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

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Lectures 2-3

Heat and Work

1

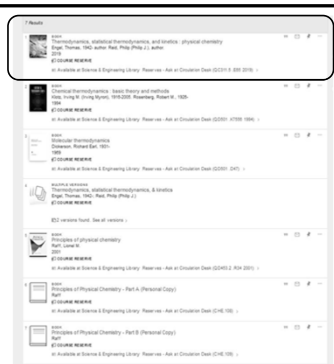
Menu: for TODAY(s)

- **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**

2

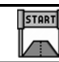
2

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



3

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

$$\oint df = 0$$

4

4

a few "FACTS OF (thermodynamic) LIFE"

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

initial state → 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** ⇒ exact differential, there is underlying **STATE FUNCTION**
- if change is path **dependent** ⇒ inexact differential, no underlying property of the state of system

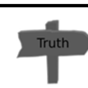
more in Lecture #5 (math !!)

5

5

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.* $\bar{d}q$ *and* $\bar{d}w$

6

6

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

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

- **U** is symbol for **INTERNAL ENERGY** of a system
- $\Delta U = q + w + \not{X}$; $dU = đq + đw + \not{\sum \ldots dn_i}$ (dn$_i$=0 closed system, *ignore for now*)
- $\Delta U_{sys} = -\Delta U_{surr}$ *(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

7

7

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

- $\frac{đq}{dT} = C$ *heat capacity* $[J\ K^{-1}]$ *extensive*

the amount (transfer) of heat required to raise substance 1K

- $\frac{đq}{dT} = n\bar{C}$ *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 $\bar{C}_P = \frac{5}{2}R$ $\neq$

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

8

8

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

change of energy by heat transfer

$đq = C\,dT = n\bar{C}\,dT$ (**C is extensive,**

$q = \int_{path} đq = \int_{path} n\bar{C}\,dT$ $\bar{C}$ **is intensive)**

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

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

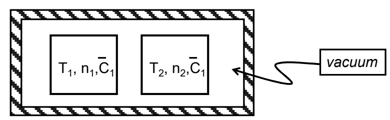
$q < 0 \Rightarrow$ **energy (heat) lost by system (exothermic)** warms surroundings

9

9

heat only transfer; thermal equlibrium (also zeroth law; E&R p11)$_{[4th]}$

initial



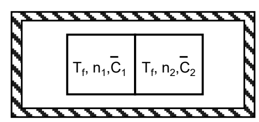
$đq_1 = n_1\bar{C}_1 dT_1$ $đq_2 = n_2\bar{C}_2 dT_2$

assume $\bar{C}$'s independent of T

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

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

final



$(T_1)_f = (T_2)_f = T_f$

10

10

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

change of energy by work done ON system

energy into system

$đw = đw_{PV} + đw_{other}$ (e.g. electrical, gravitational, etc.)

$đw_{PV} = -\underline{P_{ext}}\,dV$ (derive in a moment.)

$w_{PV} = \int_{path} đw_{PV} = \int_{path} -\underline{P_{ext}}\,dV$

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

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

11

11

processes: definitions of constraints

- *isolated* *q=0; w=0*
- *isothermal* *ΔT=0*
- *adiabatic* *q=0*
- *"against constant pressure"* P_{ext}= 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

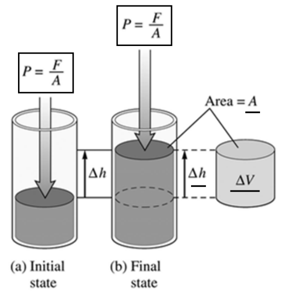
12

12

2

derivation of w = −PΔV (work of expansion or PV work)

w^*_{surr}= work done **ON SURROUNDINGS**



- pressure=~~force/area~~ P=F/A ; F= P × A
- ΔV= A × **Δh**
- w^*_{surr}= Force × Distance
- w^*_{surr}= F × **Δh**
- w^*_{surr}= P × A × **Δh**
- w^*_{surr}= P × ΔV=PΔV
- *want* w ≡ work **ON SYTEM**
- w= − PΔV to be consistent with work done **ON** system

13

13

ideal gas and energy, heat, work

for **IDEAL GAS**

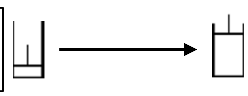
- U(≡E) depends ONLY on T *(ideal gas, previous class)*
- isothermal, ΔT=0,
  - ΔU=0=q+w *(ideal gas)*
  - q=-w
- adiabatic: q=0, ΔU=w *(in general)*
- monatomic ideal gas
  - U = (3/2) n RT
  - C_V= (3/2) n R *(~ prove later)*
  - C_P= (5/2) n R *(prove later)*

14

14

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

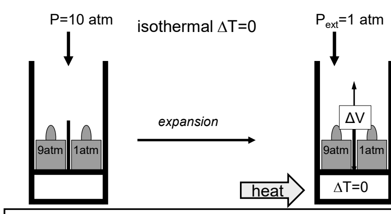
- isothermal against constant P_{ext}
- adiabatic against constant P_{ext}
- isothermal reversible
- ~~adiabatic reversible~~ *(later)*

why ??
- understanding of thermodynamic conditions
- how to calculate w=-∫ *Pdv*
- compare w_{rev} vs w_{irrev}
- AND lots of 'rewards' on HW and EXAMS

15

15

Pres... system is gas inside piston; weights are surrounding ...gainst



isothermal expansion against constant pressure (irreversible)

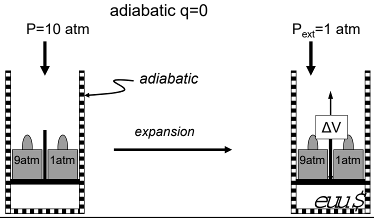
- system is piston and gas inside; weights represent external pressure of surroundings
- P_{ext}=1atm *(during volume change)* ; ΔV_{sys} > 0; w_{sys}= - P ΔV_{sys} < 0
- work (<0) is done **BY SYSTEM ON SURROUNDINGS** (1 atm weight lifted)
- E for ideal gas depends only on T
  isothermal ideal gas ΔT=0 ⇒ ΔU=0 since w< 0; q= −w > 0 ; heat absorbed by system

16

16

Pres... system is gas inside piston; weights are surrounding ...gainst

adiabatic q=0



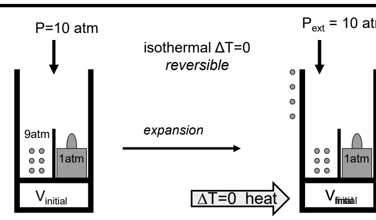
adiabatic expansion against constant pressure (irreversible)

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

17

17

Pressure-Volume work reversible expansion



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

18

18

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

change of energy by work done ON system

$$\text{đ}w = \text{đ}w_{PV} + \text{đ}w_{other}$$

$$\text{đ}w = -P_{ext}\,dV + \text{đ}w_{other}$$

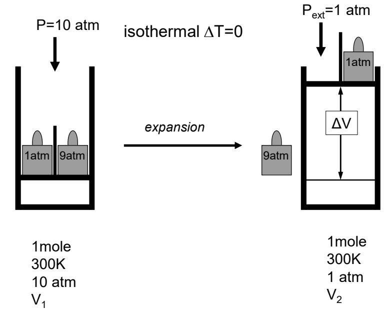
$$w = \int -P_{ext}\,dV + \int \text{đ}w_{other}$$

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 ($\mathbf{F}$), distance ($\mathbf{x}$) 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 m^2 s^{-2} = J**

19

19

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



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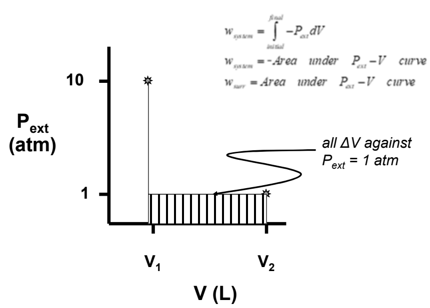
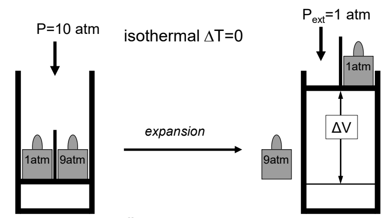
Isothermal expansion: P_{ext}= const; ideal gas; Graphical Interpretation



21

21

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



1mole
300K
10 atm
V_1

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}\,dV \qquad PV=nRT$$

$$w = -1\text{ atm}\,(V_2 - V_1)$$

$$V_2 = \frac{300\text{K R (1mol)}}{1\text{ atm}} \qquad V_1 = \frac{300\text{K R (1mol)}}{10\text{ atm}}$$

$$w = -(300\text{ K-mol})(1\text{ atm})\,R\left(\frac{1}{1\text{ atm}} - \frac{1}{10\text{ atm}}\right)$$

$$w = -2244\text{ J} = -2.244\text{ kJ}$$

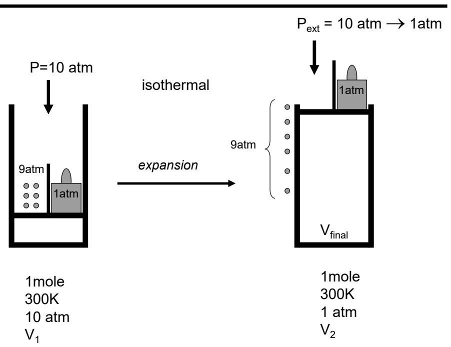
(- sign implies net work done ON surrounding)

1mole
300K
1 atm
V_2

22

22

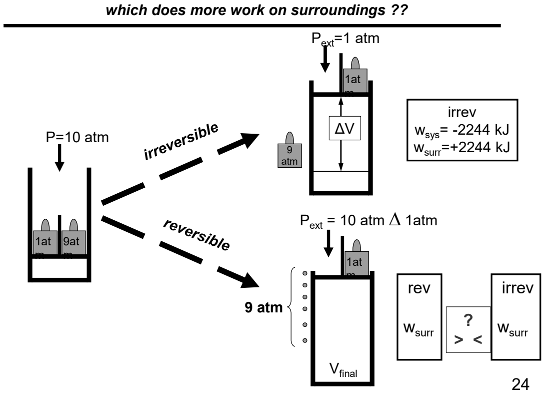
Pressure-Volume work reversible isothermal expansion; P_{ext}=P_{int}



23

23

isothermal irreversible vs isothermal reversible: which does more work on surroundings ??

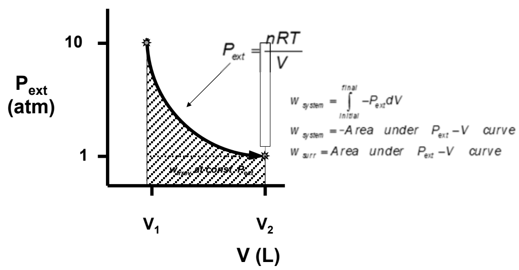


24

24

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

Isothermal expansion: $P_{ext}= P_{int}$ ideal gas; Graphical Interpretation



25

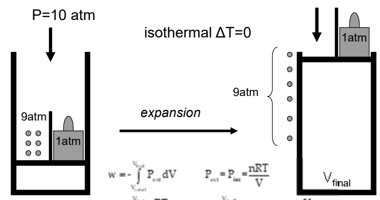
25

Pressure-Volume work reversible isothermal expansion; P_{ext}=P_{int}

P_{ext} = 10 atm→1atm

P=10 atm

isothermal ΔT=0



1mole
300K
10 atm
V_1

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}\, dV \qquad P_{ext} = P_{int} = \frac{nRT}{V}$$

$$w = -\int_{V_{initial}}^{V_{final}} \frac{nRT}{V} dV = -nRT\int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln\frac{V_2}{V_1}$$

$$V_2 = \frac{300K\ R\ (1mol)}{1\ atm} \qquad V_1 = \frac{300K\ R\ (1mol)}{10\ atm}$$

$$w = -(300\ K\text{-}mol)\ R \ln\frac{10\ atm}{1\ atm}$$

w= -5743 J= -5.743 kJ
(more work done ON surroundings
by reversible than irreversible; w_{irrev} = -2.244 kJ)

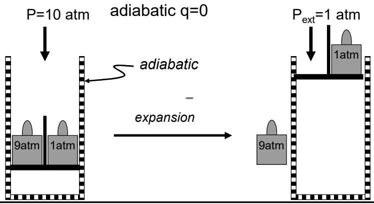
1mole
300K
1 atm
V_2

26

26

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

P=10 atm adiabatic q=0 P_{ext}=1 atm



adiabatic expansion against constant pressure (irreversible)

1mole
300K
10 atm
V_1

$$\Delta U = 0 + w = -P_{ext}(V_2 - V_1) = -1atm\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

Will soon show holds for ideal gas V **NOT** const $\Delta U = n\bar{C}_V \Delta T = \frac{3}{2} nR(T_2 - T_1)$

$$-1atm\ (1mol)\ R\left(\frac{T_2}{1atm} - \frac{300K}{10atm}\right) = \frac{3}{2}(1mol)R(T_2 - 300K)$$

brr! $T_2 = 192K \quad w = -1347\ J = -1.347\ kJ$

1mole
T_2 ? K
1 atm
V_2

no q in, less work done than isothermal ***(-2.244 kJ)*** 27

27

molecular correlates of heat and work for ideal gas

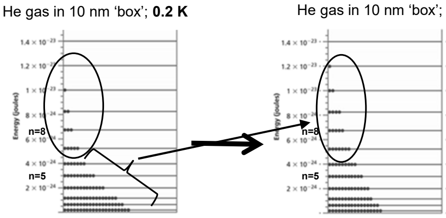
- **total energy:**
  sum of [number of particles in energy level (ν) × energy of that level (ε)]
  $E=\Sigma_n \nu_n \varepsilon_n$
- **heat only** (no work):
  redistributes particles among levels
  q>0 ⇒ more particles to higher energy levels
  q<0 ⇒ more particles to lower energy levels
- **P-V work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

28

28

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

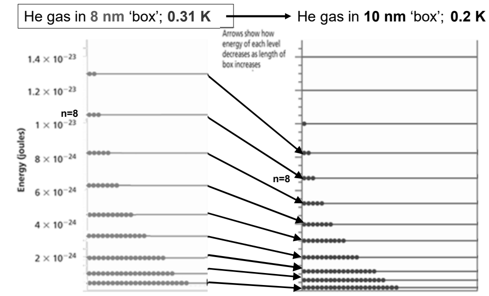
1. energy levels same spacing: *ΔV=0,* w=0 *(no change in size of box)*
2. *greater number of atoms in higher energy levels: q> 0 raises U;*
3. *ΔU>0 (ΔE>0)*

29

29

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**



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

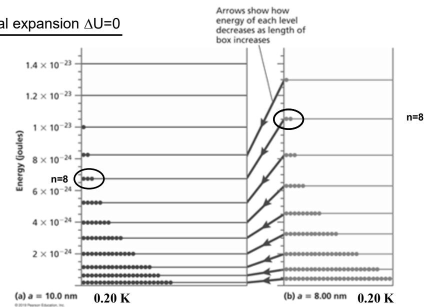
30

30

5

Figure 2-10 Energy levels for a He atom confined to a one-dimensional box. Boxes are of length (a) 10.0 nm and (b) 8.00 nm. Circles indicate the probability that the He atom has an energy corresponding to each of the energy levels at 0.20 K. Each circle indicates a probability of 0.010. For example, the probability that the energy of the He atom corresponds to the lowest energy level in the 10.0 nm box is 0.21

isothermal expansion $\Delta U=0$



$\Delta T=0$ energy levels and occupancies both change

31

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**

32

32

End of

Lectures 2-3

33