{W}_{net} = \frac{d}{dt} \left( \int_{CV} e \rho d\mathcal{V} \right) + \int_{CS} \left( h + \frac{V^2}{2} + gz \right) \rho V_n dA$$

or

$$\dot{Q} - \dot{W}_{net} = \frac{\partial}{\partial t} \int_{CV} e \rho d\mathcal{V} + \int_{CS} \left( h + \frac{V^2}{2} + gz \right) \rho V_n dA$$

or

$$\dot{Q} - \dot{W}_{net} = \frac{\partial}{\partial t} \int_{CV} e \rho d\mathcal{V} + \sum (h + \frac{V^2}{2} + gz)_e \dot{m}_e - \sum (h + \frac{V^2}{2} + gz)_i \dot{m}_i$$

## 2.5 application

- 气轮机叶轮 Turbine Wheel

$$\dot{W}_{net} = \dot{m} \left( \frac{V_1^2 - V_2^2}{2} \right)$$

- 热力发动机 Gas And Steam Turbine

$$0 = \dot{Q}_{CV} - \dot{W}_{net} + \dot{m}(h_1 - h_2)$$

$$\dot{W}_{net} = \dot{m}(h_1 - h_2)$$

- 压气机/泵 Compressor and Pump

$$0 = \dot{Q}_{CV} - \dot{W}_{net} + \dot{m}(h_1 - h_2)$$

$$\dot{W}_{net} = \dot{m}(h_1 - h_2)$$

- 喷管/扩散器 Nozzle/Diffuser

$$0 = \dot{Q}_{CV} + \dot{m} \left( h_1 + \frac{V_1^2}{2} \right) - \dot{m} \left( h_2 + \frac{V_2^2}{2} \right)$$

$$0 = (h_1 - h_2) + \left( \frac{V_1^2 - V_2^2}{2} \right)$$

- 换热器 Heat Exchanger

$$\dot{Q}_{CV} = \dot{m}(h_2 - h_1)$$

- 节流 Throttling Process

$$h_1 = h_2$$

## 3 Entropy and the Second Law of Thermodynamics

### 3.1 The Second Law of Thermodynamics

#### Clausius statement:

Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

#### Kelvin Statement:

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

**Planck's Proposition:**

It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and cooling of a heat reservoir.

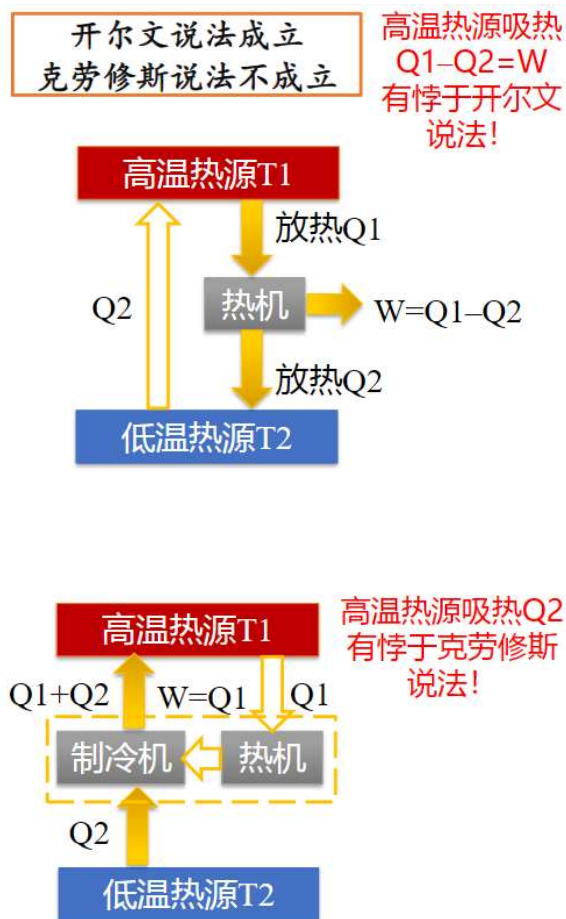
## • 克劳修斯说法:

- 热传导的不可逆性
- 无法制造理想制冷机

## • 开尔文-普朗克说法:

- 热工转换的不可逆性
- 无法制造第二类永动机
- 单一热源下不可能做正输出功

$$\oint W_{cycle} = \oint Q_{cycle} \leq 0$$



## • 熵增原理 (能量贬值原理): 孤立系统总是朝着熵增方向进行

## • 永动机:

- 第一类永动机 (违背热一定律) 凭空产生能量
- 第二类永动机 (违背热二定律) 热量100%转化为功

## • 卡诺定理:

- 卡诺第一定理: 不可能制造出在两个温度不同的热源间工作的热机, 而使其效率超过在同样热源间工作的可逆热机

- 卡诺第二定理：在两个热源间工作的一切可逆热机具有**相同的效率**
- 卡诺定理推论：在**相同两个恒温热源**间工作的一切不可逆热机的效率必小于可逆热机的效率
- 能量品位：

能量转换方向性的实质是能质有差异

- 无限可转换能—机械能，电能
- 部分可转换能—热能
- 不可转换能—环境介质的热力学能

### 3.2 Reversible Process

Reversible Process  $\iff$  No internal irreversibilities

$$\oint W_{\text{cycle}} \leq 0 \begin{cases} < 0 : \text{Internal irreversibilities present} \\ = 0 : \text{No internal irreversibilities} \end{cases} \quad (\text{single reservoir})$$

### 3.3 Propositions of The Second Law of Thermodynamics

#### I. Kelvin Scales

In Carnot Heat Engines:

$$\left(\frac{Q_C}{Q_H}\right)_{\text{rev}} = \phi(T_C, T_H) \stackrel{\text{def}}{=} \frac{T_C}{T_H}$$

#### II. Clausius Inequality

$$\oint \left(\frac{Q}{T}\right)_b = -\sigma_{\text{cycle}}, \sigma_{\text{cycle}} \begin{cases} > 0 : \text{Internal irreversibilities present} \\ = 0 : \text{No internal irreversibilities} \end{cases} \quad (\text{system boundary heat exchange})$$

#### III. Entropy

Definition:

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{rev}}$$

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev}}$$

$TdS$  equation in reversible system:

$$TdS = dU + pdV$$

$$Tds = dH - Vdp$$

$$Tds = du + pdv$$

$$Tds = dh - vdp$$

## Closed System

basic relation:

$$\oint \left( \frac{Q}{T} \right)_b = \int_1^2 \left( \frac{Q}{T} \right)_b + \int_2^1 \left( \frac{Q}{T} \right)_{rev}$$
$$\int_1^2 \left( \frac{Q}{T} \right)_b + S_1 - S_2 = -\sigma$$

differential form:

$$dS = \left( \frac{\delta Q}{T} \right)_b + \delta\sigma$$

*or*

$$dS = dS_f + \delta S_g$$

## Condition Relation:

Common:

$$dS = \left( \frac{\delta Q}{T} \right)_b + \delta\sigma$$

Adiabatic:

$$dS = \delta\sigma$$

Reversible:

$$dS = \left( \frac{\delta Q}{T} \right)_b$$

Isentropic: (  $\iff$  Adiabatic+Reversible)

$$dS = 0$$

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## IV Increase of Entropy Principle

In isolated system:

$$\left( \frac{\delta Q}{T} \right)_b = 0$$
$$dS_{iso} = \delta S_g \geq 0$$

## Open System

differential form:

$$dS_{CV} = \frac{\delta Q}{T} + \delta S_{g,CV} + d(ms)$$

Steady Flow:

$$0 = \frac{\delta Q}{T} + \delta S_{g,CV} + mds$$

time rate & integral form:

$$\left( \frac{dS}{dt} \right)_{sys} = \sum \frac{\dot{Q}}{T} + \dot{\sigma}$$



$$\sum \frac{\dot{Q}}{T} + \dot{\sigma} = \frac{\partial}{\partial t} \int_{CV} \rho s d\mathcal{V} + \int_{CS} s \rho V_n dA$$

or

$$\sum \frac{\dot{Q}}{T} + \dot{\sigma} = \frac{\partial}{\partial t} \int_{CV} \rho s d\mathcal{V} + \sum \dot{m}_e s_e - \sum \dot{m}_i s_i$$

### 3.4 Heat Engine and Heat Pump/Refrigerator

#### Heat Engine

Thermal efficiency:

$$\eta = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

$$\eta_{max} = 1 - \frac{T_C}{T_H}$$

#### Refrigerator

Thermal efficiency:

$$\varepsilon = \frac{Q_C}{W_{cycle}} = \frac{Q_C}{Q_H - Q_C}$$

$$\varepsilon_{max} = \frac{T_C}{T_H - T_C}$$

#### Heat Pump

Thermal efficiency:

$$\varepsilon' = \frac{Q_H}{W_{cycle}} = \frac{Q_H}{Q_H - Q_C}$$

$$\varepsilon'_{max} = \frac{T_H}{T_H - T_C}$$

### 3.5 application-efficiency

- isentropic turbine efficiency

$$\frac{\dot{W}_{net}}{\dot{m}} = (h_1 - h_2)$$

$$\eta_t = \frac{h_1 - h_2}{h_1 - h_{2s}}$$

- isentropic compressor and pump efficiency

$$\frac{-\dot{W}_{net}}{\dot{m}} = (h_2 - h_1)$$

$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1}$$

- isentropic nozzle efficiency

$$\frac{V_2^2}{2} = h_1 - h_2 + \frac{V_1^2}{2}$$

$$\eta_{nozzle} = \frac{V_2^2/2}{(V_2^2/2)_s}$$

### 3.6 Exergy 烟 Anergy 燃

- Exergy and Anergy in Heat

Environment at  $T_0$ , System at  $T$

Exergy:

$$E_{x,Q} = W_{max} = (1 - \frac{T_0}{T})Q$$

Anergy:

$$E_{n,Q} = Q - E_{x,Q} = \frac{T_0}{T}Q = Q_{emit}$$

- Exergy and Anergy in System

**Definition:** Maximum theoretical work from system and environment to reach an equilibrium

**Closed System**

Overall:

$$\begin{aligned} 0 &= dU_s + dU_e + dW_x \\ \delta S_g &= dS_{iso} = dS_s + dS_e \end{aligned}$$

System:

$$\begin{aligned} \delta Q_{rev} &= dU_s + \delta W_{max} \\ \delta W_{max} &= \delta W_x + p_0 dV_s \end{aligned}$$

Environment, at  $T_0, p_0$ :

$$\begin{aligned} -\delta Q_{rev} &= dU_e + p_0 dV_e \\ -\delta Q_{rev} &= T_0 dS_e \end{aligned}$$

Maximum Work:

$$\begin{aligned} \delta W_x &= -dU_s - p_0 dV_s - T_0(dS_g - dS_s) \\ W_x &= (U - U_0) + p_0(V - V_0) - T_0(S - S_0) + (E_k + E_p) - T_0 S_g \end{aligned}$$

Exergy(a kind of Potential):

$$E_x = (U - U_0) + p_0(V - V_0) - T_0(S - S_0) + (E_k + E_p)$$

or

$$E_x = (U - U_0) + p_0(V - V_0) - T_0(S - S_0)$$

$$e_x = (u + p_0 v - T_0 s) - (u_0 + p_0 v_0 - T_0 s_0)$$

Exergy Change:

$$\begin{aligned} dE_x &= dU + p_0 dV - T_0 dS \\ dE_x &= \delta Q - (\delta W - p_0 dV) - T_0(\frac{\delta Q}{T_b} + \delta S_g) \end{aligned}$$

$$\begin{aligned} dE_x &= (1 - \frac{T_0}{T_b})\delta Q - (\delta W - p_0 dV) - T_0 \delta S_g \\ E_2 - E_1 &= \int_1^2 (1 - \frac{T_0}{T_b})\delta Q - [W - p_0(V_2 - V_1)] - T_0 \Delta S_g \end{aligned}$$

- Exergy transfer of Heat transfer

$$\int_1^2 (1 - \frac{T_0}{T_b}) \delta Q$$

- Exergy transfer of Work

$$[W - p_0(V_2 - V_1)]$$

- Exergy destruction

$$T_0 \Delta S_g$$

Simplization

$$E_2 - E_1 = E_q - E_w - E_d$$

Isolated and no work process:

$$\Delta E = -E_d$$

time rate form:

$$\dot{E}_x = \sum_j (1 - \frac{T_0}{T_j}) \dot{Q}_j - [\dot{W} - p_0 (\frac{dV}{dt})] - T_0 \dot{\sigma}$$

steady state:

$$0 = \sum_j (1 - \frac{T_0}{T_j}) \dot{Q}_j - \dot{W} - T_0 \dot{\sigma}$$

**Open System**

Exergy:

$$E_x = (H - H_0) - T_0(S - S_0) + (E_k + E_p)$$

*or*

$$E_x = (H - H_0) - T_0(S - S_0)$$

$$e_x = (h - T_0 s) - (h_0 - T_0 s_0)$$

Exergy Change

time rate form:

$$\sum_j (1 - \frac{T_0}{T_j}) \dot{Q}_j - (\dot{W}_{CV} - p_0 \frac{dV_{CV}}{dt}) - T_0 \dot{\sigma} = \frac{d}{dt} \int_{CV} e_x \rho dV + \int_{CA} e_x \rho dV_n$$

steady state:

$$0 = \sum_j (1 - \frac{T_0}{T_j}) \dot{Q}_j - \dot{W}_{CV} + \sum_i \dot{m}_i e_{fi} - \sum_e \dot{m}_e e_{fe} - T_0 \dot{\sigma}$$

specific flow exergy:

$$e_f = (h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$$

$$e_f = e_x + v(p - p_0)$$

## Other System

存在非体积功输出:

$$TdS = dU + \delta W + \delta W_u$$

$$\delta W_{u,max} = TdS - dU - pdV$$

- 定温-定容

$$F = U - TS$$

$$f = u - Ts$$

$$E_x = W_{u,v,max} = (U - TS) - (U_0 - T_0 S_0) = F - F_0$$

$F$ 为亥姆霍兹自由能[强度量]

- 定温-定压

$$G = H - TS$$

$$g = h - Ts = u + pv - Ts$$

$$E_x = W_{u,p,max} = (H - TS) - (H_0 - T_0 S_0) = G - G_0$$

$G$ 为吉布斯自由能（自由焓）[强度量]

- Exergetic Efficiency

Turbines

$$e_{f1} - e_{f2} = \frac{\dot{W}}{\dot{m}} + \frac{\dot{E}_d}{\dot{m}}$$

$$\varepsilon = \frac{\dot{W}/\dot{m}}{e_{f1} - e_{f2}}$$

Compressors and Pumps

$$-\frac{\dot{W}}{\dot{m}} = e_{f2} - e_{f1} + \frac{\dot{E}_d}{\dot{m}}$$

$$\varepsilon = \frac{e_{f2} - e_{f1}}{-\dot{W}/\dot{m}}$$

Heat Exchanger Without Mixing

$$\dot{m}_h(e_{f1} - e_{f2}) = \dot{m}_c(e_{f4} - e_{f3}) + \dot{E}_d$$

$$\varepsilon = \frac{\dot{m}_c(e_{f4} - e_{f3})}{\dot{m}_h(e_{f1} - e_{f2})}$$

Heat Exchanger With Mixing

$$\dot{m}_h(e_{f1} - e_{f3}) = \dot{m}_c(e_{f3} - e_{f2}) + \dot{E}_d$$

$$\varepsilon = \frac{\dot{m}_c(e_{f3} - e_{f2})}{\dot{m}_h(e_{f1} - e_{f3})}$$

- Cost Rate

## 4 Evaluating Properties

### 4.1 Ideal gas