Chemistry 163B Winter 2014
Lectures 2-3 Heat and Work

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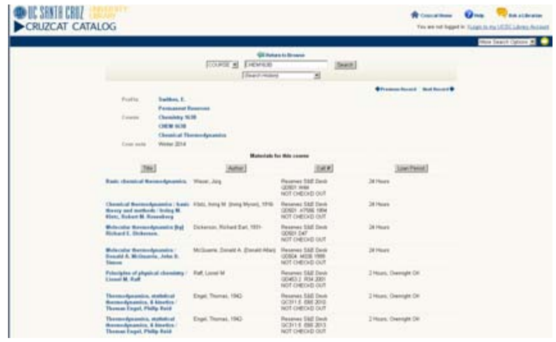
Heat and Work

Chemistry 163B reserve books 2014 (S&E Library) ⇨ *handout #7*



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heat capacity (E&R section 2.5)

$$\frac{đq}{dT} = C \qquad \textit{heat capacity } \left[J\ K^{-1}\right]$$

the amount of heat requires to raise substance 1K

$$\frac{đq}{dT} = n\bar{C} \qquad \textit{molar heat capacity } \left[J\ mol^{-1}\ K^{-1}\right]$$

the amount of heat requires to raise 1 mol substance 1K

$\bar{C}$ generally depends on T and conditions
for example ideal monatomic gas (independent of T) but
add heat at constant volume $\bar{C}_V = \frac{3}{2}R$
add heat at constant pressure $\bar{C}_P = \frac{5}{2}R$

3

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transfers of energy: **HEAT** *and work (sec 2.3)*

change of energy by heat transfer

$đq = CdT = n\bar{C}dT$ (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

q > 0 ⇒ energy (heat) gained by system (endothermic)

q < 0 ⇒ energy (heat) lost by system (exothermic)

4

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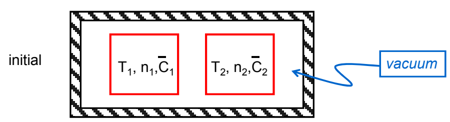
heat only transfer (also zeroth law; E&R p7)

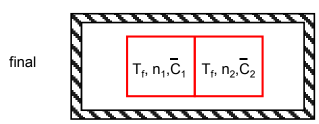


$$đq_1 = n_1\bar{C}_1 dT_1 \qquad đq_2 = n_2\bar{C}_2 dT_2$$

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

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

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



5

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transfers of energy: heat and **WORK** *(sec. 2.2)*

change of energy by work done ON system

$$đw = đw_{PV} + đw_{other}$$

$$đw_{PV} = -P_{ext}\,dV$$

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

w > 0 ⇒ energy gained by system (work done ON system)

w < 0 ⇒ energy lost by system (work done ON surroundings)

6

Chemistry 163B Winter 2014
Lectures 2-3 Heat and Work

processes: definitions of constraints

- *isolated* — *q=0; w=0*
- *isothermal* — *$\Delta T=0$*
- *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

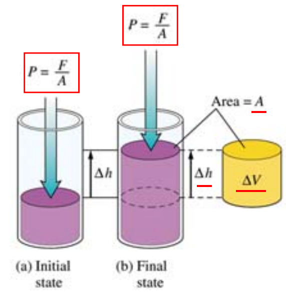
- *irreversible process*

  all other (real) processes proceeding at finite rate

7

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
- w = work **ON SYTEM**
- w= – PΔV
  to be consistent with work done **ON** system

8

ideal gas and energy, heat, work

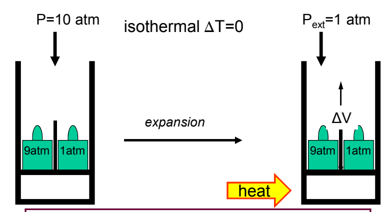
for **IDEAL GAS**

- U(E) depends ONLY on T
- isothermal, ΔT=0
  - ΔU=0=q+w
  - q=-w
- adiabatic q=0, ΔU=w
- monatomic ideal gas
  - U = (3/2) n RT
  - C_V= (3/2) n R
  - C_P= (5/2) n R

9

Pres... gainst

system is gas inside piston; weights are surrounding



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)
- *later (E for ideal gas depends only on T)*

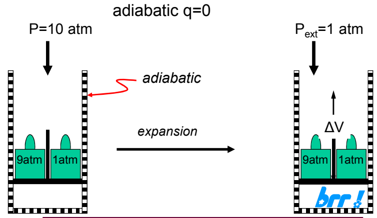
  isothermal ideal gas ΔT=0 ⟹ ΔU=0 w< 0; – w= q > 0 ; heat absorbed by system

10

Pres... gainst

system is gas inside piston; weights are surrounding

adiabatic q=0



adiabatic expansion against constant pressure

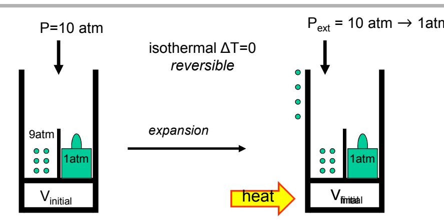
- system is piston and gas inside; weights represent external pressure of surroundings
- P_{ext}=1atm *(during volume change)*; ΔV_{sys} > 0; w_{sys}= - P_{ext} ΔV_{sys} < 0
- work (<0) is done **BY SYSTEM ON SURROUNDINGS** (1 atm weight lifted)
- *later (conservation of energy U)*

  w< 0; q=0 (adiabatic); U_{sys} < 0;

  energy (potential) of surroundings increases ⟹ energy of system decreases ⟹ gas cools

11

Pressure-Volume work reversible expansion



- w on surr rev > w on surr irrev
- w= - ∫ P_{ext}dV
- P_{ext} = P_{int} = nRT/ V ⇨ w= - ∫ nRT/ V dV
- isothermal ⇨T=const

  w = – nRT ln (V_{final}/$V_{initial}$)

12

w_{other} (E & R p. 20)

change of energy by work done ON system

$$đw = đw_{PV} + đw_{other}$$

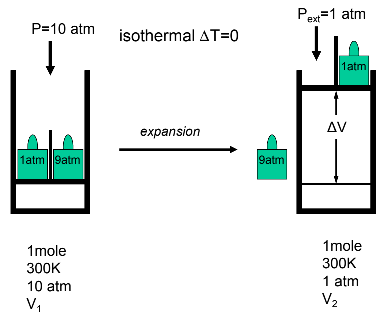
$$đw = -P_{ext}\,dV + đw_{other}$$

$$w = \int -P_{ext}\,dV + \int đw_{other}$$

TABLE 2.1 Types of Work

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int_{V_i}^{V_f} P_{external}\,dV$	Pa m³ = J
Stretching	Force (F), length (l)	$w = \int_{x_i}^{x_f} \mathbf{F}\cdot d\mathbf{l}$	N m = J
Surface expansion	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \gamma \cdot d\sigma$	($N m^{-1}$)(m^2) = J
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int_0^Q \phi\, dQ'$	V C = J
Done lifting a weight against gravity ***(weight is surroundings)***	**Mass (m), position (h)**	$w = -\int_{h_1}^{h_2} m\,g\,dh$	**kg m² s⁻² = J**

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

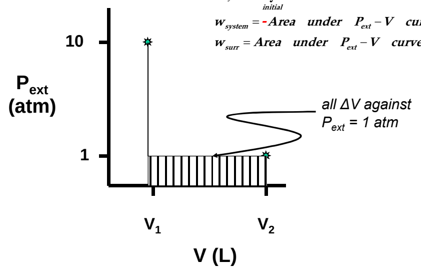


Isothermal expansion: P_{ext}= const; ideal gas; Graphical Interpretation

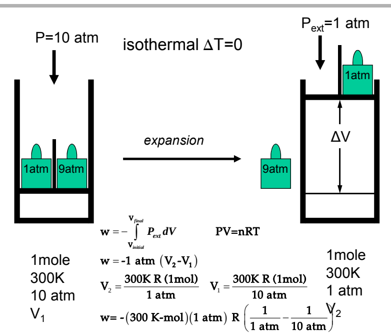
$$w_{system} = \int_{initial}^{final} -P_{ext}\,dV$$

$$w_{system} = -Area \;\; under \;\; P_{ext} - V \;\; curve$$

$$w_{surr} = Area \;\; under \;\; P_{ext} - V \;\; curve$$



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



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

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

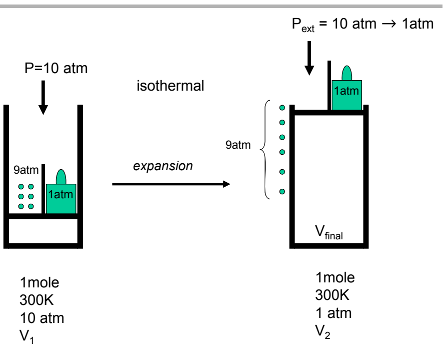
$$V_2 = \frac{300K\,R\,(1mol)}{1\text{ atm}} \qquad V_1 = \frac{300K\,R\,(1mol)}{10\text{ atm}}$$

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

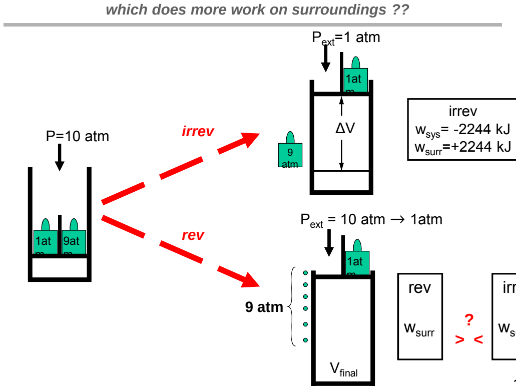
w= -2244 J= -2.244 kJ

(- sign implies net work done ON surrounding)

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

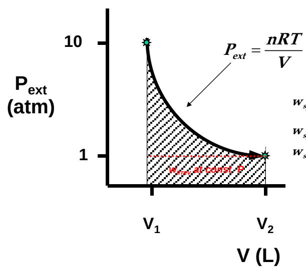


isothermal irreversible vs isothermal reversible: which does more work on surroundings ??



Chemistry 163B Winter 2014
Lectures 2-3 Heat and Work

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



$$w_{system} = \int_{initial}^{final} -P_{ext} dV$$

$$w_{system} = -Area \quad under \quad P_{ext} - V \quad curve$$

$$w_{surr} = Area \quad under \quad P_{ext} - V \quad curve$$

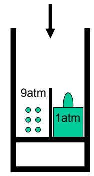
19

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

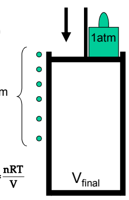
P_{ext} = 10 atm → 1atm

P=10 atm

isothermal ΔT=0



expansion



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

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

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

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

w= -5743 J= -5.743 kJ

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

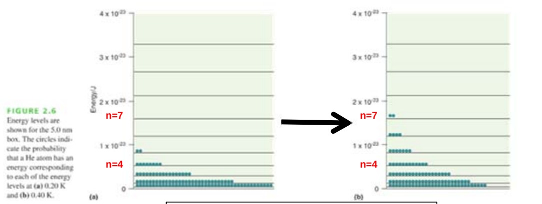
1mole
300K
10 atm
V_1

1mole
300K
1 atm
V_2

20

molecular picture of heat and work:
constant volume heating (E&R p 23-24)

He gas in 5 nm 'box'; 0.2 K — He gas in 5 nm 'box'; 0.4K



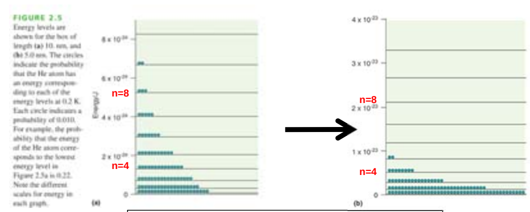
heating of He, constant V
w = 0; q > 0

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. $\Delta U>0$

21

molecular picture of heat and work:
isothermal compression (E&R p 23-24)

He gas in 10 nm 'box', 0.2K — He gas in 5 nm 'box', 0.2K



He, 0.2 K isothermal compression
w > 0; q <0

1. energy levels further apart for smaller 'box': $\Delta V<0$, w>0 , raises U
   (note E scale 10^{-24} J vs 10^{-23} J)
2. *greater number of atoms in relatively lower energy levels: q<0, lowers U;*
3. $\Delta U=0$

22

lectures next Wednesday-Friday [3X]
*(Monday 20th Jan **HOLIDAY**; exam Friday, 31st Jan)*

better make it a triple

23