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

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Lectures 2-3

Heat and Work

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Prof/ta	Switkes, E.
	Permanent Reserves
Course	Chemistry 163B
	CHEM 163B
	Chemical Thermodynamics
Cour note	Winter 2014

Materials for this course

Title	Author	Call #	Loan Period
Basic chemical thermodynamics.	Waser, Jürg.	Reserves S&E Desk QD501 .W44 NOT CHECKD OUT	24 Hours
Chemical thermodynamics : basic theory and methods / Irving M. Klotz, Robert M. Rosenberg	Klotz, Irving M. (Irving Myron), 1916-	Reserves S&E Desk QD501 .K7556 1994 NOT CHECKD OUT	24 Hours
Molecular thermodynamics [by] Richard E. Dickerson.	Dickerson, Richard Earl, 1931-	Reserves S&E Desk QD501 .D47 NOT CHECKD OUT	24 Hours
Molecular thermodynamics / Donald A. McQuarrie, John D. Simon	McQuarrie, Donald A. (Donald Allan)	Reserves S&E Desk QD504 .M335 1999 NOT CHECKD OUT	24 Hours
Principles of physical chemistry / Lionel M. Raff	Raff, Lionel M	Reserves S&E Desk QD453.2 .R34 2001 NOT CHECKD OUT	2 Hours; Overnight OK
Thermodynamics, statistical thermodynamics, & kinetics / Thomas Engel, Philip Reid	Engel, Thomas, 1942-	Reserves S&E Desk QC311.5 .E65 2010 NOT CHECKD OUT	2 Hours; Overnight OK
Thermodynamics, statistical thermodynamics, & kinetics / Thomas Engel, Philip Reid	Engel, Thomas, 1942-	Reserves S&E Desk QC311.5 .E65 2013 NOT CHECKD OUT	2 Hours; Overnight OK

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heat capacity (E&R section 2.5)

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

the amount of heat requires to raise substance 1K

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

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* $\bar{C}_P = \frac{5}{2}R$

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transfers of energy: HEAT and work (sec 2.3)

change of energy by heat transfer

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

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

$\bar{C}$ will generally depend on T and path

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

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

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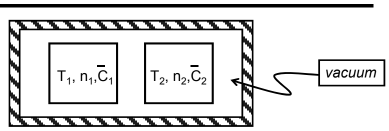
heat only transfer (also zeroth law; E&R p7)

initial



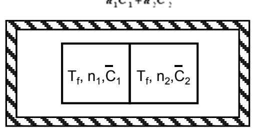
$$đq_1 = n_1\bar{C}_1 dT_1 \qquad đq_2 = n_2\bar{C}_2 dT_2$$

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

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

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

final



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

change of energy by work done ON system

$$đw = đw_{PV} + đw_{other}$$

$$đw_{PV} = -P_{ext}\,dV$$

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

$w > 0 \Rightarrow$ 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}= 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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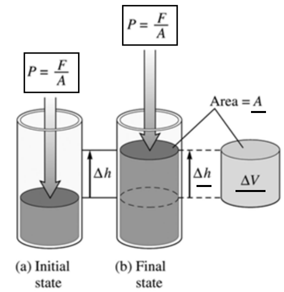
derivation of w = – PΔV (work of expansion or PV work)

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



- pressure=force/area
  P=F/A ; F= P $\times$ A
- ΔV= A $\times$ **Δh**
- w^*_{surr}= Force $\times$ Distance
- w^*_{surr}= F $\times$ **Δh**
- w^*_{surr}= P $\times$ A $\times$ **Δh**
- w^*_{surr}= P $\times$ ΔV
- w = work **ON SYTEM**
- w= – PΔV
  to be consistent with work done **ON** system

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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

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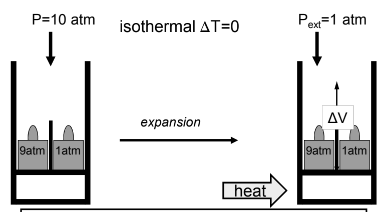
Pres *system is gas inside piston; weights are surrounding* ***gainst***



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 $\Longrightarrow$ ΔU=0 w< 0; – w= q > 0 ; heat absorbed by system

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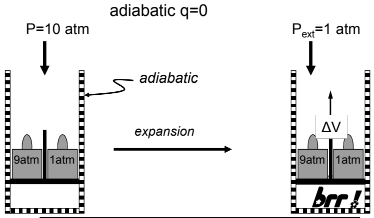
Pres *system is gas inside piston; weights are surrounding* ***gainst***

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 $\Longrightarrow$ energy of system decreases $\Longrightarrow$ gas cools

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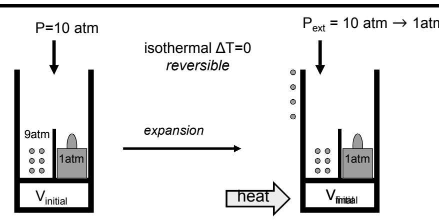
Pressure-Volume work reversible expansion



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

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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 m^3 = 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)**	$w = -\int_{h_i}^{h_f} m\,g\,dh$	**kg m^2 s^{-2} = J**

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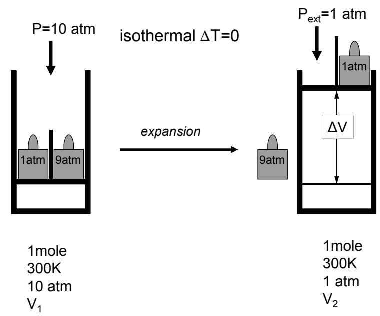
Isothermal expansion: P_{ext}= const ideal gas (irreversible)



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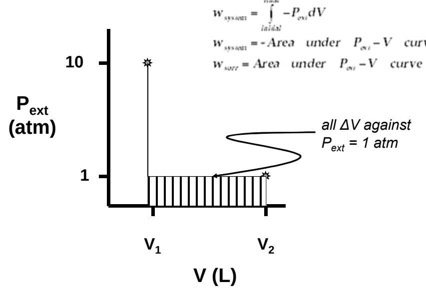
Isothermal expansion: P_{ext}= const; ideal gas; Graphical Interpretation

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

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

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



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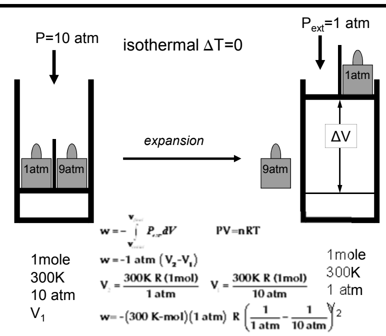
Isothermal expansion: P_{ext}= const ideal gas (irreversible)



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

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

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

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

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

(- sign implies net work done ON surrounding)

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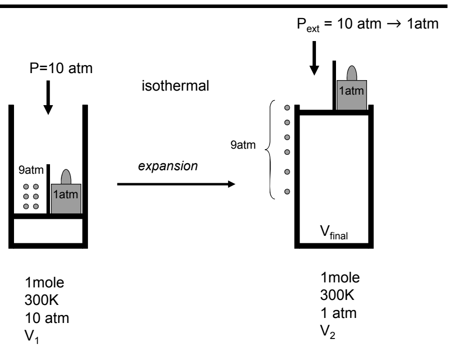
Pressure-Volume work reversible isothermal expansion; P_{ext}=P_{int}



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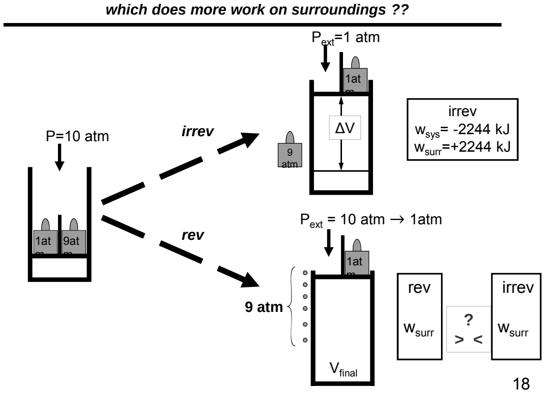
isothermal irreversible vs isothermal reversible: which does more work on surroundings ??



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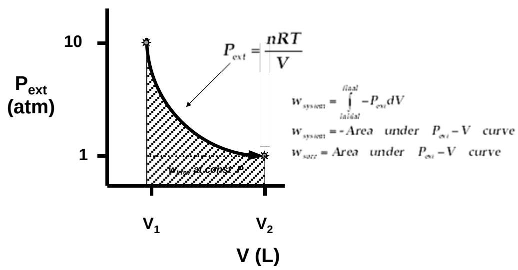
Isothermal expansion: $P_{ext}= P_{int}$ ideal gas; Graphical Interpretation



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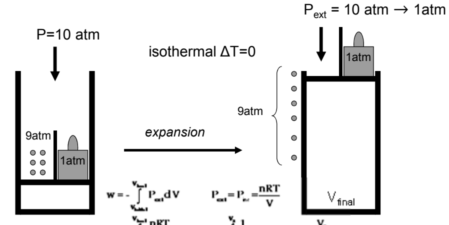
Pressure-Volume work reversible isothermal expansion; $P_{ext}=P_{int}$



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

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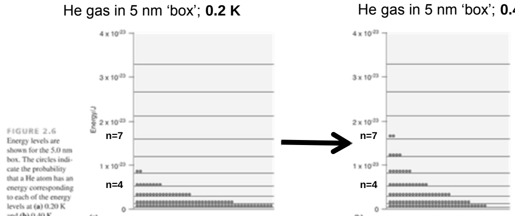
molecular picture of heat and work: constant volume heating (E&R p 23-24)

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: *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*

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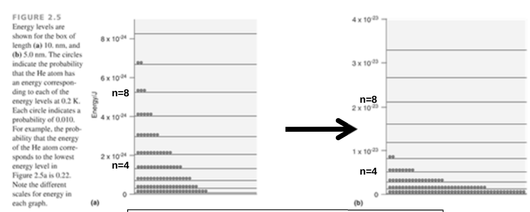
molecular picture of heat and work: isothermal compression (E&R p 23-24)

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': *ΔV <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. *ΔU=0*

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

better make it a triple

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