

Ch.2 Conservation of Mass / Energy



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1. Conservation and The Balance Equation

2. Mass Balance

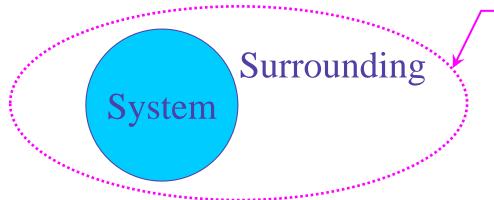
3. Energy Balance

4. Thermodynamic Properties of Matter



Conserved Quantity and Balance

- For isolated systems in the absence of nuclear reactions,
 - mass is conserved.
 - energy is conserved.
- Consequently, the Balance Concept is applicable for nonisolated systems.

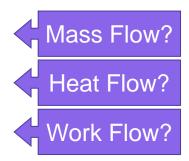


This composite system is an isolated system



Conserved Quantity and Balance

- Systems
 - Matters of interest, separated from surrounding.
 - Boundary, real or imaginary, separates a system from its surrounding.
 - Can have interactions with surroundings.
- Types of systems
 - Closed systems / Open systems.
 - Adiabatic systems / Diathermal systems.
 - Rigid systems / Deformable systems
 - Isolated systems.





- Within a specified time span, changes in the conserved quantity of the system of interest must be due to
 - Exchange of the quantity with the surrounding.

- Chemical reactions (?).

• For the system of interest, balance of quantity θ from time t to t + Δ t,

– Accumulation = Input – Output + Generation.

Integral form of the general balance equation (amount of θ in the system at time $t + \Delta t$) - (amount of θ in the system at time t) = (amount of θ that entered the system from time t to $t + \Delta t$) - (amount of θ that left the system from time t to $t + \Delta t$) + (amount of θ generated within the system at time $t + \Delta t$)

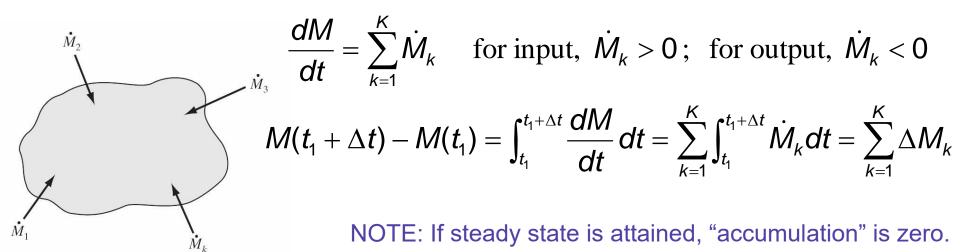


- From the integral form balance equation to the differential form balance equation,
 - "Accumulation = Input Output + Generation".
 - Divide the equation by ∆t, and let ∆t → 0, we get
 "Accumulation rate = Input rate Output rate + Generation rate".

 $\frac{d\theta}{dt} = \lim_{\Delta t \to 0} \frac{\theta(t + \Delta t) - \theta(t)}{\Delta t} = \begin{pmatrix} \text{rate of change of} \\ \theta \text{ in the system} \end{pmatrix} = \begin{pmatrix} \text{rate at which } \theta \\ \text{enters the system} \end{pmatrix} - \begin{pmatrix} \text{rate at which } \theta \\ \text{leaves the system} \end{pmatrix} + \begin{pmatrix} \text{rate at which } \theta \text{ is generated} \\ \text{within the system} \end{pmatrix} = \begin{pmatrix} \text{rate of} \\ \text{input} \end{pmatrix} = \begin{pmatrix} \text{rate of} \\ \text{output} \end{pmatrix} + \begin{pmatrix} \text{rate of} \\ \text{generation} \end{pmatrix} = \begin{pmatrix} \text{rate of} \\ \text{generation} \end{pmatrix}$



- Total mass is conserved for isolated systems. Therefore, the balance equation is applicable for "total mass".
 - "total mass" cannot be "generated" unless via nuclear reaction.
 - For systems not involving nuclear reaction, the "generation of total mass" is zero.





• Ex.2.2-1

A tank of volume 25 m³ contains 1.5×10^4 kg of water. Over a two-day period the inlet to the tank delivers 2.0×10^3 kg, 1.3×10^3 kg leaves the tank through the outlet port, and 50 kg of water leaves the tank by evaporation. How much water is in the tank at the end of the two-day period?



• Ex.

Analyze the change of your body weight from wake up to lunch time.

Analyze your bank account balance from Sept.1 till Sept. 20.

c.f., continuous process / noncontinuous process batch / semibatch process



• Ex.2.2-4

An open cylinder with a base area of 1 m² and a height of 10 m contains 5 m³ of water. As a result of corrosion, the tank leaks at its bottom at a rate following leak rate (m³/s) = $0.5\sqrt{\Delta P}$

where ΔP is the pressure difference in bar between the fluid at the base of the tank and the atmosphere. Determine the amount of water in the tank at any time.

c.f., differential (rate) form of balance eqn semibatch process



	Mass Basis	Molar Basis	
Rate-of-change for	m of the mass balance		-
General equation	$\frac{dM}{dt} = \sum_{k=1}^{K} \dot{M}_k$	$\frac{dN}{dt} = \sum_{k=1}^{K} \dot{N}_k$	
Special case:	114	JN	Only fo
Closed system	$\frac{dM}{dt} = 0$	$\frac{dN}{dt} = 0$	system
	M = constant	N = constant	withou
Difference form of	the mass balance*		reactio
00 0 0		K	
General equation	$M_2 - M_1 = \sum_{k=1}^K \Delta M_k$	$N_2 - N_1 = \sum \Delta N_k$	
	$\overline{k=1}$	$\overline{k=1}$	
Special cases:			
Closed system	$M_2 = M_1$	$N_2 = N_1$	
	Κ	K	
Steady flow	$M_2 - M_1 = \sum^K \dot{M}_k \Delta t$	$N_2 - N_1 = \sum \dot{N}_k \Delta t$	ţ
e?	$\overline{k=1}$	$\overline{k=1}$	

*Here we have used the abbreviated notation $M_i = M(t_i)$ and $N_i = N(t_i)$.



Mole Balance Equation

 $\frac{dN_{j}}{dt} = F_{j0} - F_{j} + \int F_{j} dV$

Indepodent variable : t Dependent variables: N. F. Y. V + Initial condition



Mole Balance Equation

• Ex. 2.3-2

- At high temperature, acetaldehyde dissociates into methane and CO, by $CH_3CHO \rightarrow CH_4 + CO$. At 520 °C the rate is found as $\frac{dN_{CH_3CHO}}{dt} = -0.48C_{CH_3CHO}^2 \frac{m^3}{kmol \cdot s}$ where C is in kmol/m³. The reaction occurs in a constant-volume 1-liter vessel and the initial concentration of acetaldehyde is 10 kmol/m³.
- a. If 5 moles of the acetaldehyde reacts, how much methane and CO is produced?
- b. Develop expressions for the amounts of acetaldehyde, methane, and CO present at any time, and determine how long it would take for 5 mol of acetaldehyde to have reacted.

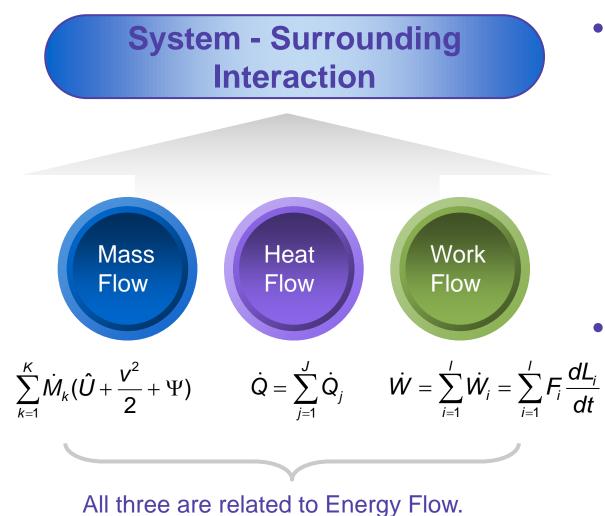
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Energy Balance Equation

- Total energy is conserved for isolated systems although the forms of energy may change. Therefore, the balance equation is applicable for "total energy".
 - "total energy" cannot be "generated" unless via nuclear reaction.
 - What forms of energy need to be considered?

$$\frac{d\theta}{dt} = \frac{d}{dt} \left(U + M(v^2/2 + \Psi) \right) = \begin{pmatrix} \text{rate of change of} \\ \text{energy in the system} \end{pmatrix} = \\ \begin{pmatrix} \text{rate at which energy} \\ \text{enters the system} \end{pmatrix} - \begin{pmatrix} \text{rate at which energy} \\ \text{leaves the system} \end{pmatrix} + \begin{pmatrix} \text{rate at which energy is generated} \\ \text{within the system} \end{pmatrix}$$



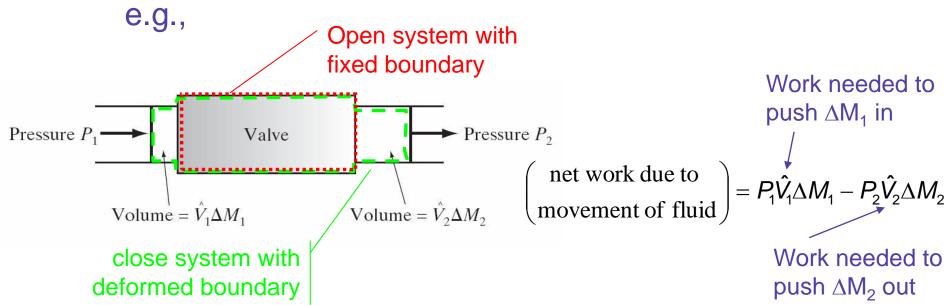


- Heat and work
 - Have the same unit as "energy"
 - Are considered as one form of energy during energy transition.
- Matters
 - Contain energy which is classified into kinetic energy, potential energy , and internal energy

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Energy Balance Equation

- Work flows (exchanges):
 - Shaft work, W_S, the mechanical energy flow that occurs without the deformation of the system boundaries, e.g., turbine. Electrical energy can also be included.
 - Work resulted from the movement of the system boundaries, which can be expressed in terms of PdV,



- In general, work flows = $\dot{W}_s P \frac{dV}{dt} + \sum_{k=1}^{\kappa} \dot{M}_k (P\hat{V})_k$
- Consequently, the energy balance equation is

$$\frac{d}{dt}\left\{U+M\left(\frac{v^2}{2}+\Psi\right)\right\}=\sum_{k=1}^{K}\dot{M}_k(\hat{U}+\frac{v^2}{2}+\Psi)_k+\dot{Q}+\dot{W}_s-P\frac{dV}{dt}+\sum_{k=1}^{K}\dot{M}_k(P\hat{V})_k$$

- Define H = U + PV, and we have

$$\frac{d}{dt}\left\{U+M\left(\frac{v^2}{2}+\Psi\right)\right\}=\sum_{k=1}^{K}\dot{M}_k(\hat{H}+\frac{v^2}{2}+\Psi)_k+\dot{Q}+\dot{W}$$

– In molar basis

$$\frac{d}{dt}\left\{U + Nm\left(\frac{v^2}{2} + \Psi\right)\right\} = \sum_{k=1}^{K} \dot{N}_k \left\{\underline{H} + m\left(\frac{v^2}{2} + \Psi\right)\right\}_k + \dot{Q} + \dot{W}$$

Usually small and negligible, esp. for gases

First Law of

Thermodynamics



Table 3.1-1 Differential Form of the Energy Balance

General equation

$$\frac{d}{dt}\left\{U+M\left(\frac{v^2}{2}+\psi\right)\right\} = \sum_{k=1}^{K} \dot{M}_k \left(\hat{H}+\frac{v^2}{2}+\psi\right)_k + \dot{Q} + \dot{W}$$
(a)

Special cases:

(i) Closed system

$$\dot{M}_k = 0, \qquad \frac{dM}{dt} = 0$$

so

$$\frac{dU}{dt} + M\frac{d}{dt}\left(\frac{v^2}{2} + \psi\right) = \dot{Q} + \dot{W}$$
(b)

(ii) Adiabatic process

in Eqs. a, b, and d
$$\dot{Q} = 0$$
 (c)

(iii) Open and steady-state system

$$\frac{dM}{dt} = 0, \qquad \frac{dV}{dt} = 0, \qquad \frac{d}{dt} \left\{ U + M\left(\frac{v^2}{2} + \psi\right) \right\} = 0$$

SO

$$0 = \sum_{k=1}^{K} \dot{M}_k \left(\hat{H} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} + \dot{W}_s$$
(d)

(iv) Uniform system

In Eqs. a and b

$$U = M\hat{U}$$
 (e)

Note: To obtain the energy balance on a molar basis, make the following substitutions:



Table 3.1-2 Difference Form of the Energy Balance

General equation

$$\left\{U + M\left(\frac{v^2}{2} + \psi\right)\right\}_{t_2} - \left\{U + M\left(\frac{v^2}{2} + \psi\right)\right\}_{t_1} = \sum_{k=1}^K \int_{t_1}^{t_2} \dot{M}_k \left(\hat{H} + \frac{v^2}{2} + \psi\right)_k dt + Q + W \quad (a)$$

Special cases:

(i) Closed system

$$\left\{U+M\left(\frac{v^2}{2}+\psi\right)\right\}_{t_2} - \left\{U+M\left(\frac{v^2}{2}+\psi\right)\right\}_{t_1} = Q+W$$
(b)

and

$$M(t_1) = M(t_2)$$

(ii) Adiabatic process

In Eqs. a and b

$$Q = 0$$
 (c)

(iii) Open system, flow of fluids of constant thermodynamic properties

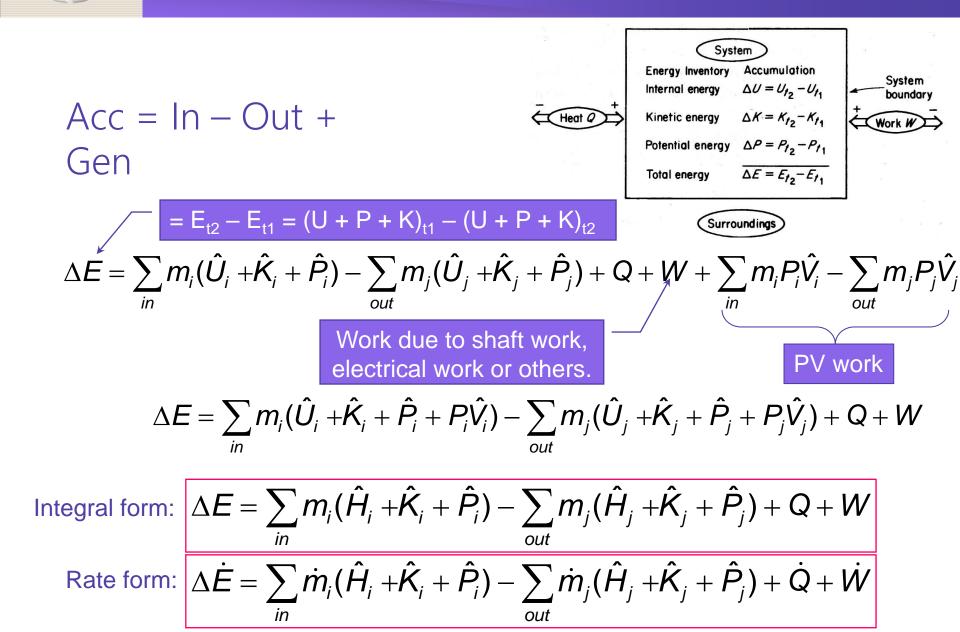
$$\sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \left(\hat{H} + \frac{v^2}{2} + \psi \right)_k dt = \sum_{k=1}^{K} \Delta M_k \left(\hat{H} + \frac{v^2}{2} + \psi \right)_k$$
(d)
in Eq. a

(iv) Uniform system

$$\left\{U + M\left(\frac{v^2}{2} + \psi\right)\right\} = M\left(\hat{U} + \frac{v^2}{2} + \psi\right)$$
 (e)
in Eqs. a and b

Note: To obtain the energy balance on a molar basis, make the following substitutions:

Governing Equation for Energy Balance



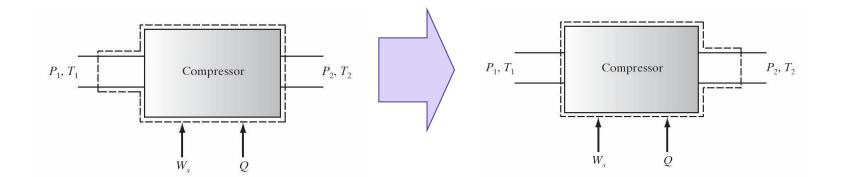
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Energy Balance Equation

• Ex. 3.2-1

A compressor is operating in a continuous, steady-state manner to produce a gas at temperature T₂ and pressure P₂ from one at T₁ and P₁. Show that for the time interval Δt , $Q + W_s = (\hat{H}_2 - \hat{H}_1)\Delta M$

Establish this result by (a) writing the balance equation for a closed system, and then (b) writing the balance equation for an open system.

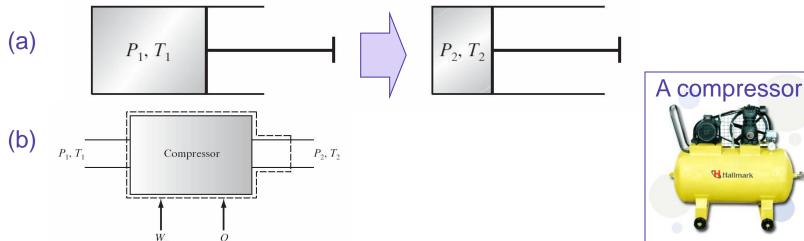


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Energy Balance Equation

• Ex. 3.2-2

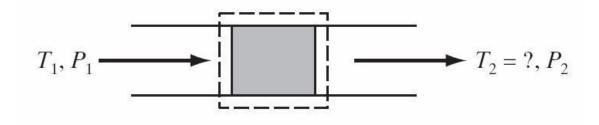
A mass M of gas is to be compressed from a temperature T_1 and pressure P_1 to T_2 and P_2 in (a) a one-step process in a frictionless piston and cylinder, and (b) a continuous process in which the mass M of gas is part of the feed stream to the compressor of the previous example. Compute the sum Q + W for each process.





• Ex. 3.2-3 (Joule-Thomson or Isenthalpic expansion)

A gas at pressure P_1 and temperature T_1 is steadily exhausted to the atmosphere at pressure P_2 through a pressure-reducing valve. Find the expression relating the downstream gas temperature T_2 to P_1 , P_2 and T_1 . Since the gas flows through the valve rapidly, one can assume that there is no heat transfer to the gas. Also, the potential and kinetic energy terms can be neglected.





Properties of Matters

- Energy associated with matters
 - Per unit mass, $\hat{E} = \hat{U} + \frac{v^2}{2} + \Psi$
 - The value depends on the state of matters (in the system)
- The state of a system
 - Can be specified by 2 independent intensive variables for single-component, single-phase system.
 - T and P are the preferred intensive variables.
 - Equation of state (EOS) of matter is important.
 - The correlation between energy (e.g., \hat{U} and \hat{H}) and the two independent variables (e.g., T, P) is important.

$$\hat{U} = \hat{U}(T, \hat{V})$$
 $\hat{U} = \hat{U}(T, P)$ or $\hat{U} = \hat{U}(P, \hat{V})$

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Properties of Matters

• EOS:

- For ideal gases, PV = RT
- For van der Waal gases, $(P + \frac{a}{V^2})(\underline{V} b) = RT$
- For others, (will be discussed in Ch.6)
- Energy
 - Usually, $\underline{U} = \underline{U}(T, \underline{V})$ and $\underline{H} = \underline{H}(T, P)$
 - Define heat capacity (from experimental observation) as $C_{v}(T,V) = \left(\frac{\partial \underline{U}}{\partial T}\right)_{v} \qquad C_{P}(T,P) = \left(\frac{\partial \underline{H}}{\partial T}\right)_{P}$

NOTE: The heat capacity concept can be verified using the energy balance



Properties of Matters

- For ideal gases (and only for ideal gases),
 EOS, PV = RT
 - $-\underline{U}=\underline{U}(T)$ and $\underline{H}=\underline{H}(T)$
 - $C_P^*(T) = \frac{d\underline{H}}{dT}$ and $C_V^*(T) = \frac{d\underline{U}}{dT}$ $C_P^* = \frac{d\underline{H}}{dT} = \frac{d(\underline{U} + P\underline{V})}{dT} = \frac{d(\underline{U} + RT)}{dT} = C_V^* + R$ $C_P^*(T) = a + bT + cT^2 + dT^3 +$ $\underline{H}^{IG}(T_2) = \underline{H}^{IG}(T_1) + \int_{T_1}^{T_2} C_P^* dT$ $\underline{U}^{IG}(T_2) = \underline{U}^{IG}(T_1) + \int_{T_1}^{T_2} C_V^* dT$

NOTE: For matters other than IG, follow the definitions and try to find EOS.



- For solids and liquids (incompressible matters), molecules are close to each other.
 - Molar volume is usually small.
 - $\underline{U} \approx \underline{H}$ because $P\underline{V} \ll \underline{U}$ (unless at very high P)

$$-\left(\frac{d\underline{V}}{dP}\right)_{T}\approx 0$$

- U, C_p, and C_v are functions of T only. For solids, the following empirical correlation (DuLong-Petit law) is found : $C_p = 3NR = 24.942N \frac{J}{mol \cdot K}$ @25 °C ?

- EOS is very different from the ideal gas law.



Properties of Matters

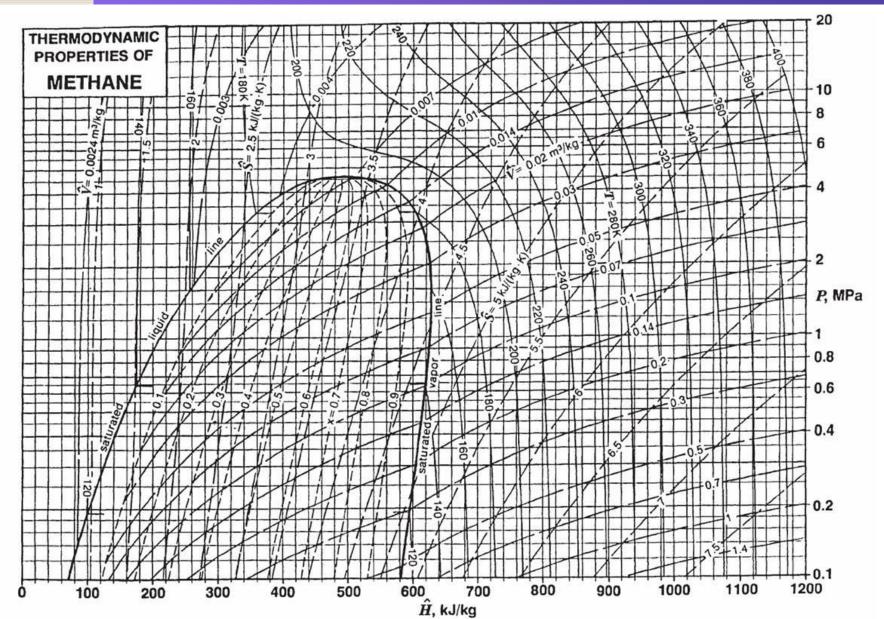
- For gases not following the ideal gas law (non-ideal gases),
 - EOS different from the ideal gas law can be found, e.g.,
 - Using the compressibility factor (called the corresponding state), i.e., PV = ZnRT.
 - van der Waal EOS (one kind of cubic EOS).
 - Cubic EOS.
 - Varial EOS.
 - Thermodynamic properties are usually expressed as functions of (T,P), or (T,V), or (P,V)



- For convenience, thermodynamic properties (and their dependency on T,P) are frequently expressed as
 - Diagrams, e.g., P-H diagrams (Fig. 3.3-2, 3.3-3, 3.3-4), T-S diagrams (Fig. 3.3-1).
 - Database, e.g., in Tables (steam table is a most frequently used one), in computerized data.



Properties of Matters



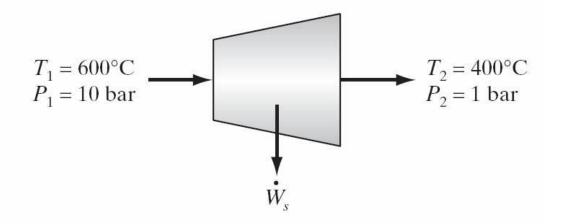


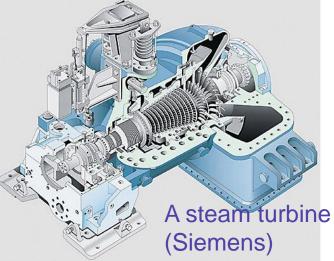
• Ex. 3.4-1 (Joule-Thompson calculation)

Steam at 400 bar and 500 °C undergoes a Joule-Thompson expansion to 1 bar. Determine the temperature of the steam after the expansion using (a) Fig. 3.3-1 and (b) steam tables (Appendix A.III).

• Ex. 3.4-2

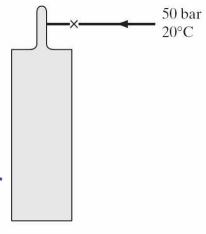
An adiabatic steady-state turbine is being designed to serve as an energy source for a small electrical generator. The inlet to the turbine is steam at 600 °C and 10 bar, with a mass flow rate of 2.5 kg/s through an inlet pipe that is 10 cm in diameter. The conditions at the turbine exit are 400 °C and 1 bar. The outlet pipe is 25 cm in diameter. Estimate the rate at which work can be obtained from this turbine.

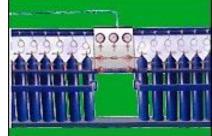




• Ex. 3.4-3

A compressed-air tank is to be pressurized to 40 bar by connecting to a high-pressure line containing air at 50 bar and 20 °C. The repressurization occurs so quickly that the process can be considered as adiabatic. Assume air as an ideal gas with $C_v = 21$ J/(mol K). (a) If the tank initially contains air at 1 bar and 20 °C, what will be the temperature of the air in the tank at the end of the filling process? (b) After long-enough time, the gas in the tank can return to room temperature because of heat exchange between the tank and the atmosphere. What is the new pressure of air in the tank?





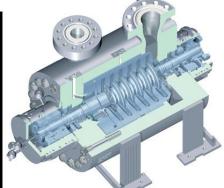
Cylinder filling station



• Ex. 3.4-4

A compressor is a gas pumping device that takes in gas at low pressure and discharges it at a higher pressure. Since the process occurs quickly compared to heat transfer, it is usually assumed to be adiabatic. Assuming that the inlet to the compressor is air (as an ideal gas with $C_P = 29.3$ J/mol K) at 1 bar and 290 K and that the discharge is at 10 bar, estimate the temperature of the exit gas and the rate at which work is done on the gas for a gas flow of 2.5 mol/s.







• Ex. 3.4-5

A gas cylinder of 1 m³ volume containing N₂ initially at a pressure of 40 bar and 200 K is connected to another cylinder of 1 m³ that is evacuated. A valve between the two cylinders is opened until the pressure in the cylinders equalize. Find the final temperature and pressure in each cylinder if no heat flows into or out of the cylinders or between the gas and the cylinder. You may assume that the gas is ideal with a constant-pressure heat capacity of 29.3 J/mol K.

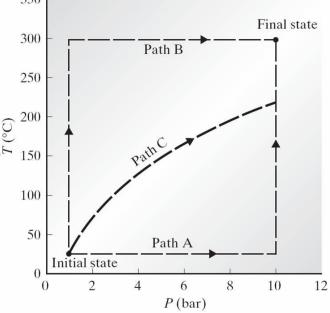
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Energy Balance Equation

• Ex. 3.4-6

It is possible to go from a given initial equilibrium state of a system to a given final equilibrium state by different paths. One gram mole of a gas at a temperature of 25 °C and 1 bar is to be heated and compressed in a frictionless piston and cylinder to 300 °C and 10 bar. Compute the heat and work along each of the following paths.

(a) Isothermal compression to 10 bar and then isobaric heating to 300 °C. (b) Isobaric heating to 300 °C following by isothermal compression to 10 bar. (c) A compression in which $PV^{\gamma} = \text{constant}, \overset{\circ}{\leftarrow}$ where $\gamma = C_P/C_V$, followed by an isobaric cooling or heating, if necessary, to 300 °C. **NOTE**: The internal energy is a state property and is independent of the path. The heat and work are, however, path-dependent quantities.



• Ex. 3.4-7

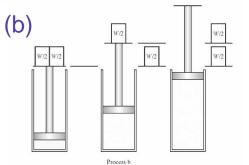
An initial pressure of 2.043 bar is maintained on a I mol of air contained in a piston and cylinder system by a set of weight \mathscr{W} . Work is obtained by removing some of the weights and allowing the air to isothermally expand at 25 °C. The process is repeated until all the weight s have been removed. The piston has a mass of 5 kg and an area of 0.01 m2. The air can be considered as an ideal gas. and 1 bar. Compute the work obtained from the isothermal expansion for each of the following:

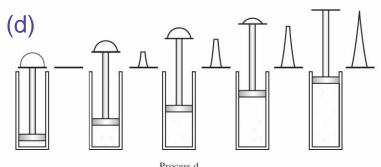
(a) The weight \mathscr{W} is taken off in one step.

(b) The weight is taken off in two steps, $\mathcal{W}/2$ removed each time.

(c) The weight is taken off in four steps, $\mathcal{W}/4$ removed each time.

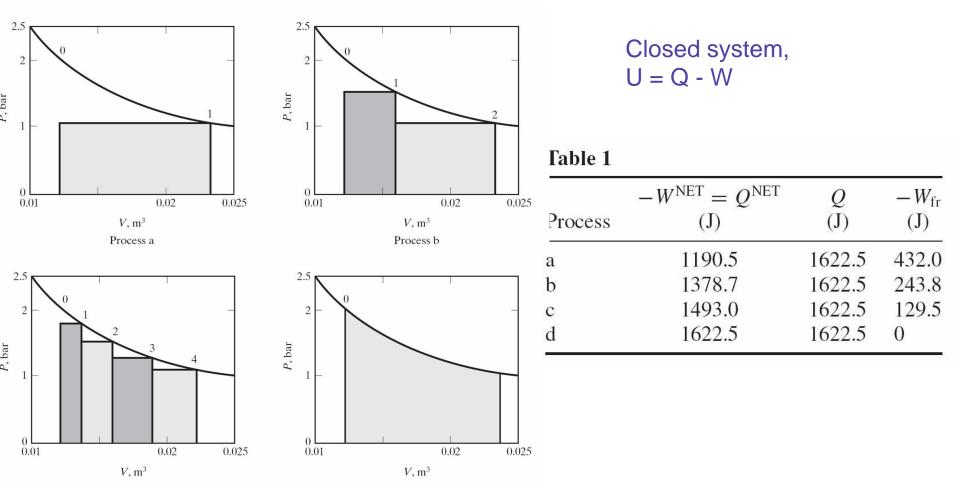
(d) The weight is replaced by a pile of sand and the grains of sand are removed one at a time.







EX. 3.4-7: All 4 processes have the same initial state, the same final state, but different paths. U is a state property while Q and W are path-dependent.



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Energy Balance Equation

• Ex. 3.4-8

Consider the cylinder filled with air and with the piston and spring arrangement shown below. The external atmospheric pressure is 1 bar, the initial temperature of the air is 25 °C, the no-load length of the spring is 50 cm, the spring constant is 40000 N/m, the frictionless piston weighs 500 kg, and the constant-colume heat capacity of air can be taken as 20.3 J/mol^oC. Compute (a) the initial pressure of the gas in the cylinder, and (b) How much heat must be added to the gas in the cylinder for the spring to compress by 2 cm.

