

Chemistry 163B Winter 2020
Lectures 2-3 Heat and Work

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Lectures 2-3

Heat and Work

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Menu: for TODAY(s)



- Heat (q), Work (w) and the First Law of Thermodynamics
 $\Delta U \equiv q + w$
- Example calculations of q , w , U for reversible and irreversible expansions of ideal gas (*comparisons and 'take home messages'*)
- Molecular picture of heat and work energy transfers


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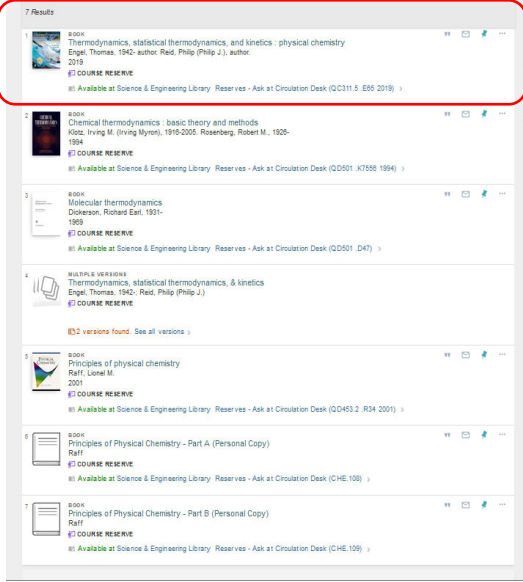
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Chemistry 163B reserve books 2020 (S&E Library)  handout #2





7 Results

- book: Thermodynamics, statistical thermodynamics, and kinetics : physical chemistry
Engel, Thomas, 1942- author; Reid, Philip J., author.
2019
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Available at Science & Engineering Library - Reserves - Ask at Circulation Desk (QD311.5 .E85 2019) >
- book: Chemical thermodynamics : basic theory and methods
Klotz, Irving M. (Irving Myron), 1916-2005; Rosenberg, Robert M., 1926-1994
COURSE RESERVE
Available at Science & Engineering Library - Reserves - Ask at Circulation Desk (QD501 .K7558 1994) >
- book: Molecular thermodynamics
Dickerson, Richard Earl, 1931-1989
COURSE RESERVE
Available at Science & Engineering Library - Reserves - Ask at Circulation Desk (QD501 .D47) >
- work in progress: Thermodynamics, statistical thermodynamics, & kinetics
Engel, Thomas, 1942-; Reid, Philip (Philip J.)
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2 versions found. See all versions >
- book: Principles of physical chemistry
Raff, Lionel M.
2001
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- book: Principles of Physical Chemistry - Part A (Personal Copy)
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a few definitions ,etc. to get us going 

- **df** is 'differential' representing an infinitesimal change
- **to calculate Δf** a finite change $\Delta f = \int_{initial}^{final} df$ 
- if **f** is a state function, the integral around a closed (cyclic) path (finish=start) is

$$\oint df = 0$$


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a few "FACTS OF (thermodynamic) LIFE"



- if the 'system' goes from one state to another by differing paths

initial state \rightarrow final state



- the change in some aspect of the system can either be
 - independent** of the path taken
(depends only on the initial and final values of the state variables)
 - or**
 - depend on** the path taken

if change is path **independent** \Rightarrow exact differential,
there is underlying **STATE FUNCTION**

if change is path **dependent** \Rightarrow inexact differential,
no underlying property of the state of system

more in Lecture #5 (math !!)

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all transfers of energy can be classified as heat (q) or work (w)

We will see (and demonstrate):



- heat (q) and work (w) are **NOT PROPERTIES** of a system but correspond to **TRANSFERS** of energy into (+)_{sys} or out of (-)_{sys} the system
[e.g. there is no underlying property "heat" of a system]
- when a system goes from an initial to a final state,
e.g. $(P_i, V_i, T_i) \Rightarrow (P_f, V_f, T_f)$ the values of **q** and **w** will **DEPEND ON THE PATH** taken between the states
- a small changes in a **path-dependent** quantities are **INEXACT DIFFERENTIALS** indicated by e.g. δq and δw

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the **FIRST LAW** of thermodynamics E&R_{4th} pp.30, 39-41

- **U** is symbol for **INTERNAL ENERGY** of a system
- $\Delta U = q + w$; $dU = \delta q + \delta w + \sum \dots dn_i$ dn_i=0 closed system, ignore for now
- $\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$ (conservation of energy)
- **U** is state function
- ΔU does not depend on path
(only on initial and final states)
- **dU** is an exact differential

equivalent statements

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heat capacity (E&R section 2.11)_[4th]

- $\frac{\delta q}{dT} = C$ heat capacity [$J K^{-1}$] extensive
the amount (transfer) of heat required to raise substance 1K
- $\frac{\delta q}{dT} = n\bar{C}$ molar heat capacity [$J mol^{-1} K^{-1}$] intensive
the amount (transfer) of heat requires to raise 1 mol substance 1K

\bar{C} generally depends on T and conditions
for example ideal monatomic gas

molar heat capacity at constant volume $\bar{C}_V = \frac{3}{2}R$
molar heat capacity at constant pressure $\bar{C}_P = \frac{5}{2}R$ ≠

$E = \frac{3}{2}nRT$ (true!!) but why does it take more heat to raise T at constant P than at constant V ??

stay tuned!!

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transfers of energy: **HEAT** and work (sec 2.2) [4th]

change of energy by heat transfer

$$\begin{aligned} \delta q &= C dT = n\bar{C}dT && (C \text{ is extensive,} \\ q &= \int_{\text{path}} \delta q = \int_{\text{path}} n\bar{C}dT && (\bar{C} \text{ is intensive}) \end{aligned}$$

\bar{C} will generally depend on T and path
(i.e. conditions)

$q > 0 \Rightarrow$ energy (heat) gained by system
(endothermic) cools surroundings



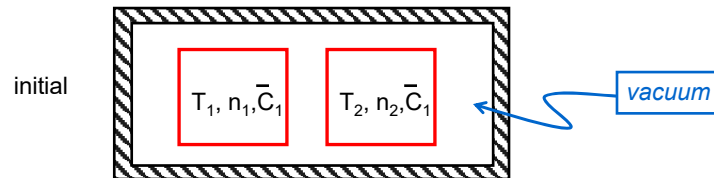
$q < 0 \Rightarrow$ energy (heat) lost by system
(exothermic) warms surroundings



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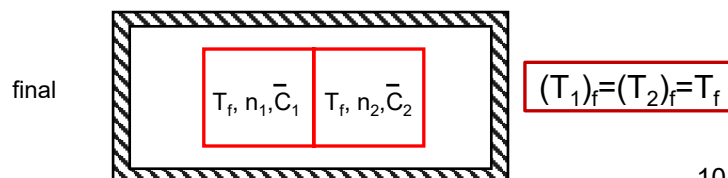
heat only transfer; thermal equilibrium (also zeroth law; E&R p11) [4th]



$$\begin{aligned} dq_1 &= n_1 \bar{C}_1 dT_1 && dq_2 = n_2 \bar{C}_2 dT_2 \\ &\text{assume } \bar{C}'\text{s independent of } T \end{aligned}$$

$$q_1 = \int_{T_1}^{T_f} n_1 \bar{C}_1 dT = n_1 \bar{C}_1 (T_f - T_1) \quad q_2 = \int_{T_2}^{T_f} n_2 \bar{C}_2 dT = n_2 \bar{C}_2 (T_f - T_2)$$

$$q_1 + q_2 = 0 \Rightarrow T_f = T_1 + \frac{n_2 \bar{C}_2 (T_2 - T_1)}{n_1 \bar{C}_1 + n_2 \bar{C}_2}$$



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*transfers of energy: heat and **WORK** (sec. 2.3) [4th]*

change of energy by work done ON system

energy into system

$$\dot{w} = \dot{w}_{PV} + \dot{w}_{other}$$

e.g. electrical, gravitational, etc.

derive in a moment.

$$\dot{w}_{PV} = -P_{ext} dV$$

$$w_{PV} = \int_{path} \dot{w}_{PV} = \int_{path} -P_{ext} dV$$

$w > 0 \Rightarrow$ energy gained by system
(work done ON system)

$w < 0 \Rightarrow$ energy lost by system
(work done ON surroundings)

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processes: definitions of constraints

- *isolated* $q=0; w=0$
- *isothermal* $\Delta T=0$
- *adiabatic* $q=0$
- *“against constant pressure”* $P_{ext} = \text{const}$
- *reversible process* $P_{int} = P_{ext}$
a (ideal) process that proceeds so slowly that an infinitesimal change of conditions causes the process to proceed in the opposite (reverse) direction
- *irreversible process*
all other (real) processes proceeding at finite rate

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derivation of $w = -P\Delta V$ (work of expansion or PV work)

w_{surr}^* = work done **ON SURROUNDINGS**

$P = \frac{F}{A}$
 (a) Initial state

$P = \frac{F}{A}$
 (b) Final state

- pressure = force/area
 $P = F/A$; $F = P \times A$
- $\Delta V = A \times \Delta h$
- $w_{\text{surr}}^* = \text{Force} \times \text{Distance}$
- $w_{\text{surr}}^* = F \times \Delta h$
- $w_{\text{surr}}^* = P \times A \times \Delta h$
- $w_{\text{surr}}^* = P \times \Delta V = P\Delta V$
- ~~want $w =$ work **ON SYSTEM**~~
- $w = - P\Delta V$
to be consistent with work done **ON** system

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ideal gas and energy, heat, work

for IDEAL GAS

- $U(\equiv E)$ depends ONLY on T (*ideal gas, previous class*)
- isothermal, $\Delta T = 0$,
 - $\Delta U = 0 = q + w$ (*ideal gas*)
 - $q = -w$
- adiabatic: $q = 0$, $\Delta U = w$ (*in general*)
- **monatomic ideal gas**
 - $U = (3/2) n RT$
 - $C_V = (3/2) n R$ (*~ prove later*)
 - $C_P = (5/2) n R$ (*prove later*)

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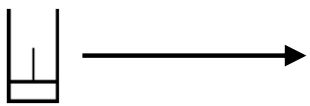
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work of expansion ideal gas (3 conditions)

P= 10atm
1 mol
T=T_{initial}
V_i = RT_i / 10atm



P= 1 atm
1 mol
T=T_{final}
V_f=RT_f/1atm

- isothermal against constant P_{ext}
- adiabatic against constant P_{ext}
- isothermal reversible
- ~~adiabatic reversible~~ (later)

why ??

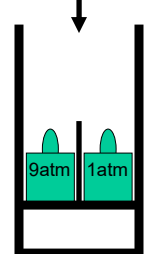
- understanding of thermodynamic conditions
- how to calculate $w = -\int P dv$
- compare w_{rev} vs w_{irrev}
- AND lots of 'rewards' on HW and EXAMS

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Pres system is gas inside piston; weights are surrounding gainst

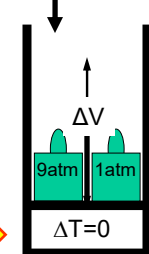
P=10 atm



isothermal $\Delta T=0$

expansion

P_{ext}=1 atm



isothermal expansion against constant pressure (irreversible)

- system is piston and gas inside; weights represent external pressure of surroundings
- P_{ext}=1atm (during volume change) ; $\Delta V_{sys} > 0$; $w_{sys} = - P \Delta V_{sys} < 0$
- work (<0) is done **BY SYSTEM ON SURROUNDINGS** (1 atm weight lifted)
- E for ideal gas depends only on T

isothermal ideal gas $\Delta T=0 \Rightarrow \Delta U=0$ since $w < 0$; $q = -w > 0$; **heat absorbed by system**

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Pressure **system is gas inside piston; weights are surrounding** against

adiabatic $q=0$

adiabatic expansion against constant pressure (irreversible)

- system is piston and gas inside; weights represent external pressure of surroundings
- $P_{\text{ext}}=1\text{atm}$ (during volume change); $\Delta V_{\text{sys}} > 0$; $w_{\text{sys}} = -P_{\text{ext}} \Delta V_{\text{sys}} < 0$
- work (<0) is done **BY SYSTEM ON SURROUNDINGS** (1 atm weight lifted)
- $w < 0$; $q=0$ (adiabatic); $E_{\text{sys}} (=U_{\text{sys}}) < 0$;
energy (potential) of surroundings increases \Rightarrow energy of system decreases \Rightarrow gas cools $\Delta T < 0$

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Pressure-Volume work **reversible expansion**

isothermal $\Delta T=0$
reversible

- w on surr **rev** $>$ w on surr **irrev** (more weights raised in irrev)
- $w = -\int P_{\text{ext}} dV$
- $P_{\text{ext}} = P_{\text{int}} = nRT/V \Rightarrow w = -\int nRT/V dV$
- isothermal $\Rightarrow T = \text{const} \Rightarrow w = -nRT \int dV/V$
 $w = -nRT \ln(V_{\text{final}}/V_{\text{initial}})$

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w_{other} (E & R p. 32)_{4th} Table 2.1 Types of Work

change of energy by work done ON system

$$d\bar{w} = d\bar{w}_{PV} + d\bar{w}_{other}$$

$$d\bar{w} = -P_{ext} dV + d\bar{w}_{other}$$

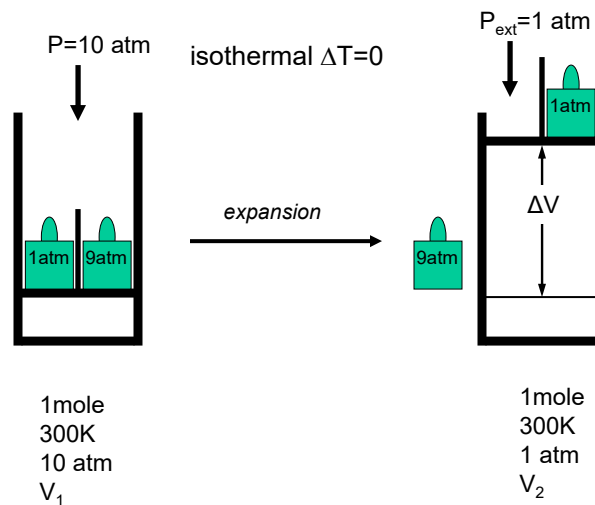
$$w = \int -P_{ext} dV + \int d\bar{w}_{other}$$

Types of Work	Variables, System definition	Equation for System-Based Work	SI Units
Gas expansion and compression	Pressure in the surroundings at the system-surroundings boundary (P_{ext}), volume (V) The gas is the system.	$-\int_{V_i}^{V_f} P_{ext} dV$	Pa m ³ = J
Spring stretching and compression	Force (F), distance (x) The spring is the system.	$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{x}$	N m = J
Bubble expansion and contraction	Surface tension (γ), surface area (σ) The content of the bubble is the system.	$w = -\int_{\sigma_i}^{\sigma_f} \gamma d\sigma$	(N m ⁻¹) (m ²) = J
Current passes through conductor	Electrical potential difference (ϕ), electrical charge (Q) The conductor is the system.	$w = \int_0^Q \phi dQ'$	V C = J
Done lifting a weight against gravity (weight is surroundings)	Mass (m), position (h)	$w = -\int_{h_i}^{h_f} m g dh$	kg m² s⁻² = J

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Isothermal expansion: $P_{ext} = \text{const}$ ideal gas (irreversible)



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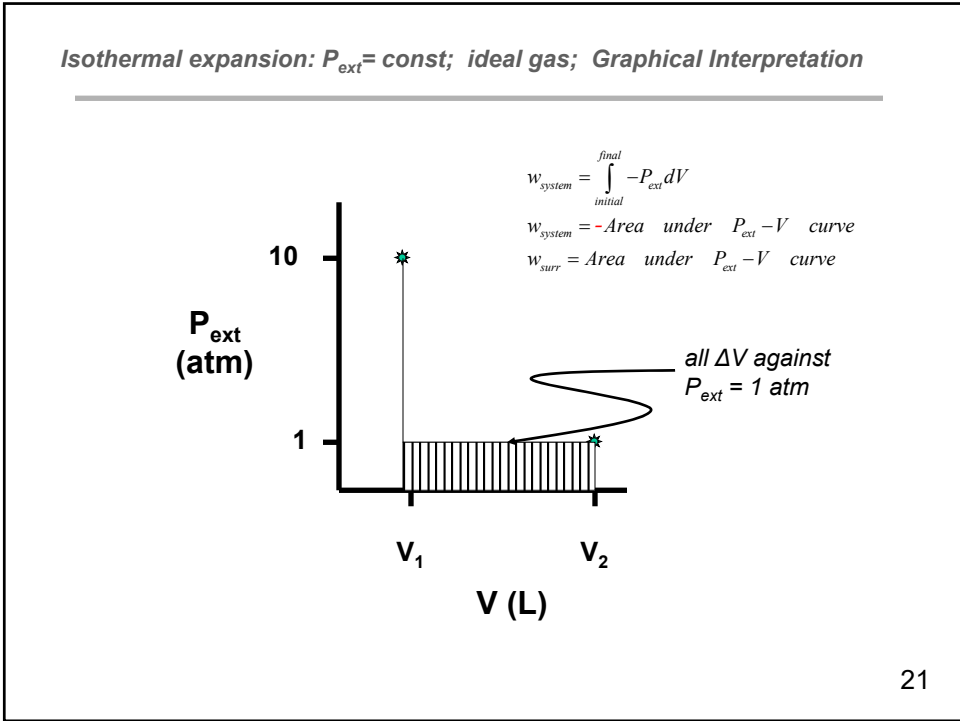
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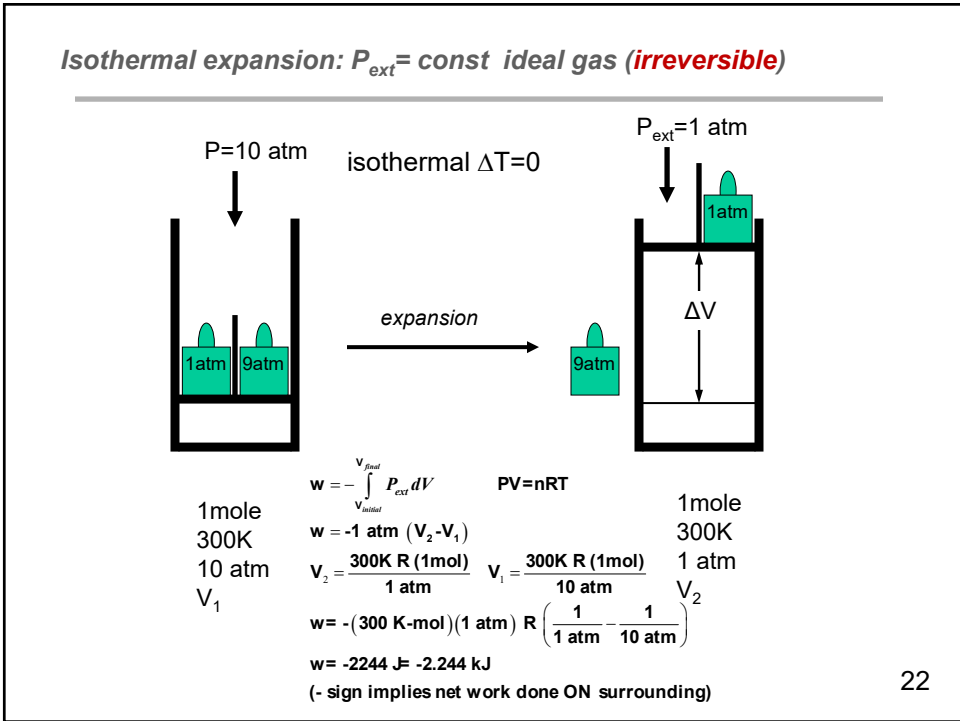
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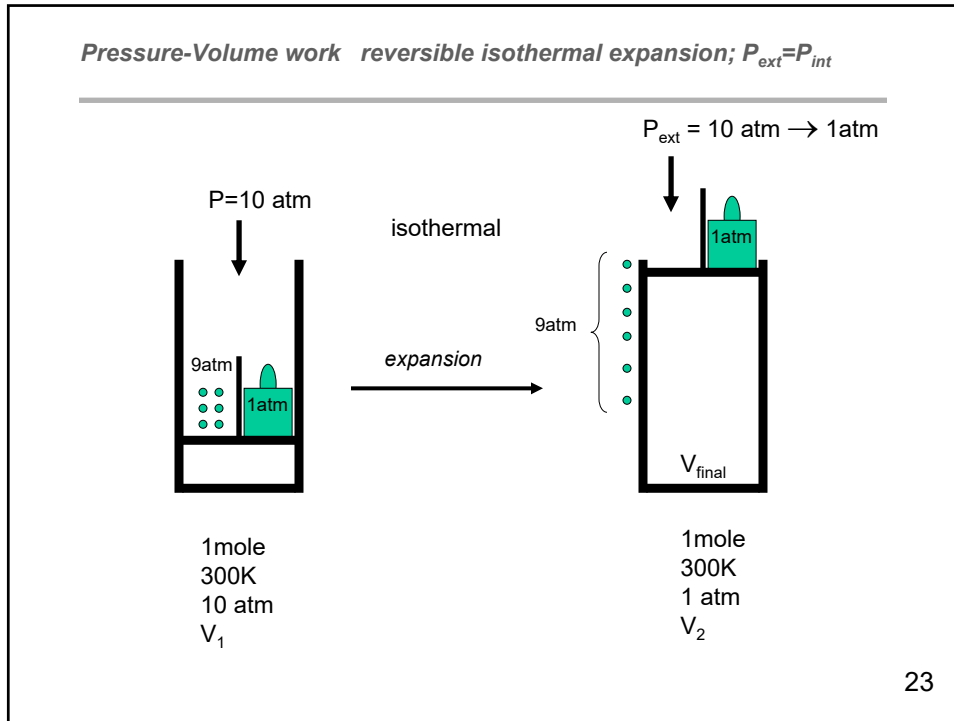


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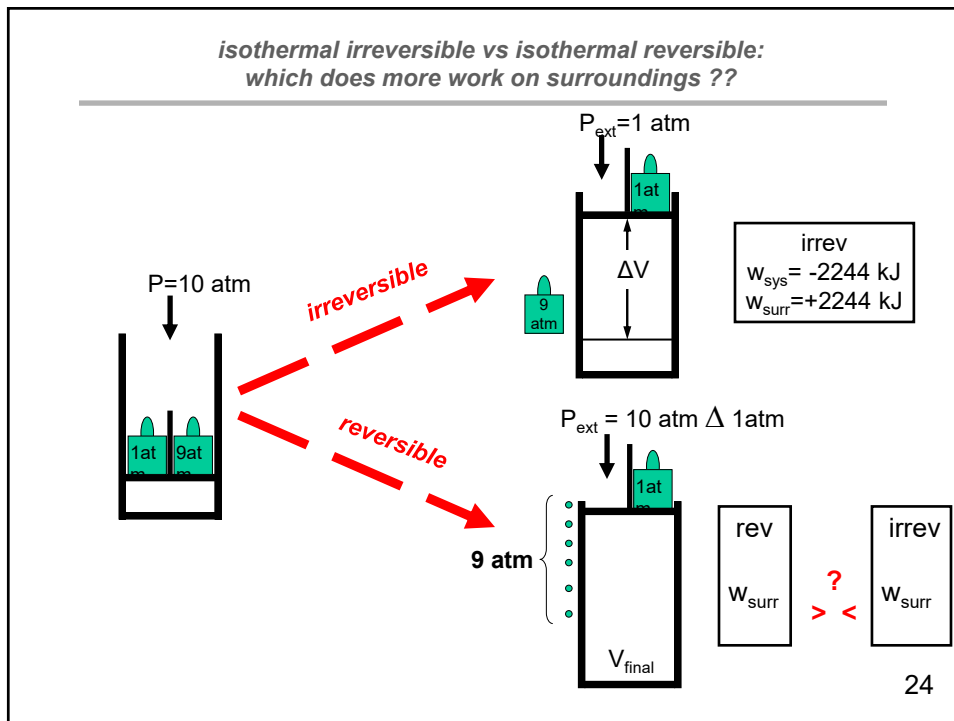


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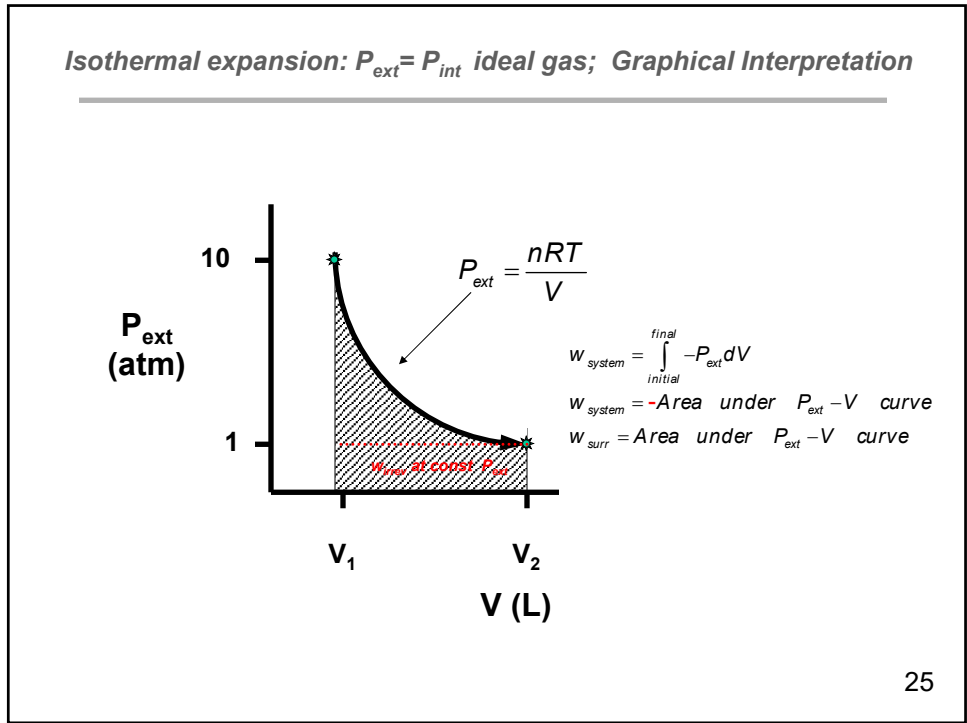


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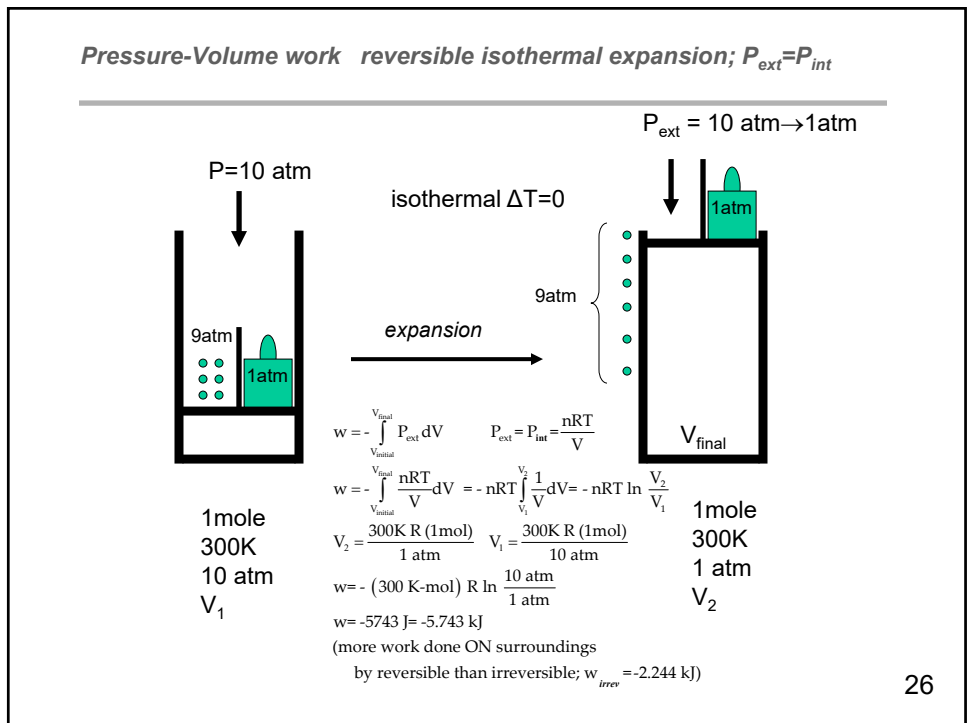


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Pressure-Volume work: irreversible adiabatic expansion $P_{\text{ext}} = \text{constant}$

adiabatic expansion against constant pressure (irreversible)

1 mole 300K 10 atm V_1	$\Delta U = 0 + w = -P_{\text{ext}}(V_2 - V_1) = -1 \text{ atm} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$ Will soon show holds for ideal gas $\Delta U = n\bar{C}_v \Delta T = \frac{3}{2} nR(T_2 - T_1)$ V NOT const $-1 \text{ atm} (1 \text{ mol}) R \left(\frac{T_2}{1 \text{ atm}} - \frac{300 \text{ K}}{10 \text{ atm}} \right) = \frac{3}{2} (1 \text{ mol}) R (T_2 - 300 \text{ K})$ brr! $T_2 = 192 \text{ K}$ $w = -1347 \text{ J} = -1.347 \text{ kJ}$	1 mole $T_2 ? \text{ K}$ 1 atm V_2
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no q in, less work done than isothermal (-2.244 kJ) 27

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molecular correlates of heat and work for ideal gas

- **total energy:**
sum of [number of particles in energy level (ν) \times energy of that level (ϵ)]
 $E = \sum_n \nu_n \epsilon_n$
- **heat only** (no work):
redistributes particles among levels
 $q > 0 \Rightarrow$ more particles to higher energy levels
 $q < 0 \Rightarrow$ more particles to lower energy levels
- **P-V work only** (adiabatic)
particle in 3D cube: **CHEM 163A DON'T FRET**
 $\epsilon_n \approx \frac{3h^2}{8mV^{2/3}} n^2$ where n is an integer (1, 2, ...)
 - larger volume ($w < 0$) \Rightarrow energy levels lower and get more closely spaced
 - smaller volume ($w > 0$) \Rightarrow energy levels higher and less closely spaced

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*molecular picture of heat and work:
constant volume heating (E&R p 44-45)^{4th}*

He gas in 10 nm 'box'; **0.2 K**

He gas in 10 nm 'box'; **0.3K**

heating of He, constant V
 $w = 0$; $q > 0$

1. energy levels same spacing: $\Delta V=0$, $w=0$ (no change in size of box)
2. greater number of atoms in higher energy levels: $q > 0$ raises U ;
3. $\Delta U > 0$ ($\Delta E > 0$)

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*molecular picture of heat and work:
reversible adiabatic expansion (E&R p Fig 2-10)^{4th}*

He gas in 8 nm 'box'; **0.31 K**

He gas in 10 nm 'box'; **0.2 K**

Arrows show how energy of each level decreases as length of box increases

- for **reversible adiabatic expansion** (no heat in) populations in levels do not change
- does total energy $E = \sum n_i \epsilon_i$ and thus temperature increase or **decrease** ??

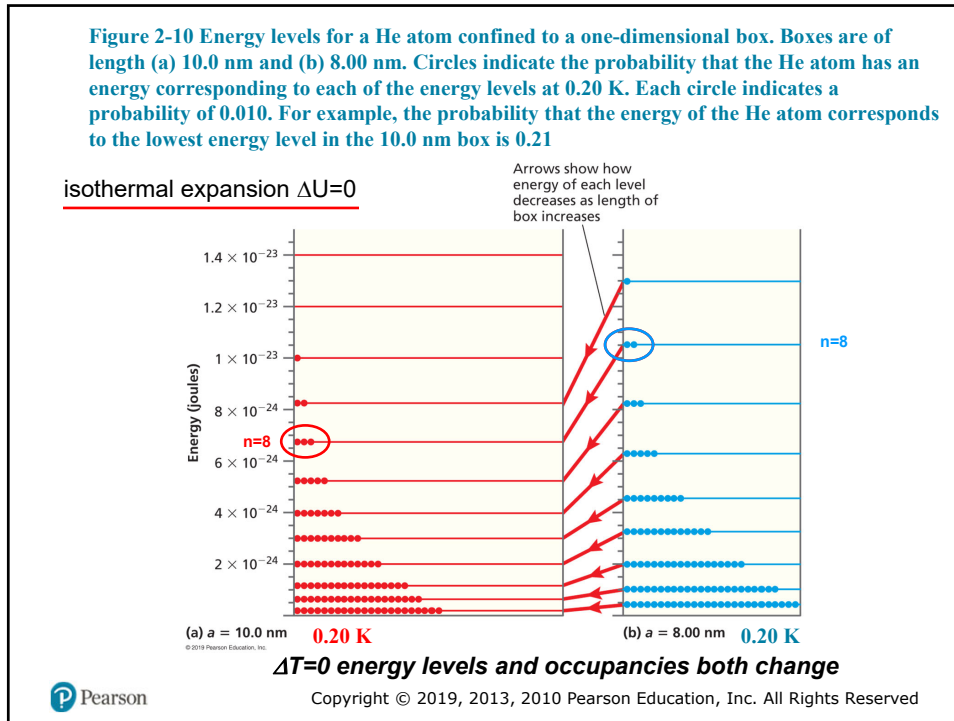
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Menu: for TODAY(s)

- ✓ **Heat (q), Work (w) and the First Law of Thermodynamics $\Delta U \equiv q + w$**
- ✓ **Example calculations of q, w, U for reversible and irreversible expansions of ideal gas (comparisons and 'take home messages')**
- ✓ **Molecular picture of heat and work energy transfers**

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End of
Lectures 2-3