06-221 Thermodynamics 9 units

Fall 2012 Tues-Thurs 12:00 – 1:20; Hamerschlag Hall B131
(100% Lecture, 0% Recitation, 0% Laboratory)

Instructor: Raj Chakrabarti **Department**: Chemical Engineering
Telephone: 8-5615
Office Hours: W 1:30 – 3:30
Office: DH 3122
E-mail: rajc@andrew.cmu.edu

Web-site: http://www.cmu.edu/blackboard
Required Text(s): S.I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics* 4th Edition, John Wiley & Sons ISBN-13: 978-0-471-66174-0
Specific Course Information: This course introduces students to the process thermodynamics of single component systems. Topics include equilibrium and thermodynamic state variables; heat and work; conservation of energy and the first law of thermodynamics; entropy balances and the second law of thermodynamics; reversibility; free energies; interconversion of heat and work via engines, refrigeration and power cycles; absolute temperature and the third law of thermodynamics; equations of state; principle of corresponding states; thermodynamic property relationships; changes of state; phase equilibrium and stability in single component systems; vapor pressure and phase transition.
Prerequisites: 06-100, 33-106 **Required:** Yes

Topics: (Chapters 1 – 7 of Sandler)

- Equilibrium and thermodynamic state variables
- Application of the first law of thermodynamics to processes where energy is converted among heat and work
- Application of the second law of thermodynamics to processes involving entropy balance and reversibility, heat engines, refrigeration cycles and power generation
- Thermodynamic properties of real substances, partial derivatives, equations of state
- Changes of thermodynamic state and principle of corresponding states
- Phase equilibrium and stability in one-component systems: molar Gibbs free energy and fugacity, vapor pressure calculations, Gibbs phase rule, phase transitions

Teaching Assistants

Chris Knapp
cknapp@andrew.cmu.edu
Office hours: F 9:30 - 11:30
DH 2208

Matt Payne
mpayne@andrew.cmu.edu
Office hours: T,W 9:00 -
10:00 DH1202

Grading: 2 midterm exams @25% each; 1 quiz @ 10%; cumulative final exam @30%; homework @10% (~ weekly)	**Prerequisites:** satisfactory completion of 06-100; mastery of unit conversions, material balances, differentiation and integration
Follow-up Courses: 06-261 Fluid Mechanics; 06-321Chemical Engineering Thermodynamics, 06-323 Heat and Mass Transfer; 06-361 Unit Operations of Chemical Engineering	

Course Overview:

Thermodynamics is one of the key engineering sciences. It teaches us how energy can be converted from one form to another or transferred from one object to another, for example when the internal energy stored in chemical bonds in a fuel may be converted to heat and transferred to another material during combustion. It also tells us how the expansion of the material that receives this heat may be used to capture mechanically useful work.

Chemical engineers excel at designing processes. A process is any procedure or set of procedures that changes a material in some way. Thermodynamics teaches us how the properties of materials change when we change their conditions and how these changes dictate the amount of work that must be done or the amount of heat that must be transferred to accomplish that change. Thermodynamics is the basis for evaluating the energy requirements of any chemical engineering process. Some of these topics will be covered in 06-221, others in 06-321.

In essence, thermodynamics can be viewed as the “science of what is physically possible.” How much work can be accomplished by a particular process? What is the maximum possible yield of some chemical reaction? Thermodynamics teaches us about equilibrium. This is the state toward which a system spontaneously evolves. Once reached, this is the resting state of the system – until an external force is applied. Thermodynamics does *not* inform us of the rate at which these processes occur. For example, thermodynamics indicates *how much* heat should be transferred to achieve equilibrium between two materials that initially have different temperatures, but to find out how quickly the temperatures change, we have to use the science of *transport phenomena*. You will learn this separate branch of engineering science later in the courses *Fluid Mechanics* and *Heat and Mass Transfer*. Both thermodynamics and transport phenomena are used to design processes.

By teaching us what is or is not possible, thermodynamics lies at the core of engineering design. No process can violate any of the laws of thermodynamics; a process design that claims to do so is invalid. There is no point in trying to design a process that aims to accomplish more than what is thermodynamically possible. It will not succeed. Thermodynamics will dictate whether a particular process is

Thermodynamics

CHE 06-221

Department of Chemical Engineering, Carnegie Mellon University

December 5, 2012

Outline

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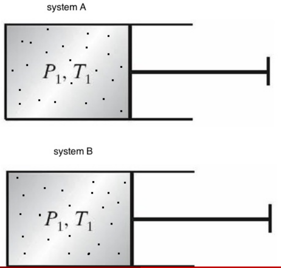
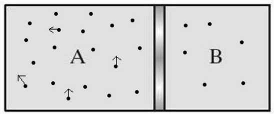
- Mechanical interaction between our system and its surroundings can then also be considered.

Examples of thermodynamic variables

- Example of macroscopic variable: **pressure**. For a sufficiently large number of molecules, if we compare several identically prepared systems, the measured pressure will be almost identical for all systems.





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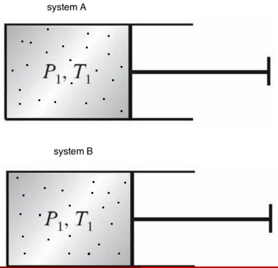

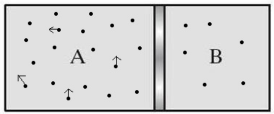

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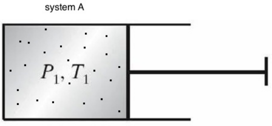
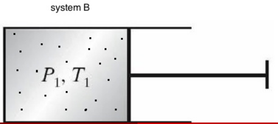
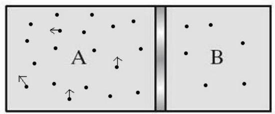
- An important macroscopic variable that is introduced in thermodynamics: **temperature**. Temperature has no analog for systems consisting of a small number of molecules.







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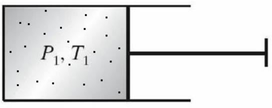
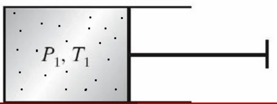
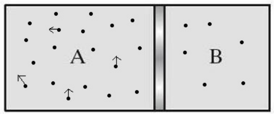


system B





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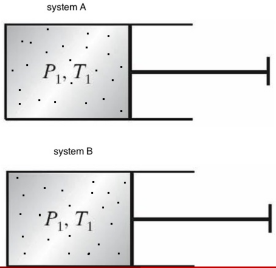
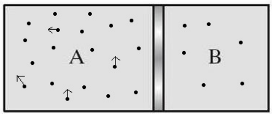
- An important macroscopic variable that is introduced in thermodynamics: **temperature**. Temperature has no analog for systems consisting of a small number of molecules.
- *Laws of thermodynamics* apply to all such macroscopic systems (under certain general assumptions)
- Other equations used in thermodynamics - for example those relating the values of temperature and pressure, are system-specific. Thermodynamics does not derive the latter equations, which depend on the molecular details, but rather establishes them based on experiment.

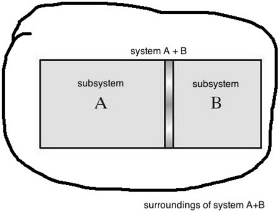


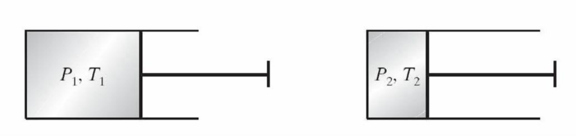


Outline

Definitions

- *System*: a region under study (e.g., in specified volume); *surroundings*: rest of universe (or specified part that does not interact with the remainder). Systems can be composed of smaller, but still macroscopic *subsystems*





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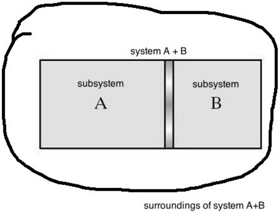

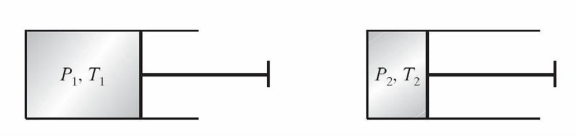

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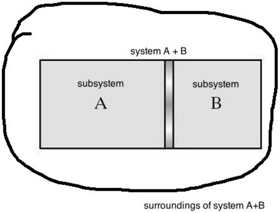

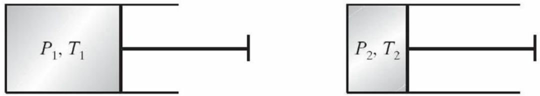

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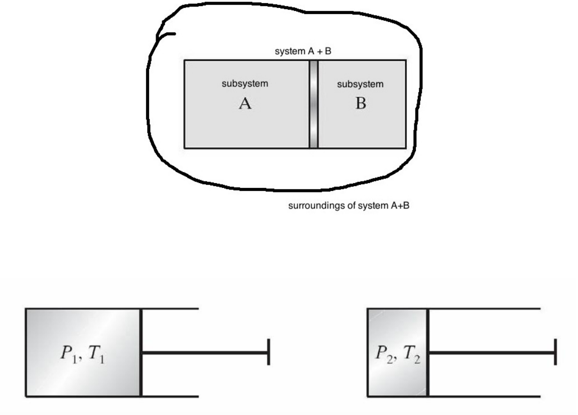
- *Phase* - "state of agglomeration" of system - whether system is a gas, liquid or solid



System classifications based on types of interaction with surroundings

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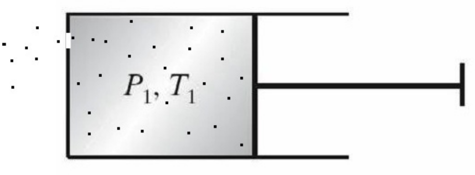

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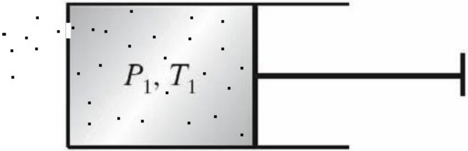

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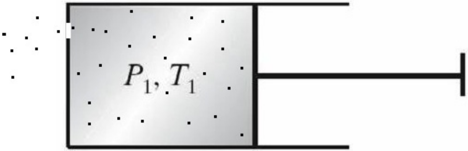

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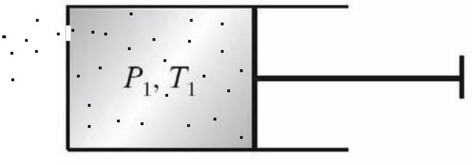

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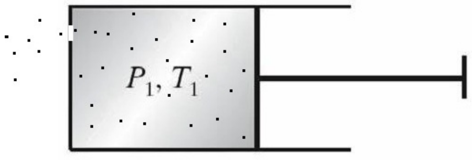
- What classifications apply to the system below?



Outline

1. What is Thermodynamics?
2. Some Thermodynamics Terminology
3. **Basic concepts of thermodynamics**
4. Thermodynamic equations of state
5. Conservation of Mass
6. Integral formulation of mass balance
7. Multicomponent mass balance
8. Conservation of energy
    - Energy balance
9. Towards the 2nd Law of Thermodynamics
10. Toward engineering applications: thermodynamic cycles and heat engines
11. Thermodynamic properties of real substances (not ideal gases)
    - Computation of heat and work for thermodynamic processes involving nonideal substances
    - Computation of entropy changes for thermodynamic processes involving nonideal substances
12. Outline of remaining topics and schedule
13. Further analysis of the behavior of real gases
14. Phase equilibrium
15. More on Gibbs free energy and applications to phase equilibrium

Thermodynamic Equilibrium

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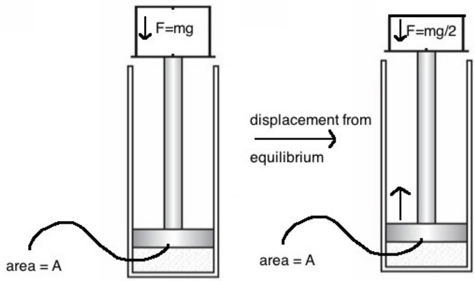

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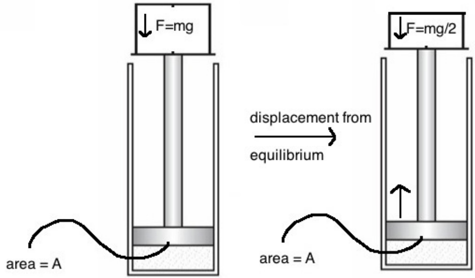

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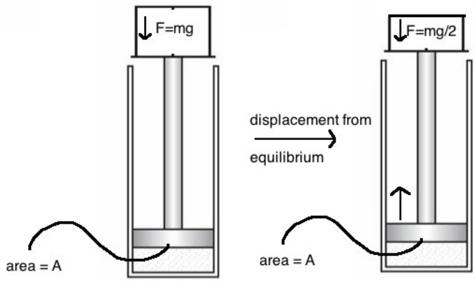
- Properties of equilibrium states:
  1. Does not vary w time
  2. System is uniform (no internal temperature, pressure, concentration gradients)
  3. Heat/mass/work flows zero (contrast w steady state where these can be nonzero)
  4. *Net* rate of chemical reactions is zero; chemical reactions may still proceed as long as rates balance



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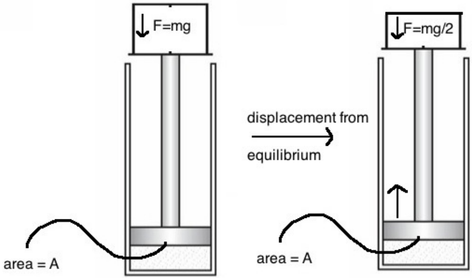
- Thermodynamic equilibrium requires both *mechanical equilibrium* (no changes to system due to mechanical contact) and *thermal equilibrium* (no changes to system due to thermal contact)



Pressure

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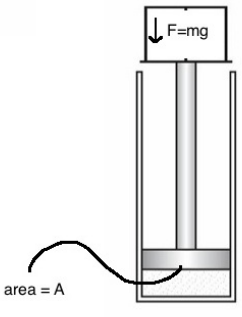

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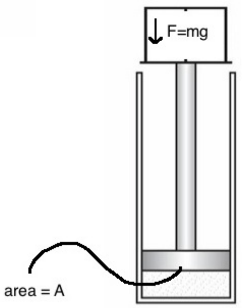

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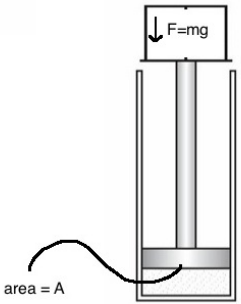
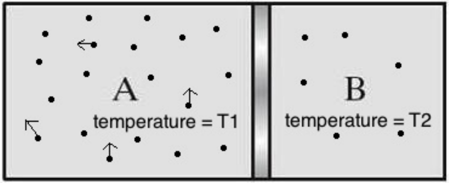
- Absolute pressure scale: $P \geq 0$ - no negative pressures allowed (this is implied by definition of pressure in terms of force exerted on container, which cannot be negative at equilibrium)



Temperature

- *Temperature*: a system property that has the same value for any two systems in thermal equilibrium (no flow of heat). Any temperature scale must satisfy this condition



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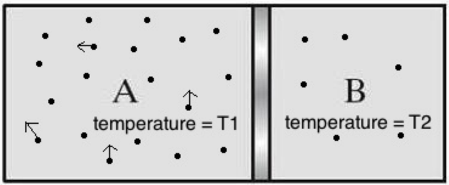

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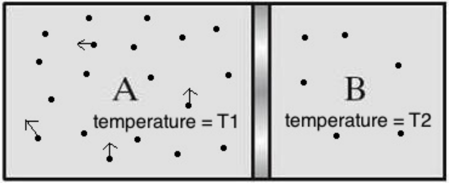

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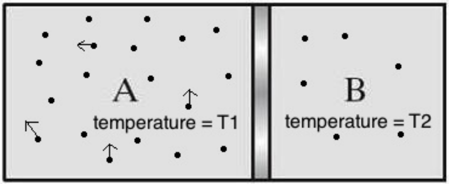
- One mole of an ideal gas with $PV = 8.314J$ is said to have temperature $T = 1\ K$; then R has units $J/mol\ K$. Having made this choice, T for a given amount of ideal gas follows from the value of PV



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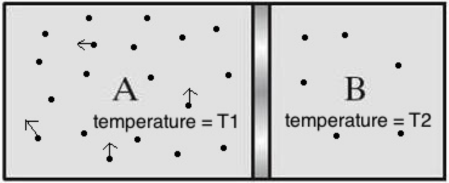
- Can define temperature scale in terms of mechanical units if we refer to experiments with a particular system; it was empirically found that low density gases obey "ideal gas law" $PV = NRT$; measure product of P, V for $N = 1\ mol$, and specify corresponding value of $T \geq 0$; then $R = \frac{PV}{NT}$ follows
- One mole of an ideal gas with $PV = 8.314J$ is said to have temperature $T = 1\ K$; then R has units $J/mol\ K$. Having made this choice, T for a given amount of ideal gas follows from the value of PV
- $T(K) = T(C) + 273.15$



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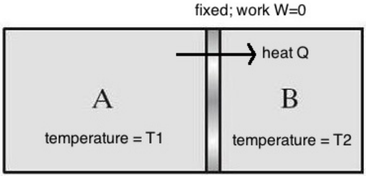
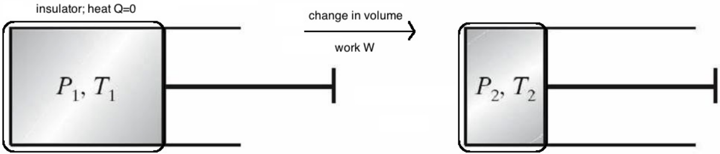
- We will provide expressions suitable for the calculation of heat and work in later lectures

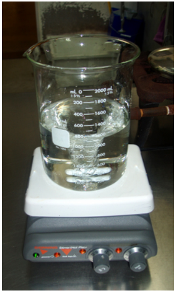
Heat, work examples





Thermal vs mechanical energy

- *Mechanical energy*: mechanical, electrical work (denoted by W)



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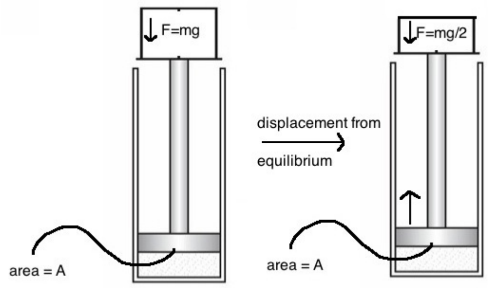

(m)

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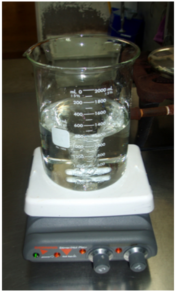

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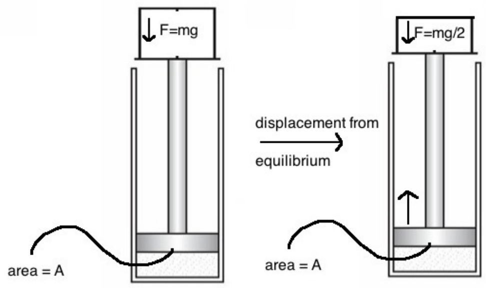

(p)

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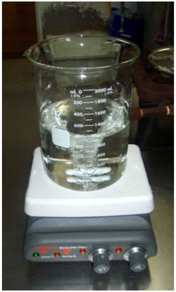
- Same internal energy change can occur through heat, mechanical or electrical work - different forms of energy change. $\Delta U = Q + W$



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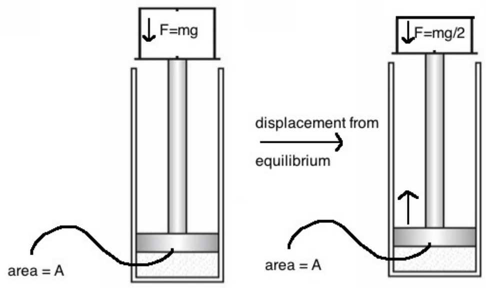

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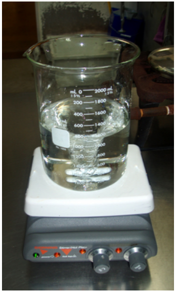
- *Conservation of energy (first law of thermodynamics)*: total energy cannot be created or destroyed, only changed in form.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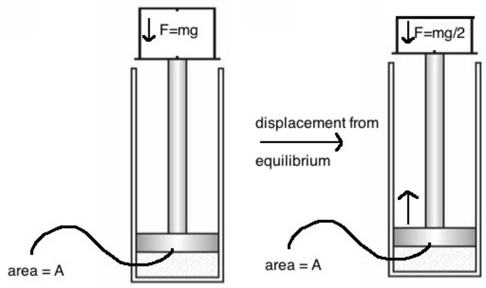
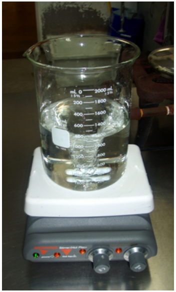


(v)

Thermal vs mechanical energy (cont'd)

- mechanical to thermal: stirring of water (mechanical energy input) increases temperature;
- thermal to thermal: heating water (initially at T_1 on table) on hot plate at temperature T_2 causes water temperature to increase (eventually to T_2 if hot plate kept at T_2); leaving hot water on table causes temperature of table to increase;
- thermal to mechanical: reducing the imposed pressure on a gas (or heating it) and then allowing it to expand - converting internal energy into mechanical work - will always result in loss of some mechanical energy in the form of heat (due to friction)



(w)

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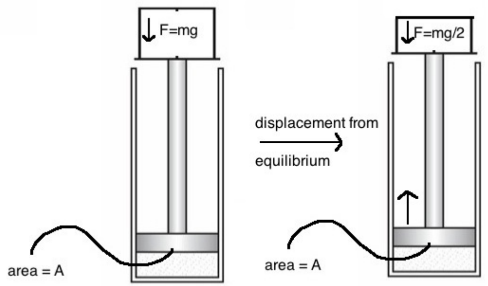

(y)

A word on units

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- *Mechanical variables*: force and pressure, volume, work
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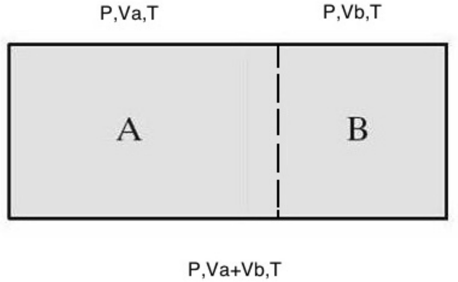
- SI units: force - newton, N ($kg\ m/s^2 = J/m$); pressure - pascal, Pa ($kg/m\ s^2 = N/m^2$); temperature - Kelvin, K; energy (also work, heat) - joule, J ($kg\ m^2/s^2 = N\ m$)

Outline

1. What is Thermodynamics?
2. Some Thermodynamics Terminology
3. Basic concepts of thermodynamics
4. **Thermodynamic equations of state**
5. Conservation of Mass
6. Integral formulation of mass balance
7. Multicomponent mass balance
8. Conservation of energy
    - Energy balance
9. Towards the 2nd Law of Thermodynamics
10. Toward engineering applications: thermodynamic cycles and heat engines
11. Thermodynamic properties of real substances (not ideal gases)
    - Computation of heat and work for thermodynamic processes involving nonideal substances
    - Computation of entropy changes for thermodynamic processes involving nonideal substances
12. Outline of remaining topics and schedule
13. Further analysis of the behavior of real gases
14. Phase equilibrium
15. More on Gibbs free energy and applications to phase equilibrium

Further classification of thermodynamic variables: extensive and intensive variables

- *Extensive variable*: scale with system size - examples are V, U. Illustration: The total volume of a system $A + B$ composed of two subsystems A, B of gas at equilibrium, with volumes V_a, V_b is $V_a + V_b$. The total internal energy of a system $A + B$ composed of two subsystems A, B of gas at equilibrium, with internal energies U_a, U_b, is $U_a + U_b$.



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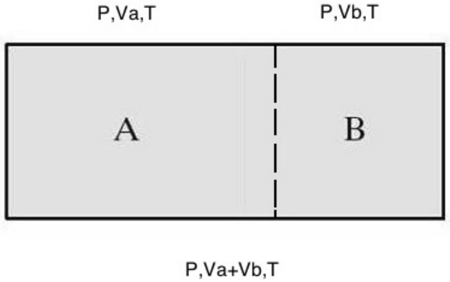

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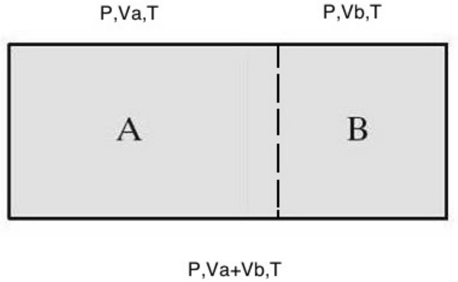
- Can convert extensive variables to intensive variables by dividing by total mass or moles N: $\hat{V} \equiv V/M$; $\bar{V} \equiv V/N$



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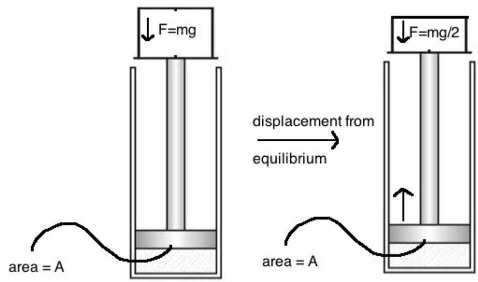
- Often it is more convenient to express equations of state in terms of extensive V (example: $PV = NRT$ vs $P\hat{V} = RT$)

What will not be covered

- How fast a system will respond to change in constraints and reattain equilibrium - relevant courses include chemical kinetics, heat/mass transfer, fluid mechanics



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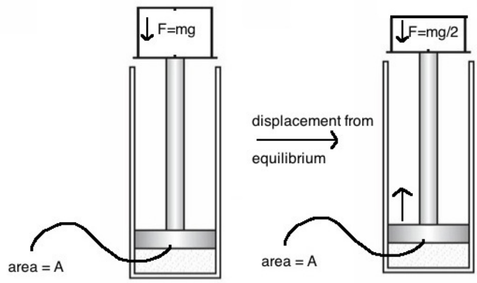

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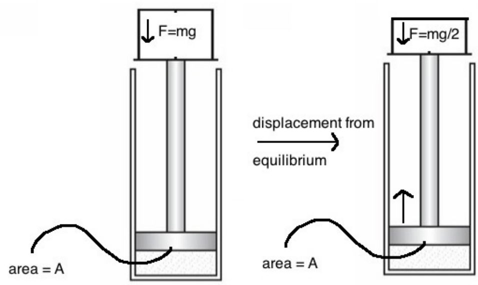

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- From the perspective of thermodynamics, mechanics refers to only macroscopic motion of systems.

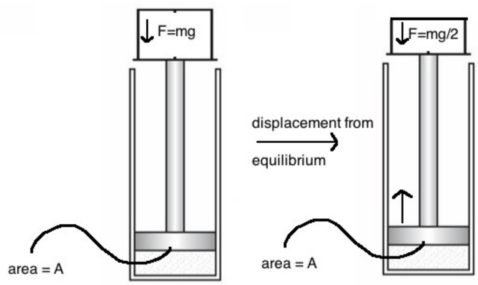

Figure :

Outline

Extensive property balances

- *Balance* equations in thermodynamics: choose a system, relate either a) instantaneous rate of change of property with rate of property entering, leaving, or being created within system; b) total change of a property of system with amounts of property that entered, left, and were created within the system

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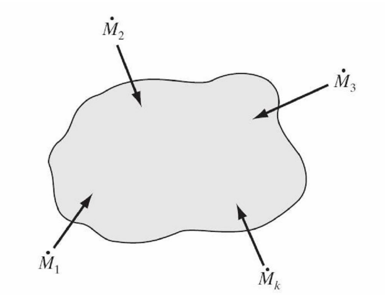
- Conserved quantities (e.g. mass of given species): 3rd term is 0

Mass flow across multiple system boundaries: rate of change



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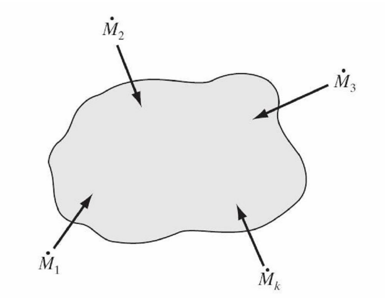

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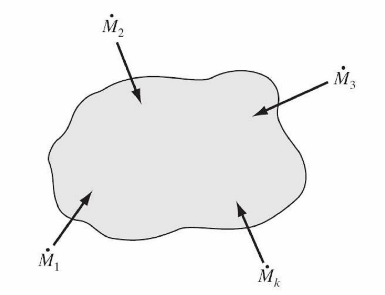

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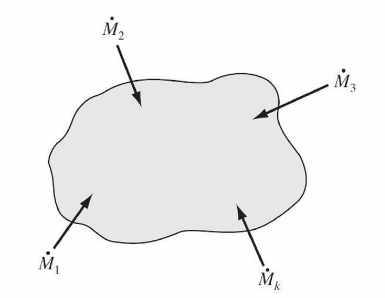

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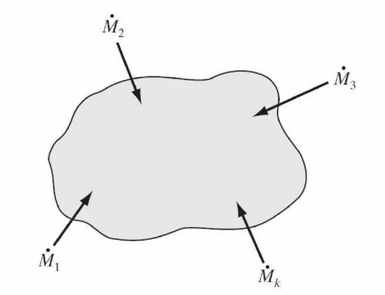

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- Sign (+/-) on each $\sum_k \dot{M}_k$, $\dot{N}_k$ is determined by direction of mass flow (flow entering system: +; flow leaving system: -)

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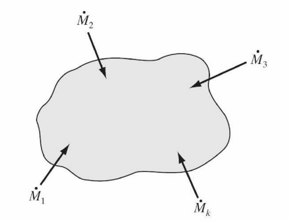
- Note: variable mass flow rate that depends on the current mass
- Use integral form of mass balance (molar basis) with a single port, solving the differential equation, to find final number of moles

$$\begin{aligned}
\frac{dN}{dt} &= -0.01N \\
\int_{t_1}^{t_2} \frac{1}{N}\frac{dN}{dt}\,dt &= \int_{t_1}^{t_2} -0.01\,dt \\
\int_{N(t_1)}^{N(t_2)} \frac{1}{N}\,dN &= -0.01(t_2 - t_1) \\
\ln(N(t_2)) - \ln(N(t_1)) &= -0.01(t_2 - t_1) \\
\ln(N(t_2)/N(t_1)) &= -0.01(t_2 - t_1) \\
N(t_2) &= N(t_1)\exp[-0.01(t_2 - t_1)] \\
&= (1000\ mol) \times \exp(-0.2)
\end{aligned}$$

Outline

Pure component vs multicomponent mass balance



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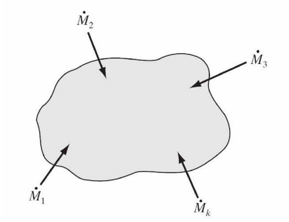

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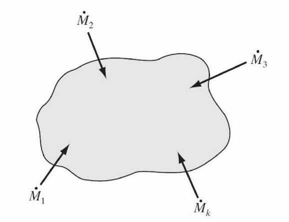

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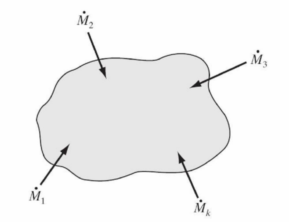

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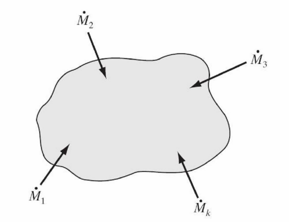

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- For example, consider both (inert) argon (species $i = 1$) and neon gas (species $i = 2$) entering through each port
- Each N_i balance can be considered separately (n independent equations for n components/species) if there are no reactions
- What if chemical reactions are possible (e.g. C_2H_4 and Cl_2 entering, where reaction $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ can occur)?

Differential formulation

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- $dN_i/dt = \sum_k (\dot{N}_i)_k + (dN_i/dt)_{rxn}$
- The second term denotes the rate of formation of species *i* due to chemical reactions (mass of species *i* no longer conserved; species can be created and destroyed)

Integral (difference) formulation

- $N_i(t_2) - N_i(t_1) = \int_{t_1}^{t_2} \sum_k (\dot{N}_i)_k + (dN_i/dt)_{rxn}\ dt$

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- First term on rhs is change in number of moles of species due to flow streams; second term on rhs is change in

Molar extent of reaction

- Note that $(dN_i/dt)_{rxn}$'s for different species are not all independent. For example, if two species are involved in the same reaction, their $(dN_i/dt)_{rxn}$'s are related by the respective stochiometric coefficients. Consider a single general chemical reaction

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- Here ν_j denotes the stochiometric coefficient of species j (here R). Assume $\nu_1 = 1$, and that after a specified time t, X moles of A are consumed. Then $((N_j)_{rxn} =)\nu_j X$ moles of R are produced in time t. X is called the molar extent of reaction.

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- We do not consider scenarios with more than one chemical reaction

Differential formulation using molar extent of reaction

- Using this notation, we have for the mass balance equations for species 1 and j

$$\begin{aligned} dN_1/dt &= \sum_k (\dot{N}_1)_k + (dN_1/dt)_{rxn} \\ &= \sum_k (\dot{N}_1)_k - (dX/dt)_{rxn} \\ dN_j/dt &= \sum_k (\dot{N}_j)_k + \nu_j (dX/dt)_{rxn} \end{aligned}$$

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- The latter equation is the general expression we will use for all species

Multicomponent mass balance involving chemical reactions: example

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- Assume stream 1 is pure C_2H_4, stream 2 is pure Cl_2. Assume all species can flow out through stream 3.
- The differential formulation of mass balance is

$$
\begin{aligned}
\frac{d}{dt}N_{C_2H_4} &= (\dot{N}_{C_2H_4})_1 + (\dot{N}_{C_2H_4})_3 + \left(\frac{dN_{C_2H_4}}{dt}\right)_{rxn} \\
\frac{d}{dt}N_{C1_2} &= (\dot{N}_{Cl_2})_2 + (\dot{N}_{Cl_2})_3 + \left(\frac{dN_{Cl_2}}{dt}\right)_{rxn} \\
\frac{d}{dt}N_{C_2H_4Cl_2} &= (\dot{N}_{C_2H_4Cl_2})_3 + \left(\frac{dN_{C_2H_4Cl_2}}{dt}\right)_{rxn}
\end{aligned}
$$

which using the molar extent of reaction notation above can be expressed

$$
\begin{aligned}
\frac{d}{dt}N_{C_2H_4} &= (\dot{N}_{C_2H_4})_1 + (\dot{N}_{C_2H_4})_3 - \frac{dX}{dt} \\
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\frac{d}{dt}N_{C_2H_4Cl_2} &= (\dot{N}_{C_2H_4Cl_2})_3 + \frac{dX}{dt}
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Total energy of system

- $E = U + M(v^2/2 + gh)$
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- We now consider energy balance formulations

Differential formulation

$$dE/dt = \text{rate energy in} - \text{rate energy out}$$

- **First law of thermodynamics**: energy is a conserved quantity; hence there is no third term pertaining to creation of energy

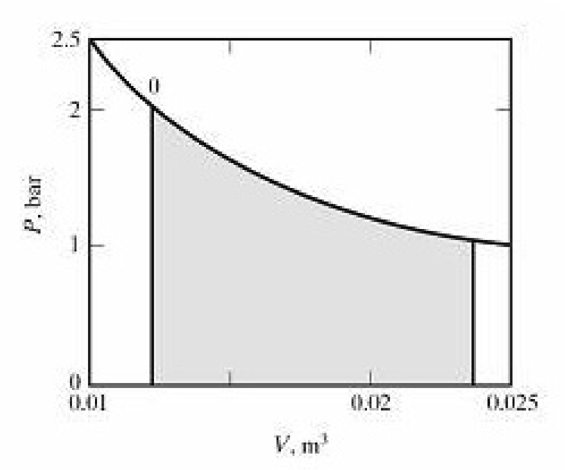
Work done by/on a system

- Mechanical work can be expressed $W = -F\Delta x$ for a constant force F. This is work done *by* a system, which reduces its energy
- For a variable force $F(x)$, we have $W = -\int_{x_1}^{x_2} F(x)\ dx$
- Infinitesimal work element: $dW = -F(x)dx$
- In thermodynamics, we are concerned with work done by or on a system, given the pressure P of the system or a system it is in contact with
- Express work in terms of pressure, volume rather than force, distance:

$$\begin{aligned} dW &= -(F(x)/A)Adx \\ &= -PdV \end{aligned}$$

- Note the internal energy of the system decreases when $\Delta V > 0$ (expansion) and increases when $\Delta V < 0$ (compression)

Rate of change of work



- For the differential form of energy balance, we need the rate of change of work.
- Now consider that V is changing with time at rate $\frac{dV}{dt}$. What is rate of change of work?
- *Work*: Rate of change of work $\frac{dW}{dt} = -PdV/dt$
- Rate of change of *heat*: assume it can enter from anywhere at a total rate of $\frac{dQ}{dt}$

Integral formulation of energy balance

- $U_2 - U_1 = Q + W$

$$\begin{aligned} Q &= \int_{t_1}^{t_2} \frac{dQ}{dt}\, dt \\ W &= \int_{t_1}^{t_2} \frac{dW}{dt}\, dt \\ &= -\int_{t_1}^{t_2} PdV/dt\; dt = -\int_{V_1}^{V_2} P\, dV \end{aligned}$$

- This energy balance follows from first law of thermo
- Change in V required for nonzero work
- How do we determine $P(V)$ in order to compute the work? Must choose a specific system since laws of thermodynamics do not specify relationships between state variables

Introducing the ideal gas

- *Ideal gas* - A gas with pressure so low that intermolecular interactions can be ignored
- Volumetric equation of state for ideal gas: $PV = NRT$ or $P\bar{V} = RT$ (intensive variables; $\bar{V}$ is molar volume)
- Given any two of the three state variables (P, V, T), this equation of state allows us to solve for the remaining state variable.
- The equation of state allows us compute the energy (U) change in response to changes of the state variable V due to work done on/by the system, since we can write $P = P(V, T)$ in the integral above
- This applies to systems not in mechanical equilibrium; work is done during process of mechanical equilibration.
- How do I compute the energy change due to heat Q exchange for interacting systems with different values of T? We have not said anything about how heat Q exchanged relates to changes in the temperature T as the systems equilibrate thermally to reach the same value of T.

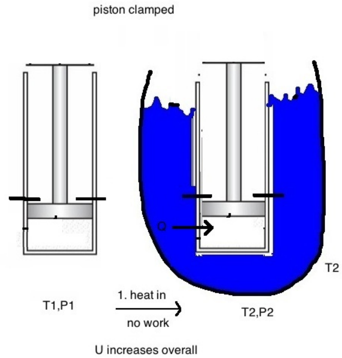
Temperature dependence of internal energy

- Assume to start that there is no work done: $\Delta V = 0$
- What is the equation used to compute Q given a specified change $\Delta T = T_2 - T_1$ of temperature of a system? The equation of state is not enough; we need an equation like $W = -P\Delta V$
- Introduce temperature dependence of internal energy per mole $(J/mol\ K)$- *constant volume heat capacity*:

  $$C_V(T, V) = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

  where $\bar{U}$ is molar internal energy
- Note that there is no macroscopic motion during equilibration analogous to change of V in mechanical equilibration above.
- Then the heat required is $Q = N \int_{T_1}^{T_2} C_V(T, V)\, dT$. Since there is no work done, the change in internal energy $\Delta U = Q$.
- For ideal gas, $C_V = C_V(T)$ and hence we can replace partial derivative with total: $C_V(T) = \frac{d\bar{U}}{dT}$
- But how do we find C_V? Temperature dependence of internal energy and enthalpy are properties of the ideal gas, and have been determined experimentally

Example: Isovolumetric heating (physical picture)



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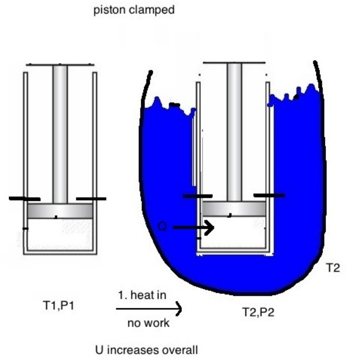

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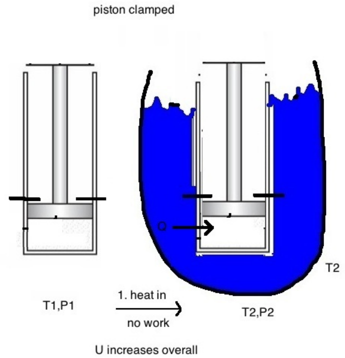

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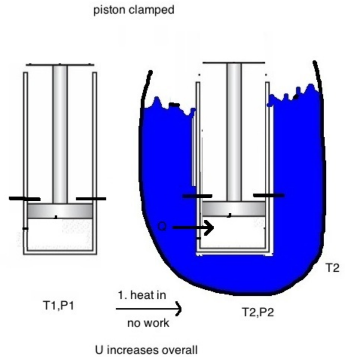

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- How much energy in the form of heat Q is absorbed by the gas?
- Answer: $Q = \Delta U = NC_v(T_2 - T_1)$ where the heat capacity C_v is an experimentally measured property of the gas.

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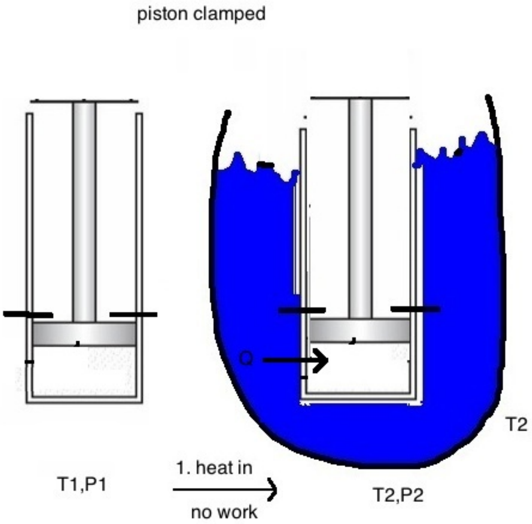
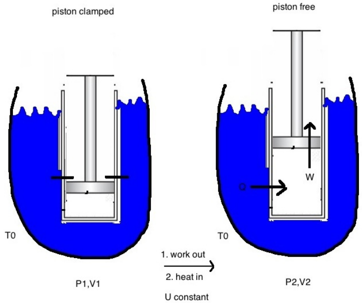


U increases overall

Example: Isothermal expansion (physical picture)



- The equation of state of a system, together with its heat capacity, allows computation of heat and work for a wide variety of processes involving different constraints on the state variables. We now consider some more examples in the case of an ideal gas.

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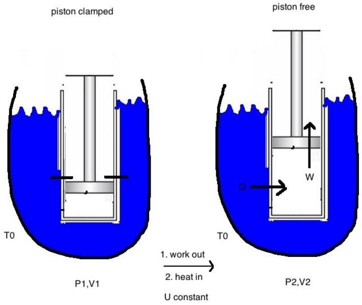

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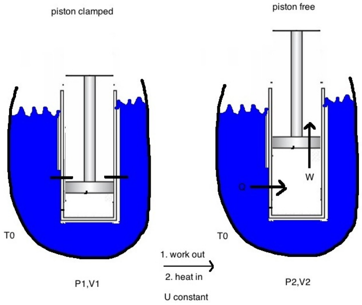

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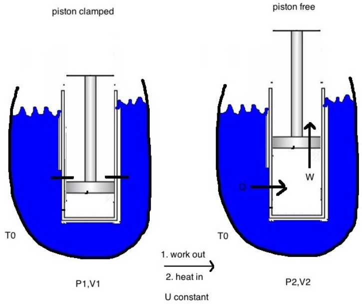

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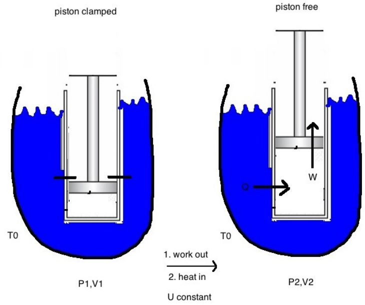

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- Suddenly, the clamp is released, so the gas expands to equilibrate mechanically. The clamp is replaced when the gas reaches volume V_2.

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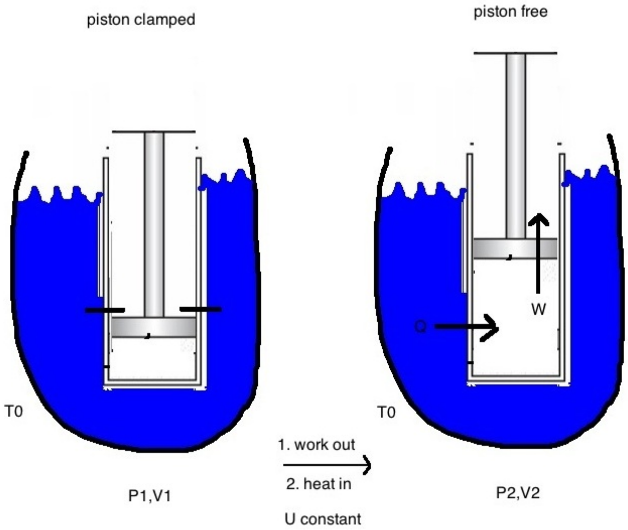

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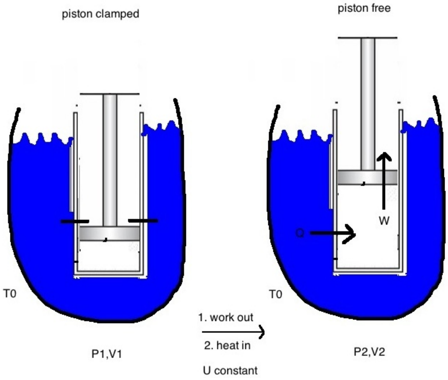

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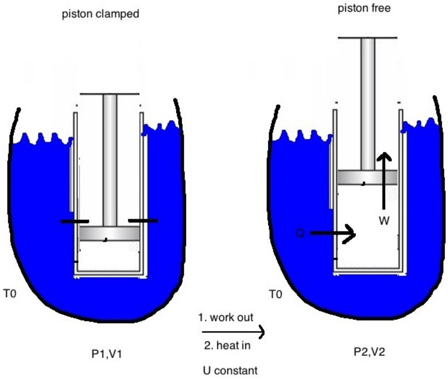

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- Energy balance: as the gas expands, doing work, $\Delta U = Q + W$ would decrease if not for heat from the bath. This would lead to a decrease in T since $U = U(T)$ for an ideal gas.

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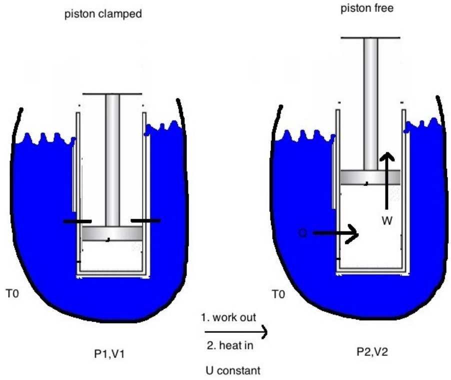

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- Energy balance: as the gas expands, doing work, $\Delta U = Q + W$ would decrease if not for heat from the bath. This would lead to a decrease in T since $U = U(T)$ for an ideal gas.
- Since the bath keeps $T = T_0$, U does not decrease. The gas absorbs heat Q from the bath so that $\Delta U = Q + W = 0$. Thus once we have found W (using the equation for work and the state equation), we can solve for Q.

Example: Isothermal expansion

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- *Isothermal* process: constraint is $T = T_0$ fixed; P, V variable; $P = P(V, T_0)$
- First compute the work W in an isothermal compression/expansion:

$$\begin{aligned} W &= -\int_{V_1}^{V_2} P(V,T)\; dV \\ P(V,T) &= P(V,T_0) \\ &= NRT_0/V \text{ from state equation} \\ W &= -\int_{V_1}^{V_2} NRT_0/V\; dV \\ &= -NRT_0 \ln(V_2/V_1) \end{aligned}$$

Isothermal expansion (cont'd)

- Now compute the heat Q exchanged using energy balance and the heat capacity equation:

$$\begin{aligned}\Delta U &= Q + W \\ &= NC_v \times (T_0 - T_0) = 0 \ \ \text{since U} = \text{U(T) for ideal gas} \\ &= 0 \\ Q &= -W\end{aligned}$$

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- Heat must be absorbed to keep T constant during the expansion since the system's internal energy decreases due to work done

Steps in setting up heat and work calculations: isothermal expansion of ideal gas

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5. Use a) the equation for heat capacity and b) the equation of state to simplify the energy balance equation. **Heat capacity:** $\mathbf{\Delta U = NC_v \times \Delta T}$; **Equation of state:** $\mathbf{P(V, T) = NRT_0/V}$

Steps in setting up heat and work calculations: isothermal expansion of ideal gas

1. What is the constraint? $\mathbf{T = T_0}$
2. Based on the answer to 1), determine whether the heat (Q), work (W) or total energy change ΔU can be set to 0. $\mathbf{\Delta U = 0}$ **since** $\mathbf{U = U(T_0)}$
3. Is it a shift away from thermal or mechanical equilibrium that initiates the change of state? **Shift from mechanical equilibrium due to release of clamp.**
4. If the change of state is initiated by a shift away from mechanical equilibrium, set up an equation for energy balance in terms of the change in volume (note name: isothermal **expansion**). (If volume is not directly given to you, use the state equation to get it.)

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6. Set terms in the energy balance to 0 based on the constraints identified above. $\mathbf{\Delta T = 0}$ **implies** $\mathbf{\Delta U = 0}$
7. Solve the equations for the Q, W and ΔU if a state variable change is specified. $\mathbf{W = -NRT_0 \ln(V_2/V_1)}$; $\mathbf{\Delta U = 0}$; $\mathbf{Q = -W}$.

Steps in setting up heat and work calculations for ideal gas processes

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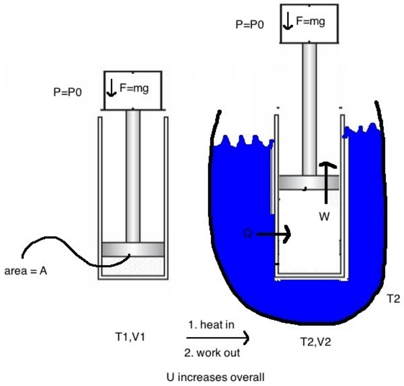
6. Set terms in the energy balance to 0 based on the constraints identified above.
7. Solve the equations for the Q, W and ΔU (if a state variable change is specified) or for the state variable change (if an energy change is specified).

Example: Isobaric heating (physical picture)



- Now consider gas inside a cylinder with piston where the pressure P is equal to that of its surroundings (mechanical equilibrium). The pressure imposed by the surroundings (by a weight on top of the piston) is P_0. The gas is initially at temperature T_1.

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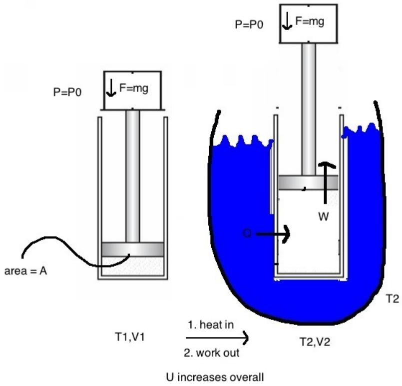

- Now consider gas inside a cylinder with piston where the pressure P is equal to that of its surroundings (mechanical equilibrium). The pressure imposed by the surroundings (by a weight on top of the piston) is P_0. The gas is initially at temperature T_1.
- The cylinder is placed on a hot plate (or immersed in a bath) at temperature T_2. The gas proceeds to thermally equilibrate with the hot plate. At every step of this process, the volume V of the gas increases due to the increase in T at constant pressure P_0.

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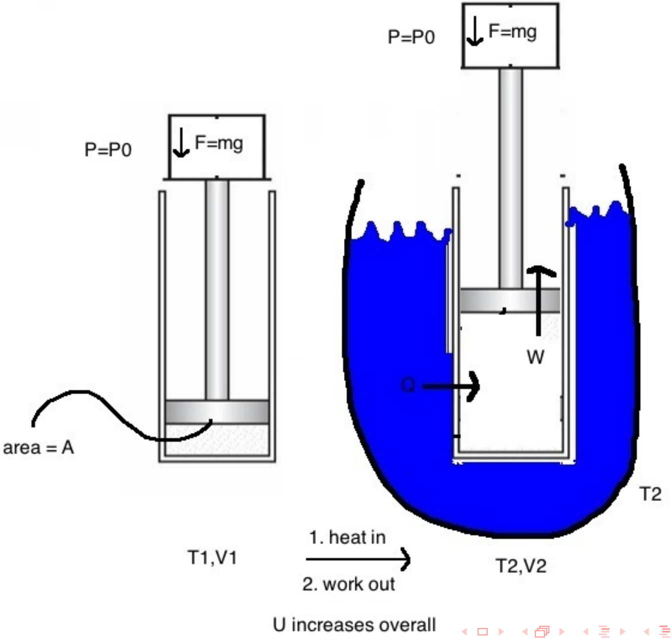
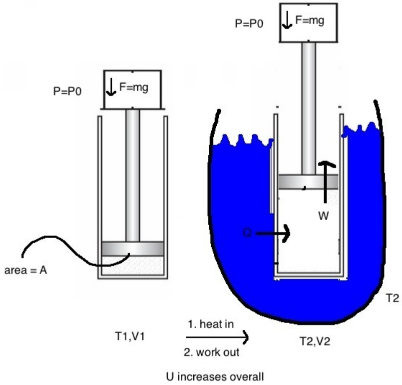
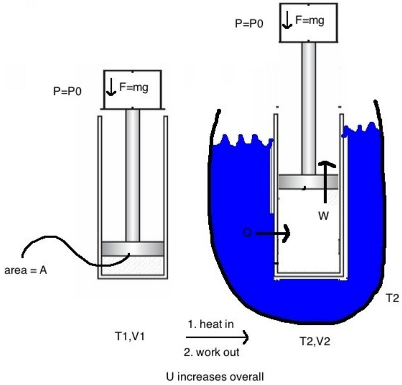




- Compute a) the work W, b) the heat Q, and c) the change in total energy ΔU for this process.



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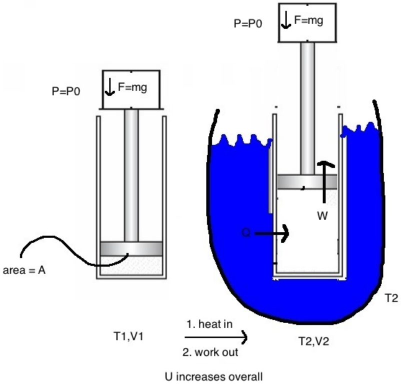
- Energy balance: as the gas is heated, ΔU increases since $U = U(T)$ for the gas. However, unlike the isovolumetric case, work is done during the free expansion. So both Q and W are nonzero.



- Compute a) the work W, b) the heat Q, and c) the change in total energy ΔU for this process.
- Energy balance: as the gas is heated, ΔU increases since $U = U(T)$ for the gas. However, unlike the isovolumetric case, work is done during the free expansion. So both Q and W are nonzero.
- We can solve for W in terms of the equation for work together with the state equation, and we can solve for ΔU using the heat capacity equation. Both should be expressed in terms of the given T_1, T_2. Once we have found these two, we can use the energy balance equation to solve for Q.

Steps in setting up heat and work calculations applied to isobaric heating of ideal gas

1. What is the constraint? $\mathbf{P} = \mathbf{P_0}$

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4. If the change of state is initiated by a shift away from thermal equilibrium, set up an equation for energy balance in terms of the change in temperature (note name: isobaric **heating**). (If temperature is not directly given to you, use the state variables provided to get it.) Use a) the equation for heat capacity and b) the equation of state to simplify the energy balance equation.

$$\Delta U = Q + W$$

$$\Delta U = Q - \int_{V_1}^{V_2} P\, dV$$

$$\Delta U = Q - P_0 \int_{V_1}^{V_2} dV$$

Heat capacity: $\mathbf{\Delta U = NC_v \Delta T}$; **From equation of state:** $\mathbf{dV = (NRdT)/P_0}$. **Hence:** $\mathbf{NC_v \Delta T = Q - \int_{T_1}^{T_2} NR\, dT = Q - NR\Delta T}$ (see below)

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2. Based on the answer to 1), determine whether the heat (Q), work (W) or total energy change ΔU can be set to 0. **none apply**
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4. If the change of state is initiated by a shift away from thermal equilibrium, set up an equation for energy balance in terms of the change in temperature (note name: isobaric **heating**). (If temperature is not directly given to you, use the state variables provided to get it.) Use a) the equation for heat capacity and b) the equation of state to simplify the energy balance equation.

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4. If the change of state is initiated by a shift away from thermal equilibrium, set up an equation for energy balance in terms of the change in temperature (note name: isobaric **heating**). (If temperature is not directly given to you, use the state variables provided to get it.) Use a) the equation for heat capacity and b) the equation of state to simplify the energy balance equation.

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5. Set terms in the energy balance to 0 based on the constraints identified above. **none**
6. Solve the equations for the Q, W and ΔU if a state variable change is specified. $\mathbf{W = -NR\Delta T}$; $\mathbf{\Delta U = NC_v \Delta T}$; $\mathbf{Q = \Delta U - W = N(C_v + R)\Delta T}$.

- *Isobaric* process: constraint is $P = P_0$ fixed; P, V variable; $P = P(V, T_0)$. How much heat Q is required to produce a given change in temperature $\Delta T = T_2 - T_1$?

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$$
\begin{aligned}
Q = \Delta U - W = N \int_{T_1}^{T_2} C_V(T)\, dT - W \\
&= N \int_{T_1}^{T_2} C_V(T)\, dT + \int_{V(T_1)}^{V(T_2)} P\, dV \\
&= N \int_{T_1}^{T_2} C_V(T)\, dT + P_0 \int_{V(T_1)}^{V(T_2)} dV \\
&= N \int_{T_1}^{T_2} C_V(T)\, dT + P_0 V_2 - P_0 V_1 \\
&= N \int_{T_1}^{T_2} C_V(T)\, dT + P_0(NRT_2/P_0) - P_0(NRT_1/P_0) \\
&= N \int_{T_1}^{T_2} C_V(T)\, dT + NR(T_2 - T_1) \\
&= N \int_{T_1}^{T_2} C_V(T) + R\, dT
\end{aligned}
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where we have applied the equation of state to rewrite the second term since we are explicitly specifying the change of T not V in the problem. **Ultimately you want to be able to recognize the type of process given its description in words and apply the appropriate equations without going through all the steps in the derivations above.**

- *Isobaric* process: constraint is $P = P_0$ fixed; P, V variable; $P = P(V, T_0)$. How much heat Q is required to produce a given change in temperature $\Delta T = T_2 - T_1$?
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Q = \Delta U - W &= N \int_{T_1}^{T_2} C_V(T)\, dT - W \\
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&= N \int_{T_1}^{T_2} C_V(T)\, dT + P_0 V_2 - P_0 V_1 \\
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- Note that if C_V is a constant, $Q = N(C_V + R)\Delta T$. $C_P = C_V + R$ is called the *constant pressure heat capacity*.

Steps in setting up heat and work calculations applied to isobaric heating of ideal gas

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Steps in setting up heat and work calculations applied to isovolumetric heating of ideal gas (revisited)

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1. What is the constraint? $\mathbf{V = V_0}$
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3. Based on the answer to 3), is it a shift away from thermal or mechanical equilibrium that initiates the change of state? **Shift from thermal equilibrium due to introduction of heater.**

Steps in setting up heat and work calculations applied to isovolumetric heating of ideal gas (revisited)

1. What is the constraint? $\mathbf{V} = \mathbf{V_0}$
2. Based on the answer to 1), determine whether the heat (Q), work (W) or total energy change ΔU can be set to 0. **$\mathbf{W} = \mathbf{0}$ since $\mathbf{V} = \mathbf{V_0}$**
3. Based on the answer to 3), is it a shift away from thermal or mechanical equilibrium that initiates the change of state? **Shift from thermal equilibrium due to introduction of heater.**
4. If the change of state is initiated by a shift away from thermal equilibrium, set up an equation for energy balance in terms of the change in temperature. (If temperature is not directly given to you, use the state equation to get it).

$$\Delta U = Q + W$$

Steps in setting up heat and work calculations applied to isovolumetric heating of ideal gas (revisited)

1. What is the constraint? $\mathbf{V} = \mathbf{V_0}$
2. Based on the answer to 1), determine whether the heat (Q), work (W) or total energy change ΔU can be set to 0. **W = 0 since V = $\mathbf{V_0}$**
3. Based on the answer to 3), is it a shift away from thermal or mechanical equilibrium that initiates the change of state? **Shift from thermal equilibrium due to introduction of heater.**
4. If the change of state is initiated by a shift away from thermal equilibrium, set up an equation for energy balance in terms of the change in temperature. (If temperature is not directly given to you, use the state equation to get it).

$$\Delta U = Q + W$$

5. Use a) the equation for heat capacity to simplify the energy balance equation. No need for equation of state. **Heat capacity:** $\mathbf{\Delta U = NC_v \times \Delta T}$, so

$$\mathbf{NC_v \times \Delta T = Q + W}$$

Steps in setting up heat and work calculations applied to isovolumetric heating of ideal gas (revisited)

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2. Based on the answer to 1), determine whether the heat (Q), work (W) or total energy change ΔU can be set to 0. $\mathbf{W} = \mathbf{0}$ **since** $\mathbf{V} = \mathbf{V_0}$
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$$\mathbf{NC_v} \times \mathbf{\Delta T} = \mathbf{Q} + \mathbf{W}$$

6. Set terms in the energy balance to 0 based on the constraints identified above. $\mathbf{\Delta V} = \mathbf{0}$ implies $\mathbf{W} = \mathbf{0}$

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6. Set terms in the energy balance to 0 based on the constraints identified above. $\mathbf{\Delta V = 0}$ implies $\mathbf{W = 0}$
7. Solve the equations for the Q, W and ΔU if a state variable change is specified. $\mathbf{\Delta U = NC_v \times \Delta T}$; $\mathbf{Q = NC_v \times \Delta T}$; $\mathbf{W = 0}$.

Additional comments on setting up heat and work calculations

- Note that in the examples above I have sometimes indicated P, T for a system, sometimes indicated P, V for a system, and sometimes indicated V, T for a system. Of course, apply the state equation to take the information given and convert it to a form that is necessary to solve the problem.

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Additional comments on setting up heat and work calculations

- Note that in the examples above I have sometimes indicated P, T for a system, sometimes indicated P, V for a system, and sometimes indicated V, T for a system. Of course, apply the state equation to take the information given and convert it to a form that is necessary to solve the problem.
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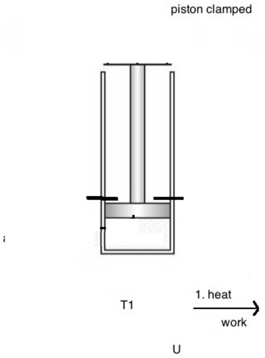
- $Q = NC_p\Delta T$ if the process occurs at constant pressure.

Example 1



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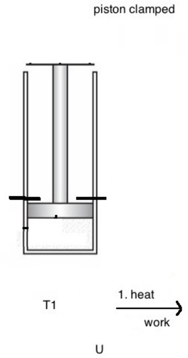

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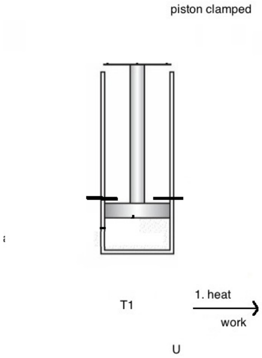

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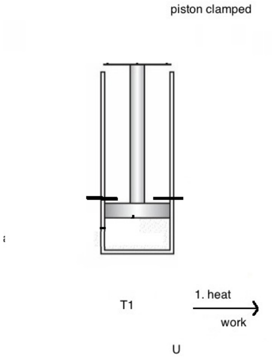

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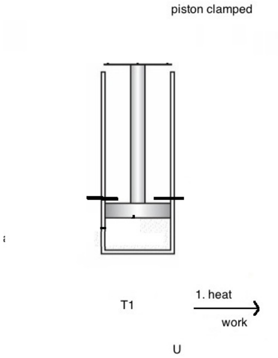

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Example 1 (cont'd)

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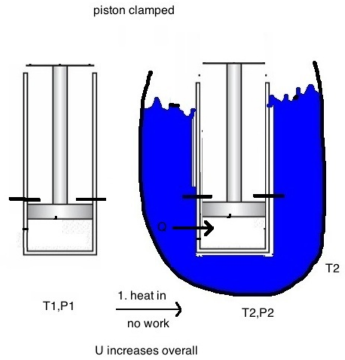
Example 1 answers



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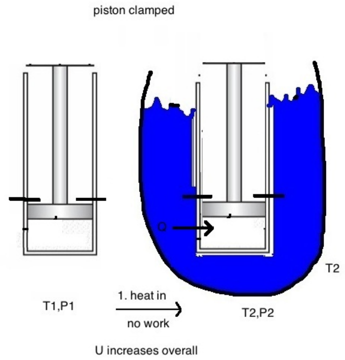

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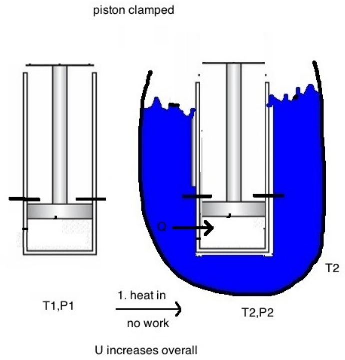

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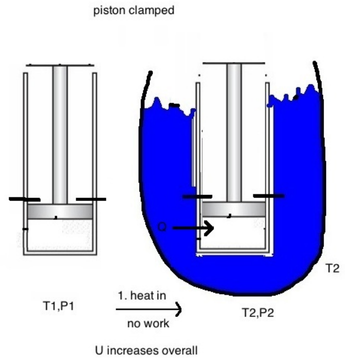

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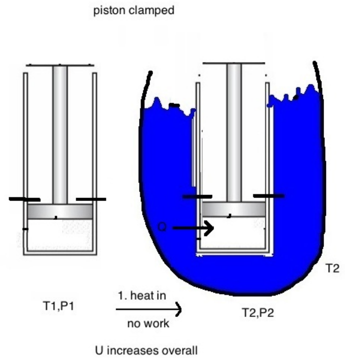

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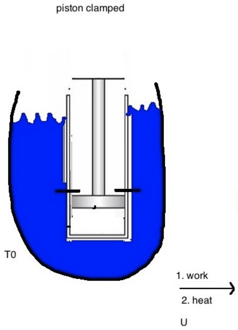

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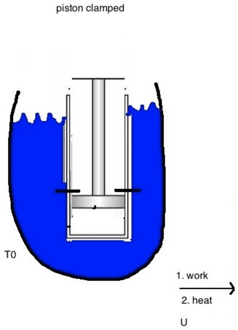

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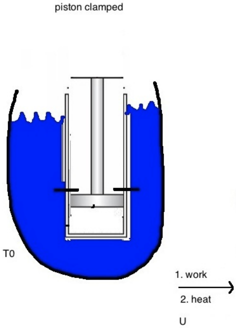

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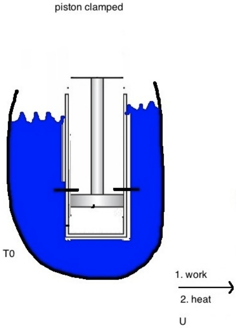

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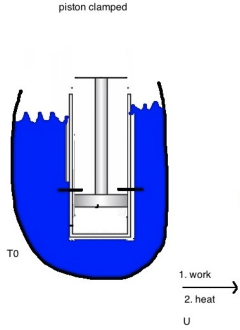

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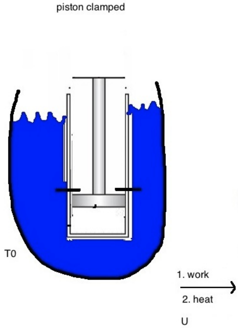

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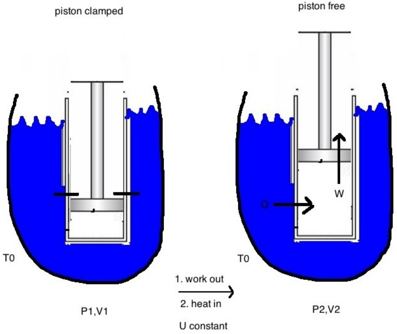
Example 2 answers



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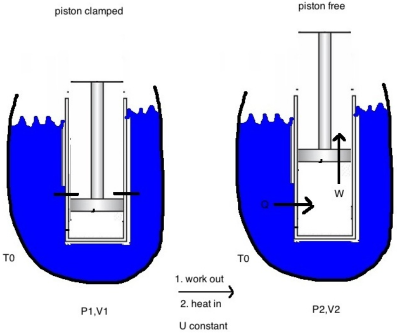

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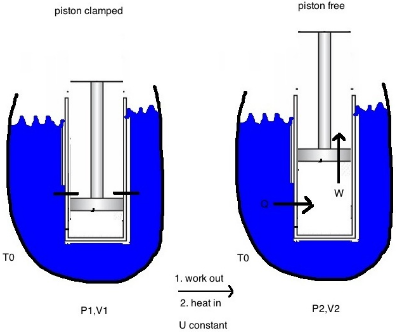

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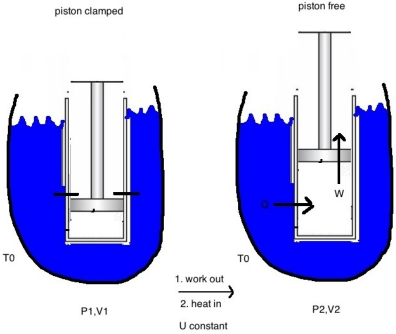

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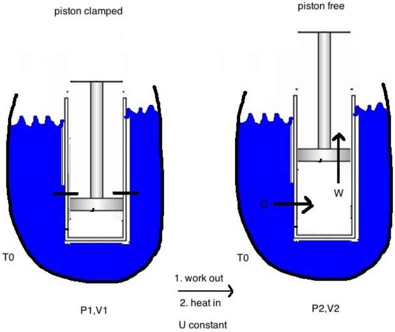
- What type of thermodynamic process is this? **Isothermal expansion**

Example 2 answers



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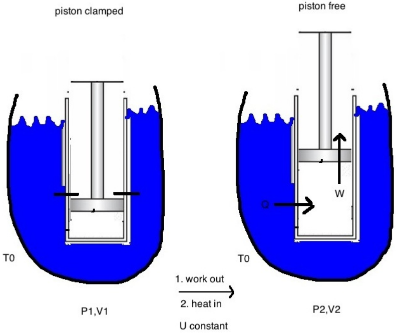

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- Draw a picture depicting the process, assuming the initial state is as shown, and indicate the heat and work flows.

Example 2 answers (cont'd)

- Write the energy balance equation in terms of the volume and temperature.

$$\Delta U = Q + W$$

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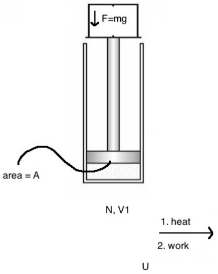
- What is the change of internal energy? $\Delta U = 0$

- True/false: the constant volume heat capacity of an ideal gas is always equal to the derivative of heat absorbed per mole with respect to the temperature.
- True/false: the constant volume heat capacity of an ideal gas is always equal to the derivative of internal energy per mole with respect to the temperature.
- True/false: the constant volume heat capacity of an ideal gas is only useful in calculations if the process occurs at constant volume.
- True/false: Heat is a form of thermal energy. Work is a form of mechanical energy. Internal energy is neither thermal nor mechanical energy.

Example 3

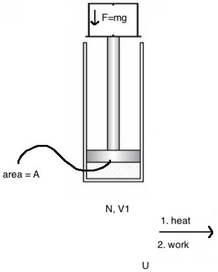


- Consider a gas inside a cylinder with piston without a clamp. A weight of mass m is sitting on top of the piston. The cross-sectional area of the piston is A. Assume the system is at equilibium and that atmospheric pressure is negligible. The number of moles of gas is N and the volume is V_1.
- The system is then immersed in a bath at temperature T_2.
- What type of thermodynamic process is this? Is the change of state initiated by a shift away from thermal or mechanical equilibrium?
- Draw a picture depicting the process and indicate the heat and work flows, assuming $T_2 < T_1$.

Example 3 (cont'd)

- Write the energy balance equation in terms of T_1 and T_2.
- What is the work done?
- What is the heat absorbed?
- What is the change in internal energy?

Example 3 answers



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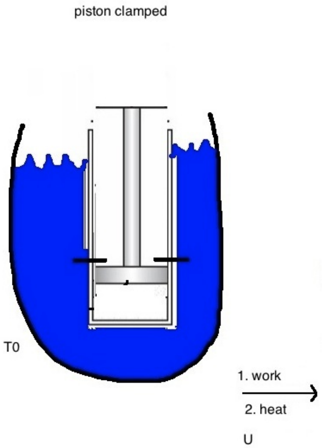
- The system is then immersed in a bath at temperature T_2.
- What type of thermodynamic process is this? **Isobaric heating/cooling.** Is the change of state initiated by a shift away from thermal or mechanical equilibrium? **Thermal**
- Draw a picture depicting the process and indicate the heat and work flows, assuming $T_2 < T_1$. **Gas compresses**

Example 3 answers (cont'd)

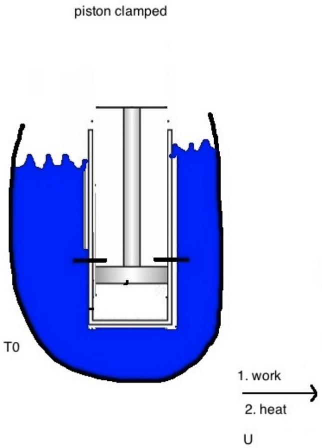
- Write the energy balance equation in terms of T_1 and T_2.

$$\begin{aligned} \Delta U &= Q + W \\ NC_v \Delta T &= Q - NR\Delta T \end{aligned}$$

- What is the work done? $W = -NR\Delta T$
- What is the heat absorbed? $Q = N(C_V + R)\Delta T$
- What is the change in internal energy? $\Delta U = NC_V \Delta T$



- Recall our picture for an isothermal process. What if there is an insulating material surrounding the cylinder, so there is no thermal contact with the surroundings?



- Recall our picture for an isothermal process. What if there is an insulating material surrounding the cylinder, so there is no thermal contact with the surroundings?
- $Q = 0$ but $W \neq 0$. This is an *adiabatic expansion*.

Adiabatic Expansion

- $W = \int_{V_1}^{V_2} \frac{NRT}{V}\, dV$; but T is no longer constant! How to integrate?

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- For every small piece of work $\frac{NRT}{V}\, dV$ done, the temperature T decreases since the energy is not replaced by heat as in the isothermal process.
- Set up the energy balance for this small change; the two sides of the equation (one in terms of T, other in terms of V) are now coupled:

$$\Delta U = W$$

$$\int_{T_1}^{T_2} NC_v\, dT = -\int_{V_1}^{V_2} \frac{NRT}{V}\, dV$$

$$\int_{T_1}^{T_2} \frac{1}{T}\, dT = -\frac{R}{C_v}\int_{V_1}^{V_2} \frac{1}{V}\, dV$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_v}}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$$

Adiabatic Expansion

- Given $T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$ for an adiabatic process, what is the $\Delta U = W$?
- $\Delta U = NC_v \Delta T = NC_v[T_2 - T_1] = NC_v T_1 \left[\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}} - 1\right]$

Constant pressure heat capacity and enthalpy

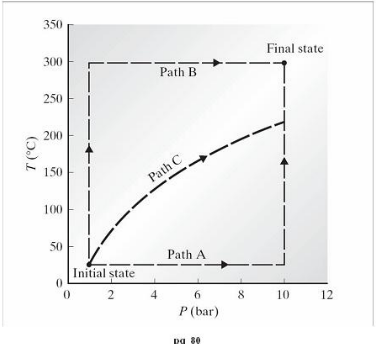
- Recall that the expression $NC_v\Delta T$ can only be used to compute the heat Q exchanged for a constant volume process.
- For an isothermal or constant pressure (isobaric) process, we have seen that the heat exchanged differs.
- We introduced the *constant pressure heat capacity*, which is also experimentally measured for various types of systems. It can be used to directly calculate the heat Q exchanged for a constant pressure process. Consider again our constant pressure process for an ideal gas

$$\begin{aligned} C_p &\equiv C_V + R \\ &= \frac{d\bar{U}}{dT} + \frac{d(RT)}{dT} \\ &= \frac{d\bar{U}}{dT} + \frac{d(P\bar{V})}{dT} \\ &= \frac{d}{dT}(\bar{U} + P\bar{V}) \end{aligned}$$

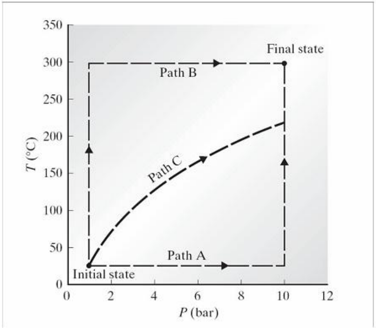
- The quantity $U + PV$ is called the *enthalpy* of the system and $\bar{U} + P\bar{V}$ its molar enthalpy. Changes in enthalpies ΔH are often reported for thermodynamic processes since it is common for processes to occur at constant pressure. $\Delta H = \Delta(U + PV)$ always, but $\Delta H = Q$ only if process occurs at constant pressure
- We then have $C_p = (\frac{\partial \bar{H}}{\partial T})_P$; compare $C_v = (\frac{\partial \bar{U}}{\partial T})_V$

Path-independence of internal energy changes (but not heat, work)

- In more complicated problems, a system may be subject to multiple thermodynamic processes in succession. (This is common in engines, which are used to convert internal energy of substances into useful work.)
- The value of ΔU is independent of the path followed by a system between two states specified by values of the state variables. Thermodynamic quantities that have this property are called *thermodynamic potentials* (compare mechanical potential energy).
- Consider a PT diagram of an ideal gas with the following two paths connecting states $(P_1, T_1), (P_2, T_2)$.



Path-independence of results



pg 80

- **Path A**: 1) *Isothermal compression*: (P_1, T_1) to (P_2, T_1); 2) *Isobaric heating*: (P_2, T_1) to (P_2, T_2)(proceeds through intermediate state (P_2, T_1))
- **Path B**: 1) *Isobaric heating*: (P_1, T_1) to (P_1, T_2); 2) *Isothermal compression*: (P_1, T_2) to (P_2, T_2) (proceeds through intermediate state (P_1, T_2))

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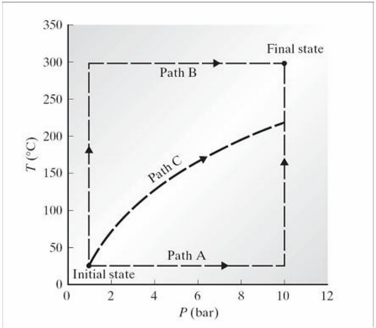

pg 80

- One mole of gas at $T_1 = 25C$ and $P_1 = 1$ bar is heated and compressed to $T_2 = 300C$ and $P_2 = 10$ bar. Compute heat and work along paths A,B
- Compute Q, W, and $\Delta U = Q + W$ as sum over paths and show ΔU is the same for both paths.

Path-independence of results (path A)

- **Path A**: $(P_1 = 1 \text{ bar}, T_1 = 298K)$ to $(P_2 = 10 \text{ bar}, T_1 = 298K)$; then to $(P_2 = 10 \text{ bar}, T_2 = 573K)$

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  1. Isothermal compression. Work:

     $$W_1 = -NRT \ln(V_2/V_1)$$

     We are given P_1, P_2, not V_1, V_2, so rewrite

     $$\ln \frac{V_2}{V_1} = \ln \frac{P_2}{P_1} = -\ln \frac{P_1}{P_2}$$

     Hence $W_1 = 8.314 J/mol\ K \times 298K \times \ln(10/1)$. For the heat, since $Q = -W$ for isothermal compression of ideal gas, we have:

     $$Q_1 = -W_1$$

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  2. Isobaric heating.

     $$W_2 = -NR(T_2 - T_1) = -8.314 J/mol\ K \times (573 - 298K)$$

     $$Q_2 = N \int_{T_1}^{T_2} C_p(T)\, dT = N(C_v + R)(T_2 - T_1) = 38 J/mol\ K \times 275K$$

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- $Q_{tot} = Q_1 + Q_2 = 4742.3\ J/mol$; $W_{tot} = W_1 + W_2 = 3421.4\ J/mol$; $\Delta U_{tot} = 8163.7\ J/mol$

Path-independence of results (path B)

- **Path B**: $(P_1 = 1 \text{ bar}, T_1 = 298\ K)$ to $(P_1 = 1 \text{ bar}, T_2 = 573K)$; then to $(P_2 = 10 \text{ bar}, T_2 = 573K)$

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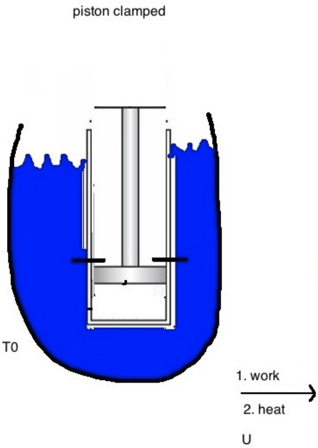
- $Q_{tot} = Q_1 + Q_2 = -522.2\ J/mol$; $W_{tot} = W_1 + W_2 = 8685.9\ J/mol$; $\Delta U_{tot} = 8163.7\ J/mol$



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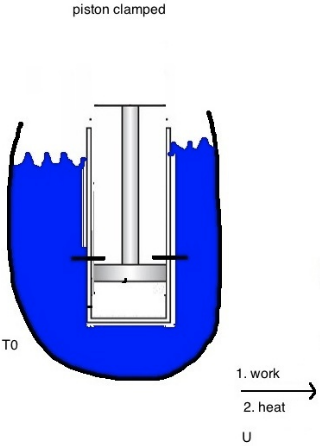

- Recall our picture for an isothermal process. What if there is an insulating material surrounding the cylinder, so there is no thermal contact with the surroundings?
- $Q = 0$ but $W \neq 0$. This is an *adiabatic expansion*.

Adiabatic Expansion

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- For every small piece of work $\frac{NRT}{V}\, dV$ done, the temperature T decreases since the energy is not replaced by heat as in the isothermal process.
- Set up the energy balance for this small change; the two sides of the equation (one in terms of T, other in terms of V) are now coupled:

$$\Delta U = W$$

$$\int_{T_1}^{T_2} NC_v\, dT = -\int_{V_1}^{V_2} \frac{NRT}{V}\, dV$$

$$\int_{T_1}^{T_2} \frac{1}{T}\, dT = -\frac{R}{C_v} \int_{V_1}^{V_2} \frac{1}{V}\, dV$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_v}}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$$

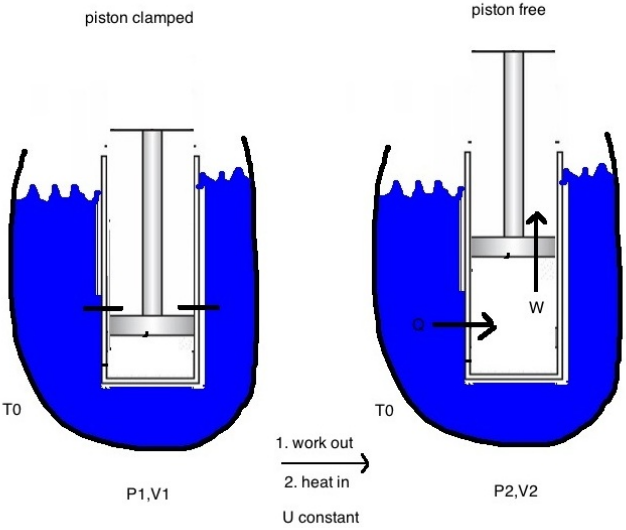
Adiabatic Expansion

- Given $T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$ for an adiabatic process, what is the $\Delta U = W$?
- $\Delta U = NC_v \Delta T = NC_v[T_2 - T_1] = NC_v T_1 \left[\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}} - 1\right]$

Outline

1. What is Thermodynamics?
2. Some Thermodynamics Terminology
3. Basic concepts of thermodynamics
4. Thermodynamic equations of state
5. Conservation of Mass
6. Integral formulation of mass balance
7. Multicomponent mass balance
8. Conservation of energy
   - Energy balance
9. Towards the 2nd Law of Thermodynamics
10. Toward engineering applications: thermodynamic cycles and heat engines
11. Thermodynamic properties of real substances (not ideal gases)
    - Computation of heat and work for thermodynamic processes involving nonideal substances
    - Computation of entropy changes for thermodynamic processes involving nonideal substances
12. Outline of remaining topics and schedule
13. Further analysis of the behavior of real gases
14. Phase equilibrium
15. More on Gibbs free energy and applications to phase equilibrium

Example 2



- Do our pictures make sense?

Spontaneous (irreversible) processes

- So far we have computed heat/work done by/on a system, but have not considered the effects on other systems in contact with our system. We now consider two systems in thermal and/or mechanical contact, which may be considered subsystems of one composite system

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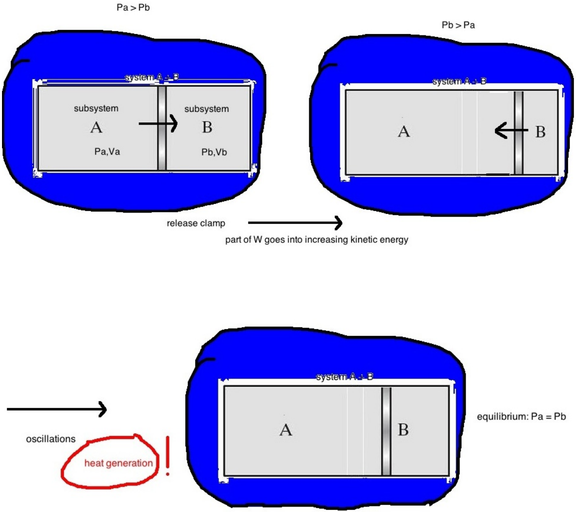
- Recall, we noted that internal energy cannot be completely converted to *useful* mechanical work.

Spontaneous (irreversible) processes



release clamp

part of W goes into increasing kinetic energy

oscillations

heat generation !

equilibrium: Pa = Pb

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- *Irreversible/spontaneous process*: any process that occurs at a finite rate due to finite difference between intensive variables of two subsystems

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$$
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- Now give the name *entropy* to this new extensive variable S; we will consider its physical meaning soon.

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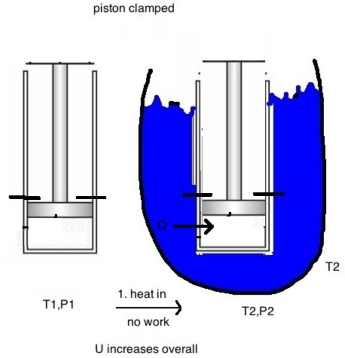
- This expression can be used to calculate entropy changes given measured heat changes dQ and temperatures T
- Note that in order to use this expression generally in computations, we will need to rewrite it in a form that allows us to explicitly integrate, as we rewrote the expression $\int_{V_1}^{V_2} P\ dV$.

Entropy change for an isovolumetric (isochoric) process



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- Track entropy changes of both system and surroundings (alternatively, treat them as two subsystems composing a larger composite system).

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- Since $T_a < T_b$, and $dQ_a > 0$, **we find $\mathbf{dS_{tot} > 0}$. Thus the total entropy increases during the heat transfer.**

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- In order to evaluate the integral, I need to express it in terms of a single variable, so I have substituted $NC_v dT = dQ$ (compare our previous experiences with such substitutions in work computations)

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- How do we compute T_2? Just apply $Q_b = -Q_a$ (energy balance for a+b) and write it in terms of temperature:

$$\begin{aligned}Q_b &= -Q_a \\ NCv, b(T_{b,2} - T_{b,1}) &= -NC_{v,a}(T_{a,2} - T_{a,1}) \\ NCv, b(T_2 - T_{b,1}) &= -NC_{v,a}(T_2 - T_{a,1})\end{aligned}$$

and solve for T_2 in terms of info given.

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- You can verify the last line by plotting the quantities on the same set of axes
- We know the total entropy change $\Delta S_{tot} > 0$ since each $dS_{tot} > 0$. But now we have obtained a numerical value for the total entropy change during equilibration.

- The key to the above analysis of why total entropy increases lies in the equation $dS_{tot} = dS_a + dS_b = \left(\frac{1}{T_a} - \frac{1}{T_b}\right)\ dQ_a$; the rest was just application of energy balance and integration

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- Net entropy change may be considered “driving force” in this example, instead of temperature difference, since we can look at driving force from perspective of extensive rather than intensive variables.
- From this perspective, the reason heat flow stops when two subsystems reach the same temperature is that there would be no increase of entropy from further passage of heat between the two subsystems

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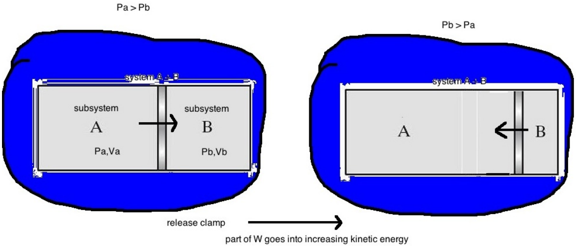
- Must keep track of entropy changes of all subsystems involved, unlike in our earlier work

Putting heat and work on an equal footing (cont'd)

- Let's return to the similarities (and differences) between heat and work



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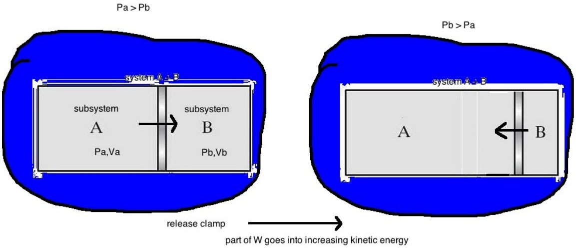

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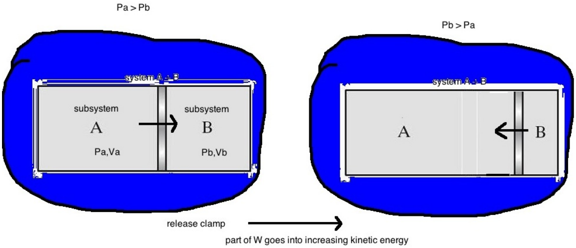

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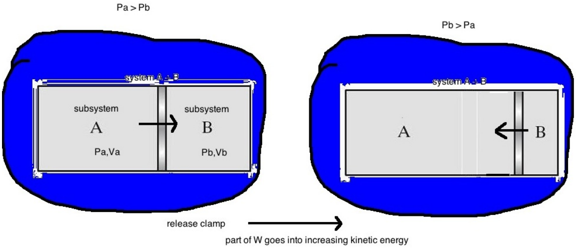

- Recall this example of a spontaneous process: V_1 increases, V_2 decreases, but the total volume change $\Delta V = 0$. So why the difference between S and V?

Putting heat and work on an "equal" footing: differences between S and V

- The reason for the difference between S_{tot} and V_{tot} - namely, that S_{tot} must increase for a real process whereas V_{tot} need not - is that *there are no equilibrium values of V_1 and V_2 for an irreversible process, until heat is liberated.*

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- Through the liberation of heat due to friction, $\Delta V_1 + \Delta V_2 = 0$ at equilibrium.

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- It is for this reason that $\Delta S_{tot} = \Delta S_1 + \Delta S_2 > 0$ for the real thermal equilibration process we studied.

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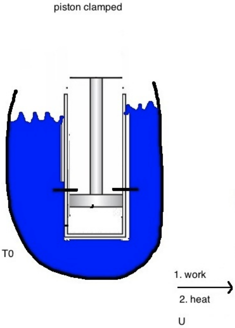
- So, as noted, it is more natural to consider the driving force for thermal equilibration to be increase in S_{tot}, whereas it is more natural to consider the driving force for mechanical equilibration to be elimination of the pressure gradient so $P_1 = P_2$
- But in general, equilibration is associated with elimination of differences between the values of intensive variables in interacting subsystems.

Entropy change example calculations: isothermal process

- Now continuing our reassessment of the pictures we've drawn, let's calculate entropy changes for both the system (gas) and its surroundings (water) in an isothermal process. Call the system a and the bath b.



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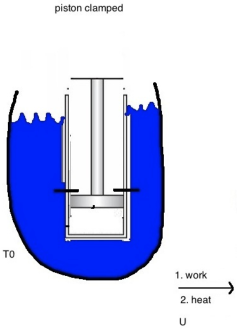
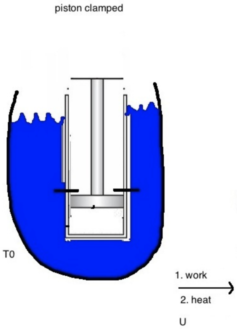
- But note that in our picture, if we suddenly remove the clamp, the gas will expand quickly and hence take on kinetic energy, as we showed. Thus entropy will increase due to heat liberated from friction in our picture.

Entropy change example calculations: adiabatic process



- Now let's consider the related adiabatic expansion process (make the cylinder well-insulated).

Entropy change example calculations: adiabatic process



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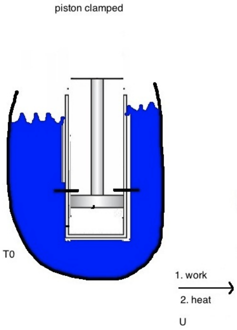

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- For this reason, a (reversible) adiabatic process is also said to be *isentropic*. Note isentropic refers to the system, not the system + surroundings.

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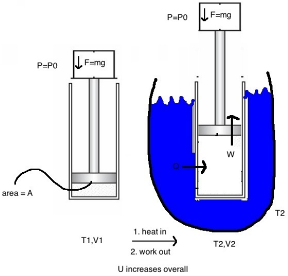
- The irreversibility originates in the finite difference in the intensive variable P upon releasing the clamp.
- In problems, the focus will be on calculating entropy changes due to heat transfer (not friction), as you saw in the homework

Entropy change example calculations: isobaric process



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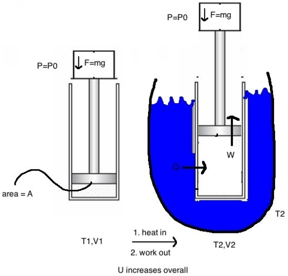

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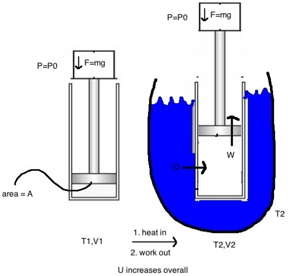

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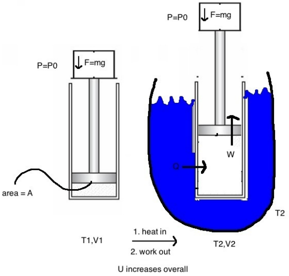

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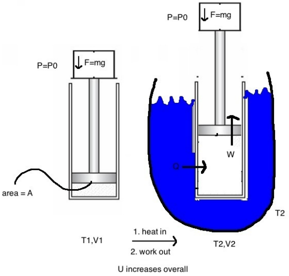

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- These heatings are irreversible as we have framed them because we have indicated that a finite difference in the intensive variable T initiated the change.

Outline

What are these processes useful for?

- Isovolumetric heating - constant V (extensive)
- Isobaric heating - constant P (intensive)
- Adiabatic (**isentropic**) expansion - constant S (extensive)
- Isothermal expansion - constant T (intensive)

Analogies between isovolumetric and isentropic processes

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- Heat engines can be fully understood by direct application of the methods we have learned

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- Avoid the heating processes we introduced, since they increase entropy due to heat transfer
- We introduced reversible isothermal and adiabatic processes: let's see how these might be used

Graphical depiction of work out and heat in for a thermodynamic cycle

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- Heat engines are run so that $W < 0$ (net work out) and $Q > 0$ (net heat in)

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- The proper choice of axes can help us determine how to close the loop

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- Thus, using TS axes will produce the simplest plot, from which it will be easy to determine where step 3 should end

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- Based on Q_2, solve for ΔV or ΔP of step 3

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Schematics of Carnot cycle steps

- Draw them!

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- See plot for details

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- Any step in the cycle that involves $|Q_{in}| > |W_{out}|$ is *irreversible* since it involves heat transfer at a finite T difference between system and surroundings
- Thus a decrease in thermodynamic efficiency is associated with $\Delta S_{tot} > 0$, which is an indication that energy was dissipated rather than being using for maximum useful work.

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- Thus, although $\Delta S_{sys} = 0$, $\Delta S_{net} = \Delta S_{2,tot} + \Delta S_{4,tot} > 0$
- Compare Carnot cycle (reversible): $\Delta S_{sys} = 0$, $\Delta S_{net} = 0$

Thermodynamic potentials revisited

- Applying our knowledge regarding the analogous formulations of Q, W in terms of intensive, extensive variables, let us write the energy balance equation in differential form

$$\begin{aligned} dU &= dW + dQ \\ dU &= -PdV + TdS \end{aligned}$$

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- We can also write changes of enthalpy (another thermodynamic potential) directly in terms of these intensive and extensive variables:

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= -PdV + TdS + PdV + VdP \\ &= VdP + TdS \end{aligned}$$

  where we have applied the product rule

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&= -PdV + TdS + PdV + VdP \\
&= VdP + TdS
\end{aligned}
$$

  where we have applied the product rule

- At constant P, $dH = TdS$ and hence change in enthalpy is equivalent to the heat exchanged, as we have seen.

Thermodynamic potentials revisited

- Applying our knowledge regarding the analogous formulations of Q, W in terms of intensive, extensive variables, let us write the energy balance equation in differential form

$$\begin{aligned} dU &= dW + dQ \\ dU &= -PdV + TdS \end{aligned}$$

  Note that we needed to introduce S in order to complete this expression in terms of our standard intensive and extensive variables (substituting $TdS = dQ$)

- We can also write changes of enthalpy (another thermodynamic potential) directly in terms of these intensive and extensive variables:

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= -PdV + TdS + PdV + VdP \\ &= VdP + TdS \end{aligned}$$

  where we have applied the product rule

- At constant P, $dH = TdS$ and hence change in enthalpy is equivalent to the heat exchanged, as we have seen.
- S is called a *state function* (as opposed to a state variable or thermodynamic potential), but specification of any two of P, V, T, S determines state. In the problems we study, it is more common to speak of entropy changes ΔS rather than absolute entropies.

Heat pumps and refrigerators: characterizing performance

- Heat pumps operate in reverse compared to heat engines
- The net heat Q_{net} is negative (net heat out) whereas the net work is positive (net work in)
- This is because Q_{out} (step 1 in the reverse Carnot cycle) is greater in magnitude than the Q_{in} (step 3 in the reverse Carnot cycle)
- Similar, the W_{in} (step 1 in the reverse Carnot cycle) is greater in magnitude than the W_{out} (step 3 in the reverse Carnot cycle)
- Instead of efficiency, it is common to use the so-called *coefficient of performance* when describing the effectiveness of a heat pump/refrigerator.
- Coefficient of performance for heating: $= \frac{|Q_{out}|}{|W_{net}|} = \frac{T_1}{T_1 - T_2}$, which is just the inverse of the Carnot efficiency, since Q_{out} is equal in magnitude to Q_{in} for the Carnot cycle, and W_{net}'s are also equal in magnitude.
- Note that the coefficient of performance for heating is always > 1 (since its reciprocal, the Carnot efficiency, was < 1).

Heat pumps and refrigerators: coefficient of performance, cooling

- Coefficient of performance for cooling: commonly used in refrigeration
- In *refrigeration*, one wants to remove heat from a body at a low temperature; in this case, it can be considered to be the heat bath at $T_2 < T_1$
- The coefficient of performance commonly used for refrigeration is the ratio of the amount heat removed at the lower temperature to the net work required to run the refrigerator.
- Coefficient of performance for cooling: $= \frac{|Q_{in}|}{|W_{net}|}$
- See TS axis plot

Rate of change and integral formulations of energy balance

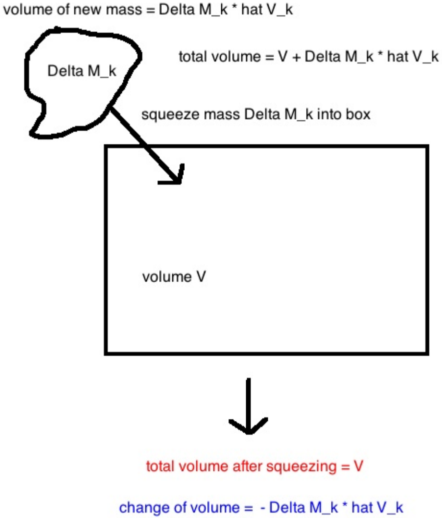
- $U_2 - U_1 = Q + W$

$$
\begin{aligned}
Q &= \int_{t_1}^{t_2} \frac{dQ}{dt}\ dt \\
W &= \int_{t_1}^{t_2} \frac{dW}{dt}\ dt \\
&= -\int_{t_1}^{t_2} PdV/dt\ dt = -\int_{V_1}^{V_2} P\ dV
\end{aligned}
$$

- We can also consider energy flow rates due to mass flow in/out of the system

Rate of change of energy due to mass flow

- We can also consider energy flow due to mass flow in/out of the system
- This is needed for engineering applications since we **often build engines and refrigerators fluid flowing through pipes and devices**, rather than keeping our fluid within a cylinder



volume of new mass = Delta M_k * hat V_k

Delta M_k

total volume = V + Delta M_k * hat V_k

squeeze mass Delta M_k into box

volume V

total volume after squeezing = V

change of volume = - Delta M_k * hat V_k

Rate of change of work due to mass flow

- A given amount of mass ΔM_k about to enter through port k has volume $\Delta M_k \times \hat{V}_k$. The total volume of the original system plus this mass is $V + \Delta M_k \times \hat{V}_k$, where $\hat{V}_k$ is volume per unit mass of the material entering through port k.
- For processes involving mass flow, it is more common to use $\hat{V}$ (volume per unit mass) or $\bar{V}$ (molar volume) of the gas rather than V, since the total amount of material we are looking may be changing but with a given density.
- When the new mass is squeezed into the container, the total volume becomes V.
- This squeezing caused the total volume of the original system plus new mass to decrease by $\Delta M_k \times \hat{V}_k$. Thus the overall system was compressed during squeezing. This means work was done on the system by the process of squeezing new mass in.
- The rate of change of volume of the system is $dV/dt = -\sum_k \dot{M}_k \hat{V}_k$. Thus the work (done on the system) due to mass flow $= \sum_k \dot{M}_k (P\hat{V})_k$

- There is a rate of internal energy flow accompanying mass flow: $\sum_k \dot{M}_k \hat{U}_k$, since the new mass has these forms of energy as well.
- Putting it all together,

$$dU/dt = \underbrace{\frac{dQ}{dt}}_{\text{heat}} - \underbrace{PdV/dt}_{\text{work due to expansion}} + \underbrace{\sum_k \dot{M}_k (P\hat{V})_k}_{\text{work due to mass flow}} + \underbrace{\sum_k \dot{M}_k \hat{U}_k}_{\text{U from mass flow}}$$

Applications of energy flow during mass flow: compressors

- A *compressor* is a device that takes in a fluid at pressure P_1 and emits it at some higher pressure $P_2 > P_1$ (or equivalently, lower molar volume); we can later do work with the pressurized fluid. It takes the place of the compression steps in the cycles we have studied so far

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- See picture
- Consider mass ΔN_1 entering the inlet port of a compressor
- Over the same period of time, mass ΔN_2, which is now compressed, exits the outlet port of the compressor
- Assume the compressor is operating at "steady-state", meaning the total amount of material inside at any time is the same. Thus $\Delta N_2 = -\Delta N_1 = -\Delta N$

Applications of energy flow by mass flow: compressors (cont'd)

- Inlet port: ΔN is flowing in at pressure P_1; its volume $V_1 = \bar{V}_1 \Delta N$

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- The compressor must push the gas out into the outlet stream, which is at higher pressure.
- Overall work due to pushing the gas through the device across the pressure difference (increase): $W = P_1 \bar{V}_1 \Delta N - P_2 \bar{V}_2 \Delta N = P_1 V_1 - P_2 V_2$; $P_2 > P_1$

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- First term is work done on the system since we are squeezing material into the compressor and the second term is work done by the system in pushing the material out of the compressor.

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Applications of energy flow by mass flow: compressors (cont'd)

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- For the differential formulation, we have $\frac{dW}{dt} = \sum_k P_k \bar{V}_k \dot{N}_k$ where here k runs from 1 to 2 for the inlet and outlet ports
- Note that the work required to push the material through the device is not being applied to change the state of another system (hence is not useful)

Ideal gas compressors

- Consider an ideal gas working fluid
- Inlet stream at $P_1, \bar{V}_1, T_1$; outlet stream at $P_2, \bar{V}_2, T_2$. Within the device, the gas is compressed such that $P_2 > P_1$, $\bar{V}_2 < \bar{V}_1$.
- According to above analysis for energy flow accompanying mass flow, the change of energy of the compressor is:

$$\begin{aligned}\Delta U &= \underbrace{P_1\bar{V}_1\Delta N - P_2\bar{V}_2\Delta N}_{\text{work due to mass flow}} + \underbrace{\Delta N C_v(T_1 - T_2)}_{\text{internal energy change to due to mass flow}} \\ &= (RT_1 - RT_2)\Delta N + \Delta N C_v(T_1 - T_2) \\ &= -R(T_2 - T_1)\Delta N - \Delta N C_v(T_2 - T_1)\end{aligned}$$

- The first work term is work needed to push the fluid through the device by pushing the fluid in front of ΔN out of the way. This is the important new term that will be appearing in these problems.
- Let's look at the simplest, isothermal example: then $\Delta U = 0$. There is no work needed to push the fluid across the pressure difference for this example
- What about the work needed to compress the gas within the device? As before, this is W_{in}:

$$W_{in} = -\Delta NRT \ln(\bar{V}_2/\bar{V}_1)$$

  which is positive since $\bar{V}_2 < \bar{V}_1$
- For T to remain constant, this must be matched by $Q_{out} = \Delta NRT \ln(\bar{V}_2/\bar{V}_1)$ (negative)

Applications of energy flow by mass flow: turbines

- A turbine is a device that takes in fluid at high P and emits it at low P, using expansion of the fluid to do work.
- See picture
- Inlet port: ΔN is flowing in at pressure P_1; its volume $V_1 = \hat{V}_1 \Delta N$
- Outlet port: ΔN is flowing out at pressure $P_2 < P_1$, $V_2 > V_1$
- Overall work due to pushing the gas through the device across the pressure difference (decrease): $W = P_1 \bar{V}_1 \Delta N - P_2 \bar{V}_2 \Delta N = P_1 V_1 - P_2 V_2$
- First term is work done on the system since we are squeezing material into the compressor and the second term is work done by the system in pushing the material out of the compressor from 1 to 2 for the inlet and outlet ports

Ideal gas turbines

- Consider an ideal gas working fluid for a turbine as well
- Inlet stream at P_1, $\bar{V}_1$, T_1; outlet stream at P_2, $\bar{V}_2$, T_2. Within the device, the gas is expanded such that $P_2 < P_1$, $\bar{V}_2 > \bar{V}_1$. Let's look at the simplest, isothermal example.
- $\Delta U = 0$ again since it's isothermal
- What about the work done due to expansion of the gas within the device? As before, this is W_{out}

  $$W_{out} = -\Delta NRT \ln(\bar{V}_2/\bar{V}_1)$$

  which is negative since $\bar{V}_2 > \bar{V}_1$. This is the point of running the turbine: to do useful work
- For T to remain constant, this must be match by $Q_{out} = \Delta NRT \ln(\bar{V}_2/\bar{V}_1)$ (positive)
- In the differential formulation we will write these as rates of heat and work in terms of $\dot{N}$ flow rate

  $$W_{out} = -\dot{N}RT \ln(\bar{V}_2/\bar{V}_1)$$
  $$Q_{out} = \dot{N}RT \ln(\bar{V}_2/\bar{V}_1)$$

- The W_{out} here is useful

Ideal gas heaters

- Consider a heating device for an ideal gas working fluid
- Inlet stream at $P_1, \bar{V}_1, T_1$; outlet stream at $P_2, \bar{V}_2, T_2$. Within the device, the gas is heated such that $T_2 > T_1$. **First assume this heating is done isovolumetrically** so $\bar{V}_2 = \bar{V}_1$
- According to above analysis for energy flow accompanying mass flow, the change of energy of the heater is (again):

$$\begin{aligned}\Delta U &= \underbrace{P_1\bar{V}_1\Delta N - P_2\bar{V}_2\Delta N}_{\text{work due to mass flow}} + \underbrace{\Delta N C_v(T_1 - T_2)}_{\text{internal energy change to due to mass flow}} \\ &= (RT_1 - RT_2)\Delta N + \Delta N C_v(T_1 - T_2) \\ &= -R(T_2 - T_1)\Delta N - \Delta N C_v(T_2 - T_1)\end{aligned}$$

- Now $T_2 > T_1$ so there must be a source of net energy input to enact this change
- Compensating energy input comes from heat

$$Q_{in} = R(T_2 - T_1)\Delta N + \Delta N C_v(T_2 - T_1)$$

- To get the signs right, note that the energy input (here in the form of heat) must be equal in magnitude and opposite in sign to the ΔU in order to compensate and keep the device at steady state

Use of thermodynamic cycles involving mass flow for engines

- As example of a thermodynamic cycle for a heat engine involving mass flow, consider one called a Stirling cycle (isovolumetric/isothermal); similar to cycle we studied on HW 4 but with mass flow
- See depiction of cycle with compressor and turbine: the compression and expansion are done isothermally using the devices we just discussed
- Now must express heat and work in terms of rates of change, using known rates of mass flow $\dot{N}$. Problems are usually formulated in this way: given flow rates $\dot{N}$ and $P, \bar{V}, T$ changes across the devices
- The heatings and coolings between T_1 and T_2 are done using heat exchangers, isobarically - devices that transmit heat to and from flowing mass

Illustration of Stirling cycle using ideal gas

- **Step 1: isothermal turbine (expansion)**

$$\begin{aligned} 0 &= \dot{Q} + \dot{W} \\ \dot{W} &= -\dot{N}RT_1 \ln(V_2/V_1) \\ \dot{Q} &= \dot{N}RT_1 \ln(V_2/V_1) \end{aligned}$$

- **Step 2: isovolumetric cooling**

$$\dot{Q} = \dot{N}(C_v + R)(T_2 - T_1)$$

- **Step 3: isothermal compressor**

$$\begin{aligned} \dot{W} &= -\dot{N}RT_2 \ln(V_4/V_3) \\ \dot{Q} &= \dot{N}RT_2 \ln(V_4/V_3) \end{aligned}$$

- **Step 4: isovolumetric heating**

$$\dot{Q} = \dot{N}(C_v + R)(T_1 - T_2)$$

Use of heat exchangers in thermodynamic cycles involving mass flow

- The efficiency of engines using mass flow can be improved by using heat exchangers
- In Stirling cycle, note

$$\dot{Q}_2 = \dot{N}(C_v + R)(T_2 - T_1)$$
$$\dot{Q}_4 = \dot{N}(C_v + R)(T_1 - T_2)$$

- Hence $\dot{Q}_2 = -\dot{Q}_4$. Why not use the heat liberated during the cooling step to heat the stream during the heating step?
- This principle is called *heat exchange*.
- Heat exchange can increase the efficiency of an engine:

$$\dot{Q}_{in} = \dot{Q}_1 = \dot{N}RT_1 \ln(V_2/V_1)$$
$$\dot{W}_{out} = \dot{W}_1 + \dot{W}_3$$
$$\text{Efficiency} = \frac{|\dot{W}_1 + \dot{W}_3|}{\dot{Q}_1}$$

- Note that we have omitted other sources of heat input because of the heat exchanger
- See schematic of the Stirling cycle with heat exchanger

Ideal gas heaters (cont'd)

- For an **isobaric heating in a mass flow device**, since work is done within the device during the heating, there must be a source of additional energy; this would require additional Q_{in}:

$$\begin{aligned} Q_{in} &= R(T_2 - T_1)\Delta N + \Delta N(C_v + R)(T_2 - T_1) \\ &= \Delta N(C_v + 2R)(T_2 - T_1) \end{aligned}$$

- In the book it is assumed that the additional energy required for the expansion work is provided by the device and Q_{in} is listed as the same for isobaric and isovolumetric heatings
- It is a matter of how you account for the energy changes; we will clarify when asking you questions on this

Outline

From thermodynamics of ideal to thermodynamics of non-ideal substances

- Ideal gas has some special properties
- Its state equation is particularly simple (all state variables enter linearly)
- Consider a nonideal gas equation of state:

$$PV = NRT\left(1 + \frac{B_1(T)}{\bar{V}} + \frac{B_2(T)}{\bar{V}^2} + \cdots\right)$$

- This is called the virial equation of state
- Note that as molar volume decreases, the correction terms after the 1 become more important (due to molecular interactions in the gas)

- Computation of internal energy changes of an ideal gas were particularly simple since

$$dU = N\bar{C}_v dT$$

  i.e. the energy does not explicitly depend on V or P and U can be written as $U = U(T)$. Microscopically, this is because the gas molecules do not interact

- Note that I have used the notation $\bar{C}_v$ for the molar heat capacity; this will allow me to drop the N when writing expressions in terms of C_v, which I will now use to refer to the total heat capacity:

$$dU = C_v dT$$

  for an ideal gas

From thermodynamics of ideal to thermodynamics of nonideal substances

- For a nonideal substances, the internal energy can depend on state variables other than T (cannot always write $U = U(T)$)
- As we mentioned previously, $C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V$ (which is equal to $\frac{dU}{dT}$ for an ideal gas).
- In general, a thermodynamic potential like U can be written in terms of (as an explicit function of) any two state variables (since any two state variables determine the third)
- Changes in any thermodynamic potential can be written in terms of corresponding changes in these two state variables
- **What is the appropriate general expression for dU in terms of dT and dV?** I.e., how can we write $U = U(T, V)$ for a nonideal substance?

Towards a general expression for internal energy changes in terms of temperature and volume

- Recall our general expression for dU in terms of differential heat and work contributions:

$$dU = TdS - PdV$$

- Here the first term is dQ and the second term is dW. This equation always holds for any substance. This assumes $U = U(S, V)$, which is not convenient since we generally do not measure changes in S directly
- In the language of partial derivatives, we have

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$
$$P = -\left(\frac{\partial U}{\partial V}\right)_S$$

- A total differential like dU can thus be written in terms of the sum of 1) the partial derivative with respect to state variable 1, at constant value of the 2nd state variable, times the infinitesimal change in the 1st variable; 2) the partial derivative with respect to state variable 2, at constant value of the 1st state variable, times the infinitesimal change in the 2nd variable:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

- Now, we want an expression of the form

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \, dT + \left(\frac{\partial U}{\partial V}\right)_T \, dV$$
$$= N\bar{C}_v \, dT + \left(\frac{\partial U}{\partial V}\right)_T \, dV$$

  where we have substituted the definition of C_v.
- So our question is, what is $\left(\frac{\partial U}{\partial V}\right)_T$?

Towards a general expression for internal energy changes in terms of temperature and volume

- What do we know about the term $\left(\frac{\partial U}{\partial V}\right)_T dV$?
  1. It is equal to zero for an ideal gas
  2. It must have a contribution from $-PdV$, i.e., the work done due to change of volume
- Thus this term has the form

$$\left(\frac{\partial U}{\partial V}\right)_T dV = [?? - P]\, dV$$

where $?? - P = 0$ for an ideal gas

Towards a general expression for internal energy changes in terms of temperature and volume

- Thus this term has the form

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- It turns out that the expression is

$$\left(\frac{\partial U}{\partial V}\right)_T dV = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

  as we can show explicitly later, but this is an identity that you can remember for now

- Verify that it $= 0$ for an ideal gas, by substituting the equation of state $PV = NRT$:

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T dV &= \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \\ &= T\left(\frac{\partial \frac{NRT}{V}}{\partial T}\right)_V dV - PdV \\ &= (NRT/V)dV - PdV \\ &= (P - P)dV \\ &= 0\end{aligned}$$

- Note that this follows from the linearity of the equation of state in T

Towards a general expression for internal energy changes in terms of temperature and volume

- You can view the term $T\left(\frac{\partial P}{\partial T}\right)_V$ as a "correction required to convert the term TdS into $C_v dT$"
- So we have

$$dU = N\bar{C}_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

as an alternative to

$$dU = TdS - PdV$$

when we want to express $U = U(T, V)$

- This expression is fully general, and applies to nonideal substances
- Note the advantages of this expression for dU for practical calculations: **you can compute changes in internal energy purely in terms of the heat capacity and the equation of state, and you do not need to measure changes in entropy to do it**

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  as an alternative to

$$dU = TdS - PdV$$

  when we want to express $U = U(T, V)$

- This expression is fully general, and applies to nonideal substances
- Note the advantages of this expression for dU for practical calculations: **you can compute changes in internal energy purely in terms of the heat capacity and the equation of state, and you do not need to measure changes in entropy to do it**
- Next we will compute ΔU's for nonideal substances given their heat capacities and equations of state

ΔU for isothermal expansion of a nonideal gas

- **Example**: what is ΔU for an isothermal expansion of a nonideal gas? Note that it is not necessarily $= 0$ as for an ideal gas; the internal energy can depend explicitly on the volume (the interactions between gas molecules are not negligible)
- Isothermal process:

$$\begin{aligned} dU &= N\bar{C}_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \\ &= \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \end{aligned}$$

- Integral formulation:

$$\Delta U = \int_{V_1}^{V_2} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

- Note $\Delta U \neq 0$ for an isothermal process!
- Evaluation of ΔU requires an equation of state.

Equations of state for nonideal gases

- Nonideal gas equations of state, like the ideal gas law, are often determined empirically by measurements of state variables of a gas under different conditions
- *van der Waals* equation of state:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

  Physical interpretation: b is the molar volume excluded by the finite size of the gas molecules; a is a measure of the strength of attraction between gas molecules (note that at the same T, P is lower due to attraction at smaller $\bar{V}$).

- *Peng-Robinson* equation of state (extension of van der Waals equation):

$$P = \frac{RT}{\bar{V} - b} - \frac{a(T)}{\bar{V}(\bar{V} + b) + b(\bar{V} - b)}$$

- *Virial* equation of state:

$$P\bar{V} = RT\left(1 + \frac{B_1(T)}{\bar{V}} + \frac{B_2(T)}{\bar{V}^2} + \cdots\right)$$

  Physical interpretation: the correction terms are are expansion in powers of the density $\frac{1}{\bar{V}}$ of the gas, with the ideal gas law holding at very low densities

ΔU for isothermal expansion of a nonideal gas (cont'd)

- Now consider calculation of ΔU for the isothermal expansion of a gas that obeys the van der Waals equation of state.
- Isothermal process:

$$dU = N\bar{C}_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$
$$= \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

- van der Waals:

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

- So $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}-b}$ and

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{\bar{V}-b} - \frac{RT}{\bar{V}-b} + \frac{a}{\bar{V}^2}$$
$$= \frac{a}{\bar{V}^2}$$

ΔU for isothermal expansion of a nonideal gas (cont'd)

- ΔU for isothermal expansion of van der Waals gas:

$$\begin{aligned}\Delta U &= \int_{V_1}^{V_2} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \\ &= \int_{V_1}^{V_2} \frac{a}{\bar{V}^2} dV \\ &= \int_{V_1}^{V_2} \frac{N^2 a}{V^2} dV \\ &= -\frac{N^2 a}{V_2} + \frac{N^2 a}{V_1}\end{aligned}$$

- $\Delta U > 0$ for an expansion $(V_2 > V_1)$ because we needed to pull gas molecules apart, which required the input of energy

Computation of internal energy changes for nonideal gases: changes in T and V

- Now consider computation of the internal energy change for a nonideal gas that undergoes a change from V_1, T_1 to V_2, T_2
- $\Delta U = U(T_2, V_2) - U(T_1, V_1)$
- We can choose any path we want in order to do the computation; for convenience choose those consist of steps where only one state variable is changing at a time
- Consider first path consisting of i) a step from T_1, V_1 to T_1, V_2, followed by ii) a step from T_1, V_2 to T_2, V_2; $\Delta U = \Delta U_1 + \Delta U_2$
- Step i): $\Delta U_1 = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_{T=T_1} dV$ - internal energy change due to volume change at constant temperature (this term is 0 for an ideal gas). **We just looked at this term.**
- Step ii): $\Delta U_2 = N \int_{T_1}^{T_2} \bar{C}_v(V_2, T)\, dT$.
- See state variable diagram

Computation of heat for ideal vs nonideal gas processes

- Now consider the computation of heat for a nonideal gas process. We first start by recalling our results for ideal gases. Assume one mole of gas.
- For an ideal gas undergoing constant volume process, $dQ = N\bar{C}_v dT$,
- For a constant pressure (isobaric) process,

$$\begin{aligned} dQ &= N\bar{C}_p dT \\ &= N\bar{C}_v dT + NRdT \end{aligned}$$

Computation of heat for nonideal gas processes

- In general, from $dU = dQ + dW$,

$$\begin{aligned} dQ &= dU - dW \\ &= dU + PdV \end{aligned}$$

- Check consistency: for an ideal gas undergoing an isobaric process,

$$\begin{aligned} dQ &= dU + PdV \\ &= N\bar{C}_v dT + Pd(RT/P) \\ &= N\bar{C}_v dT + NRdT \\ &= N(\bar{C}_v + R)dT \end{aligned}$$

which is consistent with the expression we have used above.

Computation of heat for nonideal gas processes (cont'd)

- In general, we have

$$dQ = dU + PdV$$

- This is expression is always true, but we want the rhs to be expressed in terms of dT and dV
- To achieve this, just substitute our expression for dU in terms of changes in temperature and volume, to get

$$\begin{aligned} dQ &= N\bar{C}_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV + PdV \\ &= N\bar{C}_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dV \end{aligned}$$

  This is a general expression for heat exchanged, given in terms of changes in state variables
- Note we still have $dW = -PdV$ for work

Example: Heat Q and work W for isothermal expansion of a nonideal gas

- Now consider calculation of Q for the isothermal expansion of a gas that obeys the van der Waals equation of state.
- Isothermal process:

$$\begin{aligned} dQ &= N\bar{C}_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \\ &= T\left(\frac{\partial P}{\partial T}\right)_V dV \end{aligned}$$

  since isothermal.
- van der Waals:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

- Recall from above that $T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{\bar{V}-b}$. Hence for heat we have

$$\begin{aligned} Q &= \int_{V_1}^{V_2} \frac{RT}{\frac{V}{N} - b} dV \\ &= NRT \ln\left(\frac{\frac{V_2}{N} - b}{\frac{V_1}{N} - b}\right) \end{aligned}$$

Example: Heat Q and work W for isothermal expansion of a nonideal gas (cont'd)

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- For work we have

$$\begin{aligned} W &= -\int_{V_1}^{V_2} PdV \\ &= -\int_{V_1}^{V_2} \frac{RT}{\frac{V}{N} - b} - \frac{N^2 a}{V^2} dV \\ &= -NRT \ln\left(\frac{\frac{V_2}{N} - b}{\frac{V_1}{N} - b}\right) + N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right) \end{aligned}$$

- Compare $Q = NRT \ln\left(\frac{V_2}{V_1}\right)$, $W = -NRT \ln\left(\frac{V_2}{V_1}\right)$ for an ideal gas

Summary of equations for internal energy, work, heat and entropy for nonideal substances, in terms of T, V

- Listing our new equations:
  1. Internal energy: $dU = N\bar{C}_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$
  2. Work: $dW = -PdV$
  3. Heat: $dQ = dU - dW = N\bar{C}_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$
  4. Entropy: $dS = dQ/T = \frac{1}{T}N\bar{C}_v dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
- Remember that you need heat capacity information and an equation of state to apply these expressions

Computation of entropy changes for ideal vs nonideal gases

- Now consider the computation of ΔS for a nonideal gas. We first start by recalling our results for ideal gases. Recall $dS = \frac{1}{T}dQ$. Assume one mole of gas.
- For an ideal gas undergoing constant volume process, since $dQ = N\bar{C}_v dT$, we used $dS = \frac{1}{T}N\bar{C}_v dT$.
- For a constant pressure (isobaric) process, since $dQ = N\bar{C}_p dT$, we used

$$\begin{aligned} dS &= \frac{1}{T}dQ \\ &= \frac{1}{T}N\bar{C}_p dT \\ &= \frac{1}{T}N(\bar{C}_v + NR)dT \\ &= \frac{1}{T}N\bar{C}_v dT + \frac{1}{T}NRdT \end{aligned}$$

Computation of entropy changes for nonideal gases (cont'd)

- In general, we have

$$\begin{aligned} dS &= \frac{1}{T} dQ \\ &= \frac{1}{T} (dU - dW) \\ &= \frac{1}{T} dU + \frac{P}{T} dV \end{aligned}$$

- This is expression is always true, but we want the rhs to be expressed in terms of dT and dV
- To achieve this, just substitute our expression for dU in terms of changes in temperature and volume, to get

$$\begin{aligned} dS &= \frac{1}{T} \left\{ N\bar{C}_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \right\} + \frac{P}{T} dV \\ &= \frac{N\bar{C}_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dV \end{aligned}$$

  This is a general expression for heat exchanged, given in terms of changes in state variables
- For an ideal gas, $dS = \frac{1}{T} N\bar{C}_v dT + \frac{NR}{V} dV$
- Remember that entropy changes ΔS are independent of path but heat Q exchanged is not

Computation of internal energy changes for nonideal gases: changes in T and V

- Given heat capacity information and an equation of state, we can compute ΔU for any thermodynamic process for any substance.
- Heat capacities are usually tabulated at (or provided as functions with parameters given at) very low pressures (i.e., ideal gas limit). These heat capacities are denoted by a $*$; e.g., C_v^*. This will typically be given to us directly.
- Hence we typically use paths where we only need to know the heat capacity (or heat capacity as function of T) for the corresponding ideal gas.
- Thus consider the following alternate path for the process above:
- Step i): $\Delta U_1 = \int_{V_1}^{\infty} \left(\frac{\partial U}{\partial V}\right)_{T=T_1} dV$ - internal energy change due to volume change at constant temperature (this term is 0 for an ideal gas)
- Step ii): $\Delta U_2 = \int_{T_1}^{T_2} N\bar{C}_v^*(T)\, dT$
- Step iii): $\Delta U_3 = \int_{\infty}^{V_2} \left(\frac{\partial U}{\partial V}\right)_{T=T_2} dV$
- See state variable diagram

Computation of internal energy changes for nonideal gases: changes in T and V

- Consider again the van der Waals gas:

$$\begin{aligned}\Delta U_1 &= \int_{V_1}^{\infty} \left(\frac{\partial U}{\partial V}\right)_{T=T_1} dV \\ &= \int_{V_1}^{\infty} \frac{a}{\bar{V}^2}\, dV \\ &= \frac{N^2 a}{V_1}\end{aligned}$$

- $\Delta U_2 = \int_{T_1}^{T_2} N\bar{C}_v^*(T)\, dT$
- $$\begin{aligned}\Delta U_3 &= \int_{\infty}^{V_2} \left(\frac{\partial U}{\partial V}\right)_{T=T_2} dV \\ &= \int_{\infty}^{V_2} \frac{a}{\bar{V}^2}\, dV \\ &= -\frac{N^2 a}{V_2}\end{aligned}$$
- $\Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3$

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- Note for the latter, we need to consider details of the path; the calculations can be a little more complicated
- However, recall that for isobaric processes, we applied $Q = \Delta H$. We may revisit these problems later
- On the homework, you are studying changes in thermodynamic potentials for isobaric processes, which are diagonal lines on V, T plots

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- You can apply same principles we learned to calculate ΔG's for real gases
- We will study practical applications of ΔG shortly.

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- Thurs Dec 6th: Working on practice problem set in class

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- Note that if we specify P, T for a van der Waals equation of state, V is not uniquely determined - there are in fact multiple solutions for $\bar{V}$. See $P\bar{V}$ diagram of a vdW isotherm

Equations of state of real gases and appearance of a second phase

- Recall we said that if we specify any two state variables of a system, the third is determined by the state equation
- For the ideal gas law $PV = NRT$, we can see that the state equation *uniquely* determines the third state variable
- We have previously looked at isotherms of ideal gases (e.g., for isothermal expansions)
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- Note that if we specify P, T for a van der Waals equation of state, V is not uniquely determined - there are in fact multiple solutions for $\bar{V}$. See $P\bar{V}$ diagram of a vdW isotherm
- How can we explain multiple solutions for $\bar{V}$ by just looking at the state equation?

Equations of state of real gases and vapor-liquid equilibria

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- Above a critical temperature T_c, there is only one viable solution for $\bar{V}$ given P, T and the liquid phase no longer coexists above this temperature

Understanding the shape of isotherms for a van der Waals gas

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

- To understand shape of vdW isotherms, look at the derivative (slope). $P = P(T, V)$ so we need a partial derivative

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Finding critical points of real gases

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- With these two equations, we can find two unknowns $\bar{V}_c, T_c$ given the equation of state of the gas, i.e., the vdW equation with a, b specified. Exercise with solving such equations.

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- Now solve for T_c by substituting $\bar{V}_c$ into the solution to the first equation:

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- So we have obtained $\bar{V}_c, T_c$ in terms of the parameters a, b of the gas. Can find P_c from equation of state

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- **Problem type 2: How to find a, b given $P_c, \bar{V}_c, T_c$ of a real gas from experimental measurements?**

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vdW isotherms

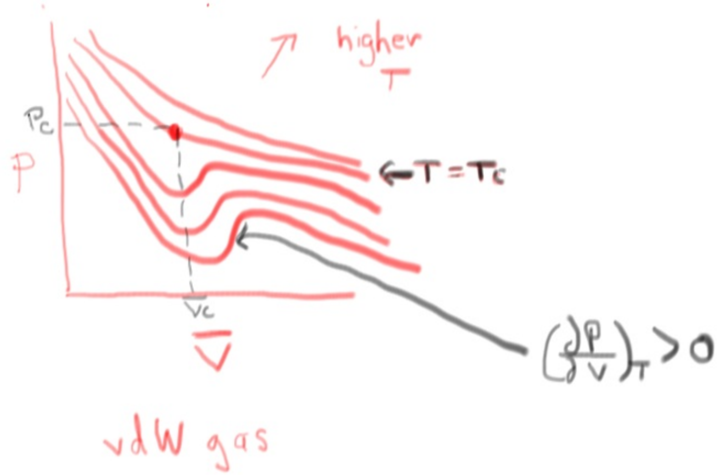

Figure :

Generalized equations of state

- Inserting these expressions for a, b in terms of $\bar{V}_c, T_c$ into the vdW equation we can rewrite the eqn in terms of $\bar{V}_c, T_c$, or using the shorthand notation for *relative state variables* $T_r \equiv \frac{T}{T_c},\ P_r \equiv \frac{P}{P_c},\ \bar{V}_r = \frac{\bar{V}}{\bar{V}_c}$, as

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Corresponding states

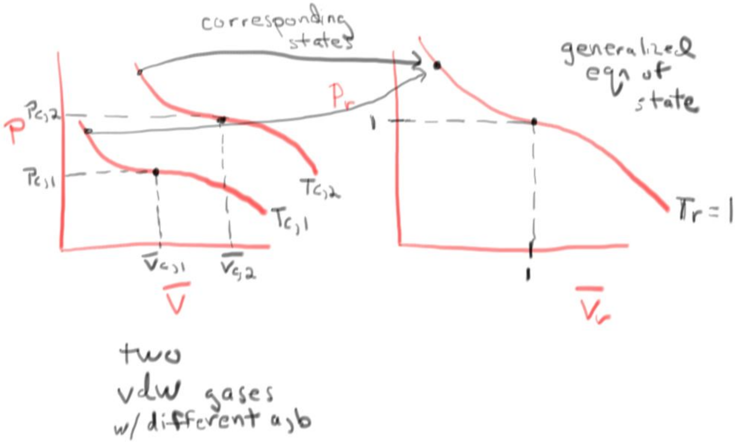

Figure :

Critical points of real gases (cont'd)

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- Solve for $\bar{V}_2$, T_2 from these equations and then P_2 from equation of state

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Outline

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Phase coexistence line

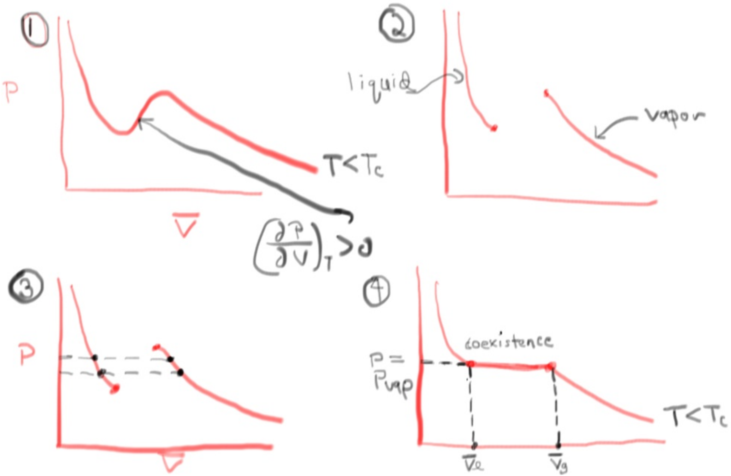
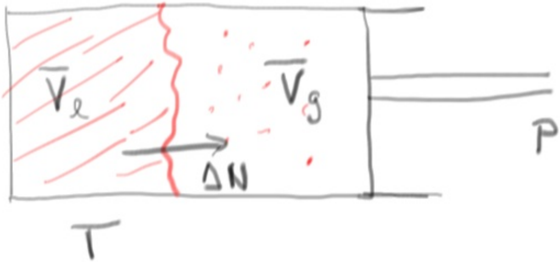


Figure :

Phase equilibrium



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- We haven't previously discussed equilibrium with respect to flow of mass

Phase equilibrium problems

- *Phase coexistence* means equilibrium with respect to mass transfer between liquid, gas subsystems at a given P, T
- Above P_{vap}, only liquid; below P_{vap}, only gas - two phases cannot exist at equilibrium
- To place the line, we need some quantitative way of understanding the conditions for phase equilibrium
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- **Material for midterm ends here**

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- $\bar{G}(T, P)$ is the appropriate intensive variable:

$$\bar{G}_a(T, P) = \bar{G}_b(T, P)$$

  sets P_{vap}. These are either tabulated or can be computed from equations of state. If $\bar{G}_a > \bar{G}_b$, material flows from a to b.

Gibbs free energy and phase equilibrium

- Why the Gibbs free energy? Recall that for processes without mass flow

$$\begin{aligned} dG &= dU + d(PV) - d(TS) \\ dG &= dU + PdV + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

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- Just like T, P, $\bar{G}$ is an intensive variable associated with a certain type of equilibrium - here it is phase equilibrium. N is the extensive variable.

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- Note that the above expression can be used to show that mass flows from a to b when $\bar{G}_a > \bar{G}_b$, and that no mass flows when $\bar{G}_a = \bar{G}_b$, thus deriving these results

Outline

1. What is Thermodynamics?
2. Some Thermodynamics Terminology
3. Basic concepts of thermodynamics
4. Thermodynamic equations of state
5. Conservation of Mass
6. Integral formulation of mass balance
7. Multicomponent mass balance
8. Conservation of energy
    - Energy balance
9. Towards the 2nd Law of Thermodynamics
10. Toward engineering applications: thermodynamic cycles and heat engines
11. Thermodynamic properties of real substances (not ideal gases)
    - Computation of heat and work for thermodynamic processes involving nonideal substances
    - Computation of entropy changes for thermodynamic processes involving nonideal substances
12. Outline of remaining topics and schedule
13. Further analysis of the behavior of real gases
14. Phase equilibrium
15. **More on Gibbs free energy and applications to phase equilibrium**

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- ΔS_{extra} originates due to some chemical process, like phase equilibrium, occurring within the system (container). It is usually not given to us directly.

Phase equilibrium

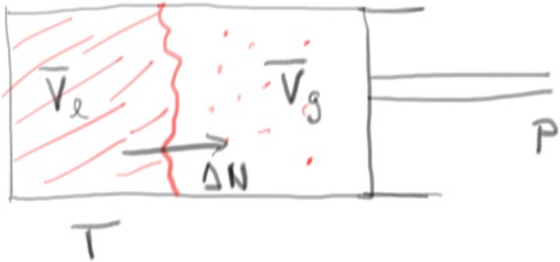

Figure :

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- So we see that $-\frac{\Delta G}{T}$ for a process at constant T, P equals ΔS_{extra}. $\Delta S_{tot} = \Delta S_{extra}$ because heat transfer at constant T does not contribute to total entropy.

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- ΔG associated with passage of ΔN_a moles of liquid into the vapor phase subtracts off the contribution from $\Delta S_{sys,heat}$ since it is isothermal heat and cannot contribute to the driving force for the process:

  $$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ \Delta N_a(\bar{G}_a - \bar{G}_b)a &= \Delta N_a(\bar{H}_a - \bar{H}_b) - T\Delta N_a(\bar{S}_{a,heat} - \bar{S}_{b,heat}) - T\Delta N_a(\bar{S}_{a,extra} - \bar{S}_{b,extra}) \\ &= -T\Delta N_a(\bar{S}_{a,extra} - \bar{S}_{b,extra}) \end{aligned}$$

  So we have successfully isolated the contribution from the extra entropy, which is the driving force for equilibration

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Application to phase equilibrium (cont'd)

$$\begin{aligned}
\Delta G &= \Delta H - T\Delta S \\
\Delta N_a(\bar{G}_a - \bar{G}_b) &= \Delta N_a(\bar{H}_a - \bar{H}_b) - T\Delta N(\bar{S}_{a,heat} - \bar{S}_{b,heat}) - T\Delta N(\bar{S}_{a,extra} - \bar{S}_{b,extra}) \\
&= -T\Delta N_a(\bar{S}_{a,extra} - \bar{S}_{b,extra})
\end{aligned}$$

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- All the above expressions can be written in terms of dN, and hence dG rather than ΔN and ΔG 5

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- E.g., for an isothermal/isovolumetric path,

$$\begin{aligned} \Delta U &= \Delta U_1 + \Delta U_2 \\ &= \int_{V_1}^{V_2} T\left(\frac{\partial P}{\partial T}\right)_V - P\ dV + \int_{T_1}^{T_2} N\bar{C}_v dT \\ Q &= \Delta U + P\Delta V \end{aligned}$$

- Note that $Q = \Delta H$ for the isobaric process - a shortcut!