


Chemistry 163B Winter 2014

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

heat capacity (E&R section 2.5)

$$\frac{d\dot{q}}{dT} = C \quad \text{heat capacity [J K}^{-1}\text{]}$$

the amount of heat requires to raise substance 1K

$$\frac{d\dot{q}}{dT} = n\bar{C} \quad \text{molar heat capacity [J mol}^{-1}\text{ K}^{-1}\text{]}$$

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

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

change of energy by heat transfer

$$d\mathbf{q} = C dT = n\bar{C} dT \quad (C \text{ is extensive,}$$

$$q = \int_{\text{path}} d\mathbf{q} = \int_{\text{path}} n\bar{C} dT \quad \bar{C} \text{ is intensive)}$$

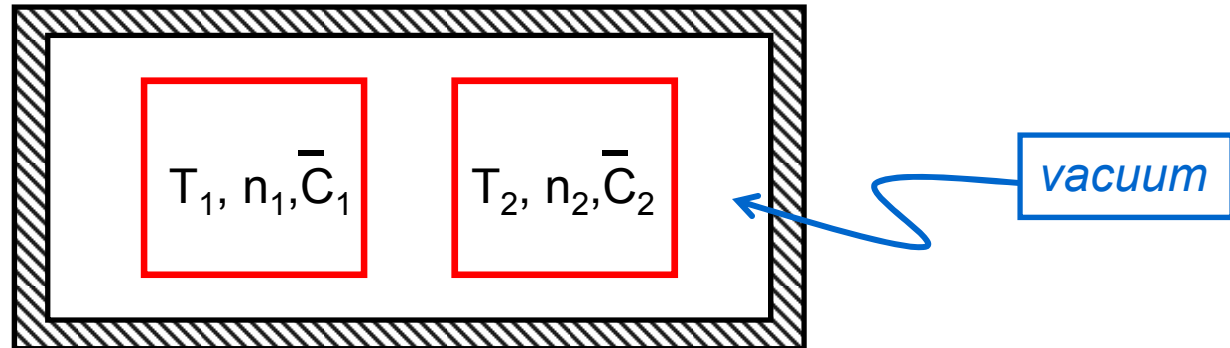
\bar{C} will generally depend on T and path

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

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

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

initial



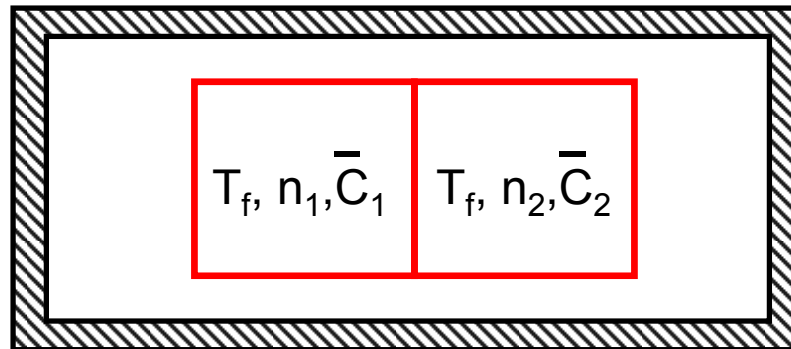
$$dq_1 = n_1 \bar{C}_1 dT_1 \quad dq_2 = n_2 \bar{C}_2 dT_2$$

assume \bar{C} 's independent of T

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

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

final



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

change of energy by work done ON system

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

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

$$w_{PV} = \int_{path} d\mathbf{w} = \int_{path} -P_{ext} dV$$

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

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

processes: definitions of constraints

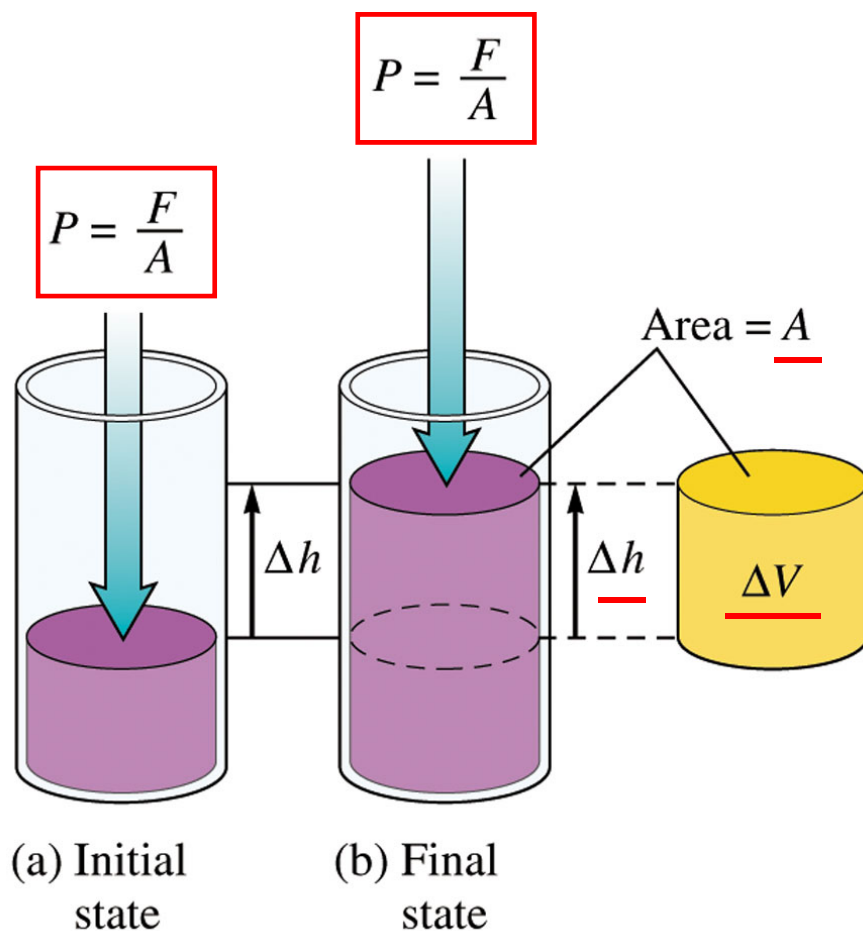
- *isolated* $q=0; w=0$
- *isothermal* $\Delta T=0$
- *adiabatic* $q=0$
- *“against constant pressure”* $P_{\text{ext}} = \text{const}$
- *reversible process* $P_{\text{int}} = P_{\text{ext}}$

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

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

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



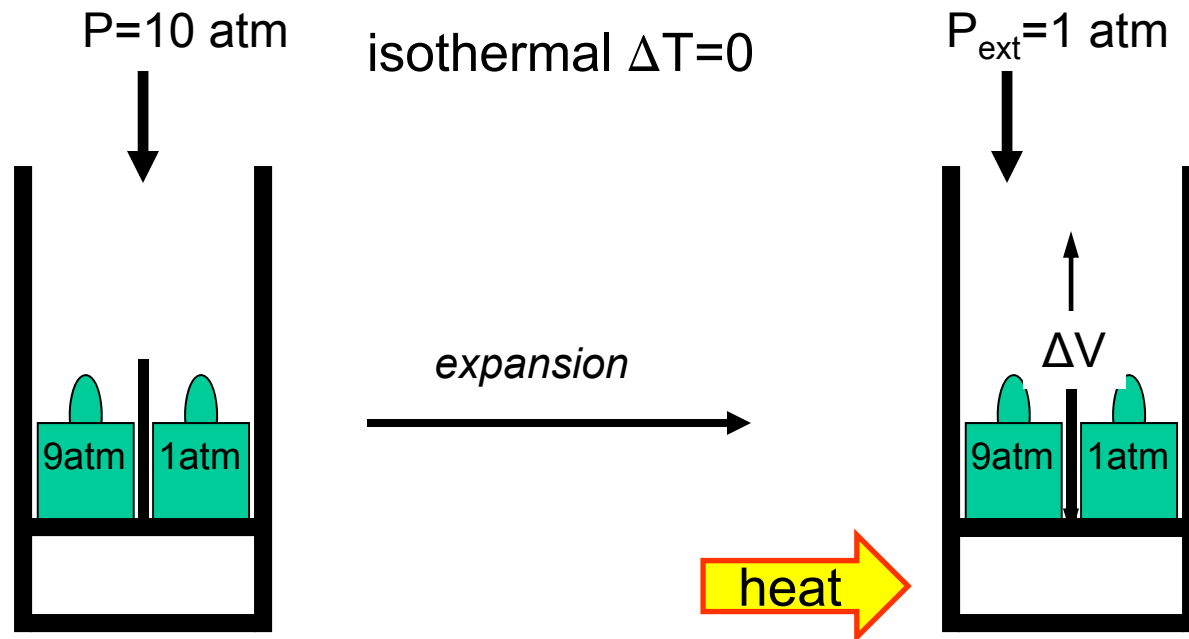
- pressure=force/area
 $P = F/A$; $F = P \times A$
- $\Delta V = A \times \Delta h$
- $w^*_{\text{surr}} = \text{Force} \times \text{Distance}$
- $w^*_{\text{surr}} = F \times \Delta h$
- $w^*_{\text{surr}} = P \times A \times \Delta h$
- $w^*_{\text{surr}} = P \times \Delta V$
- ~~$w = \text{work ON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

ideal gas and energy, heat, work

for **IDEAL GAS**

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

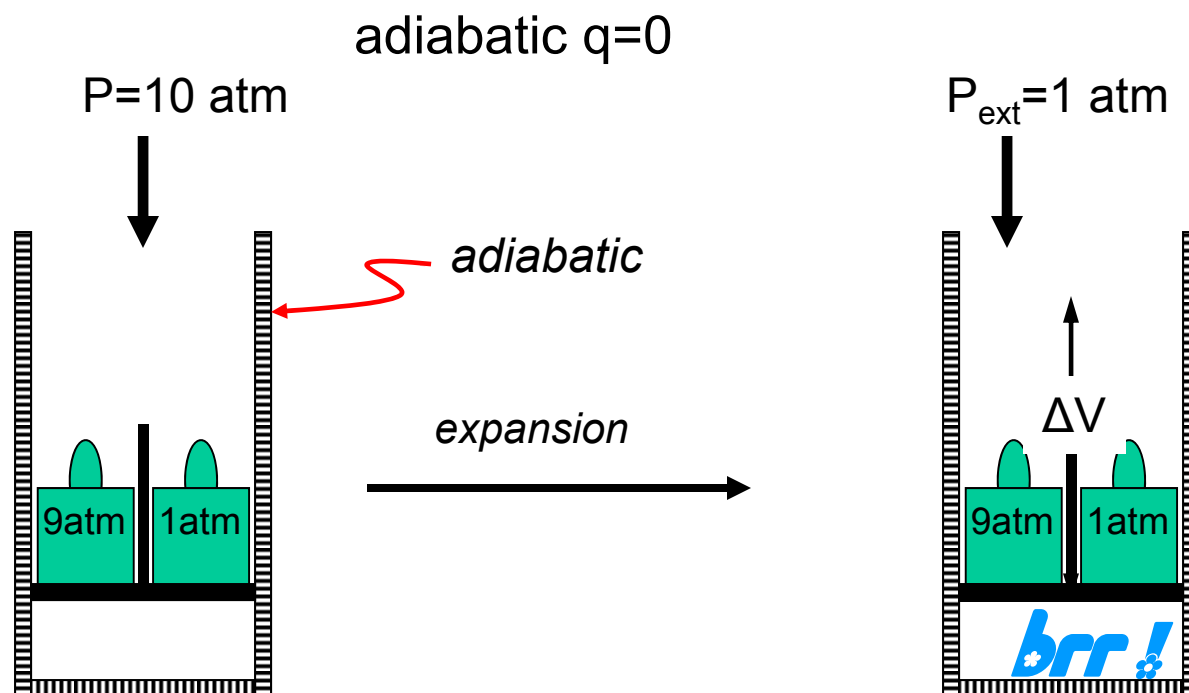
Pressure **system is gas inside piston; weights are surrounding** against



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) ; $\Delta V_{\text{sys}} > 0$; $w_{\text{sys}} = - P \Delta V_{\text{sys}} < 0$
- work (< 0) is done **BY SYSTEM ON SURROUNDINGS** (1 atm weight lifted)
- later (E for ideal gas depends only on T)
 isothermal ideal gas $\Delta T = 0 \implies \Delta U = 0$ $w < 0$; $-w = q > 0$; **heat absorbed by system**

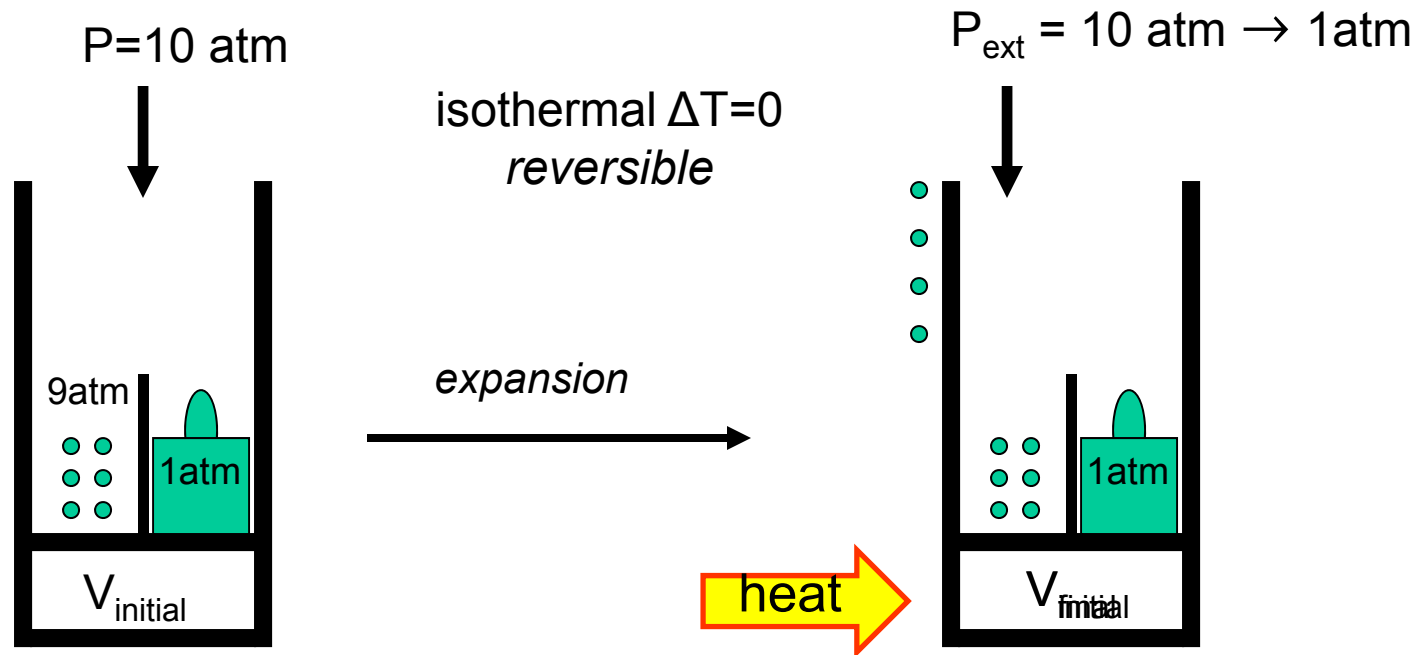
Pressure **system is gas inside piston; weights are surrounding** against



adiabatic expansion against constant pressure

- 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)
- *later (conservation of energy U)*
 $w < 0$; $q=0$ (adiabatic); $U_{\text{sys}} < 0$;
 energy (potential) of surroundings increases \Rightarrow energy of system decreases \Rightarrow gas cools

Pressure-Volume work reversible expansion



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

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

change of energy by work done ON system

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

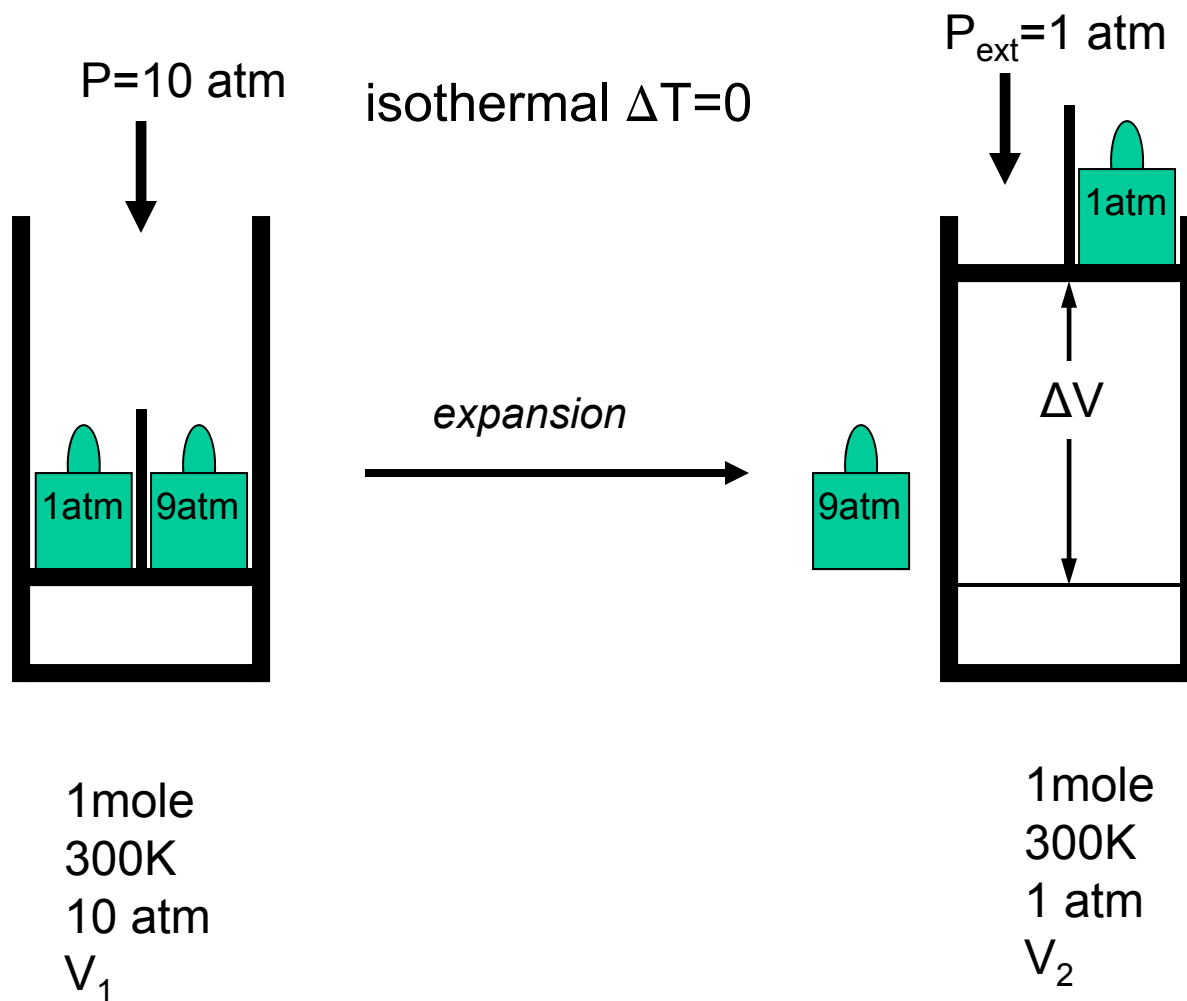
$$d\mathbf{w} = -P_{ext} dV + d\mathbf{w}_{other}$$

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

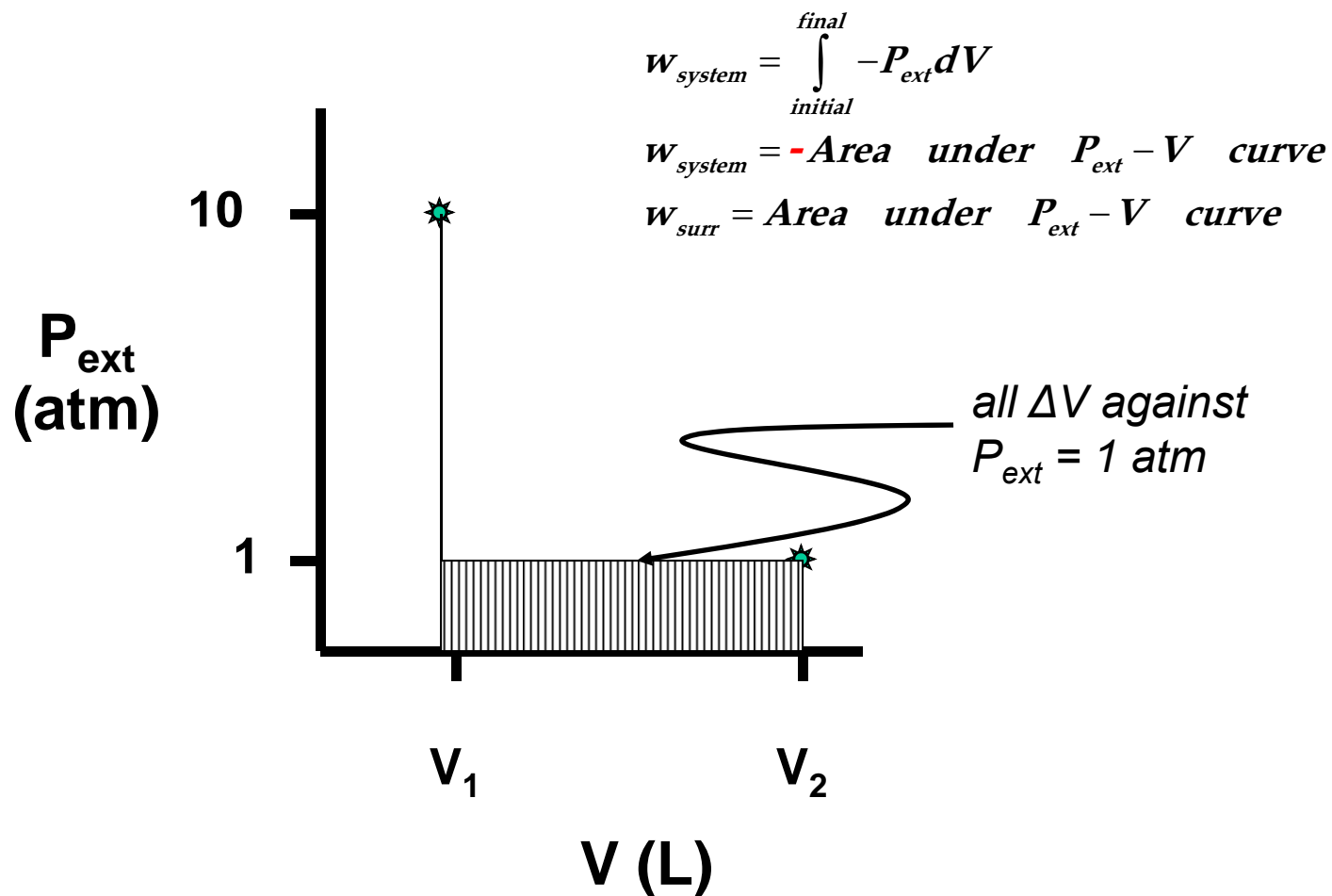
TABLE 2.1 Types of Work

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = - \int_{V_i}^{V_f} P_{external} dV$	$\text{Pa m}^3 = \text{J}$
Stretching	Force (F), length (l)	$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{l}$	$\text{N m} = \text{J}$
Surface expansion	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \gamma \cdot d\sigma$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int_0^Q \phi dQ'$	$\text{V C} = \text{J}$
Done lifting a weight against gravity (weight is surroundings)	Mass (m), position (h)	$w = - \int_{h_1}^{h_2} m g dh$	$\text{kg m}^2 \text{s}^{-2} = \text{J}$

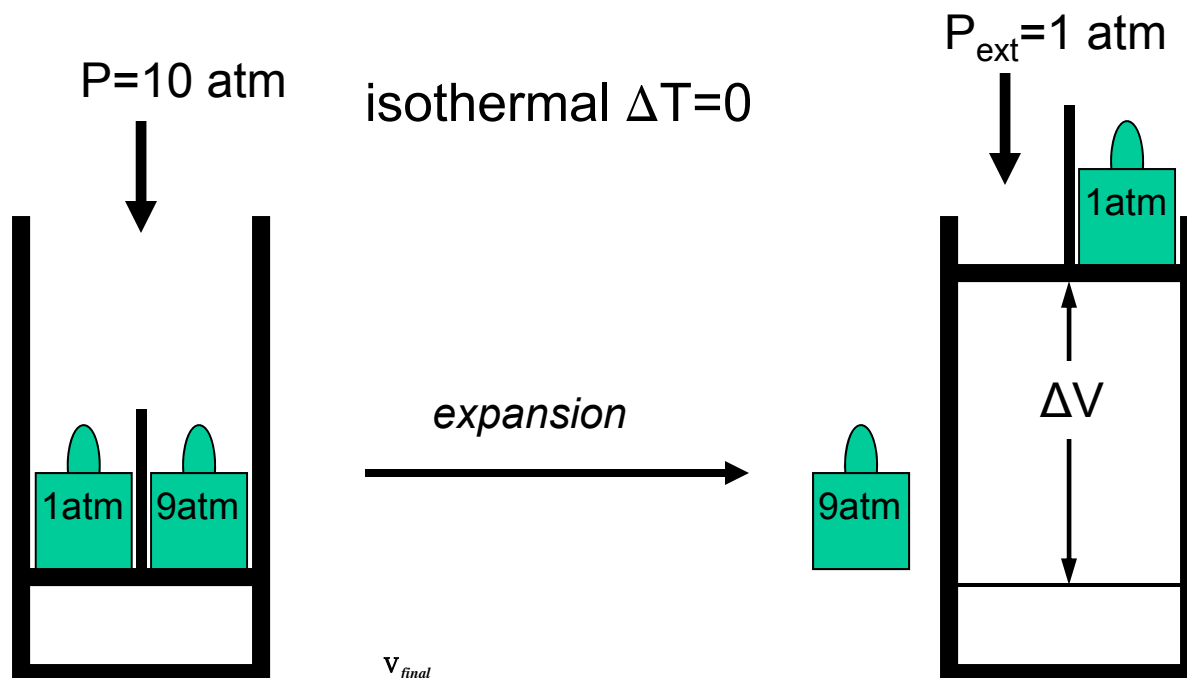
Isothermal expansion: $P_{\text{ext}} = \text{const}$ ideal gas (irreversible)



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



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



isothermal $\Delta T = 0$

expansion

$$w = - \int_{V_{initial}}^{V_{final}} P_{ext} dV$$

$$PV = nRT$$

1 mole
300K
10 atm
 V_1

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

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

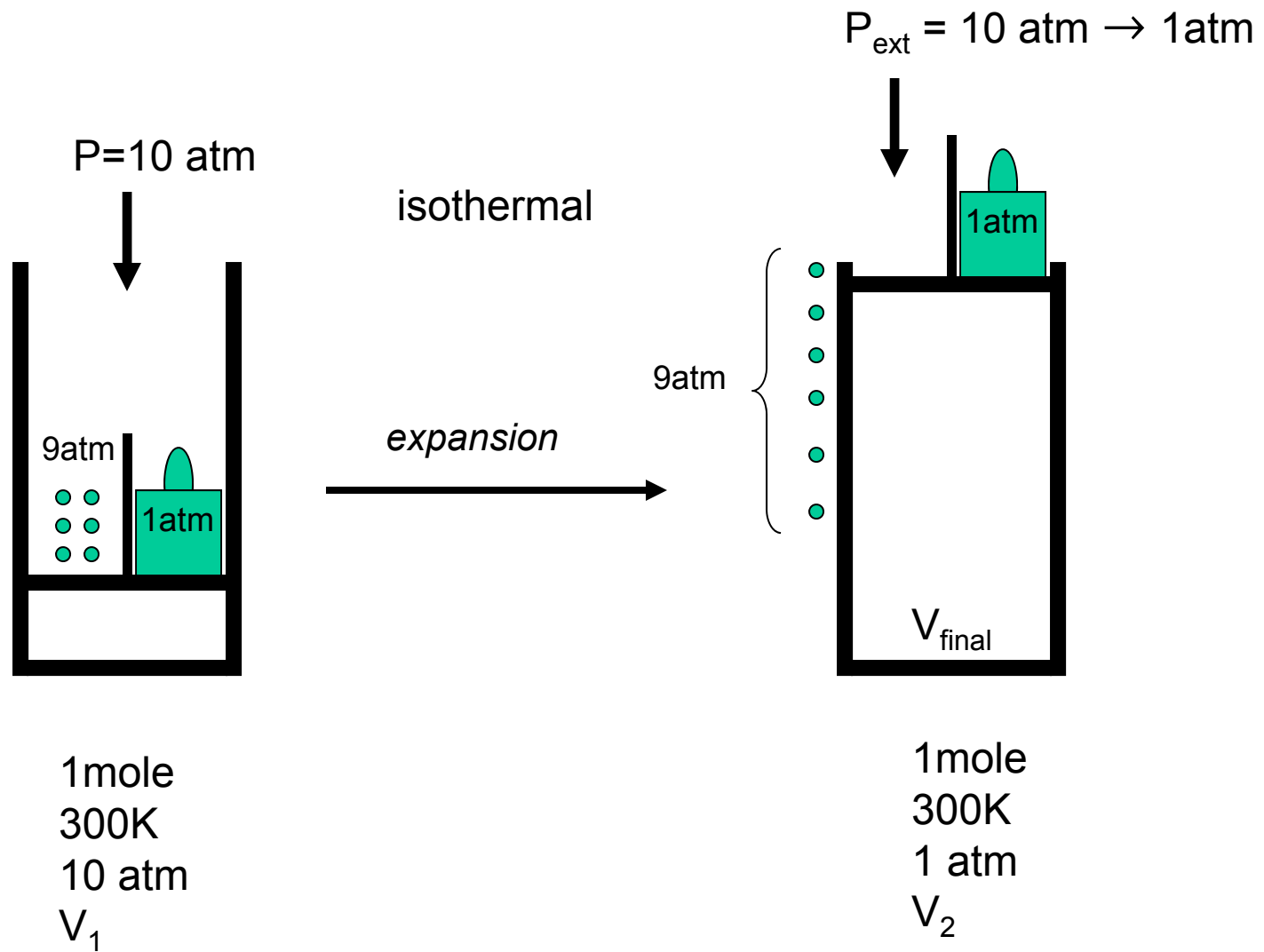
1 mole
300K
1 atm
 V_2

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

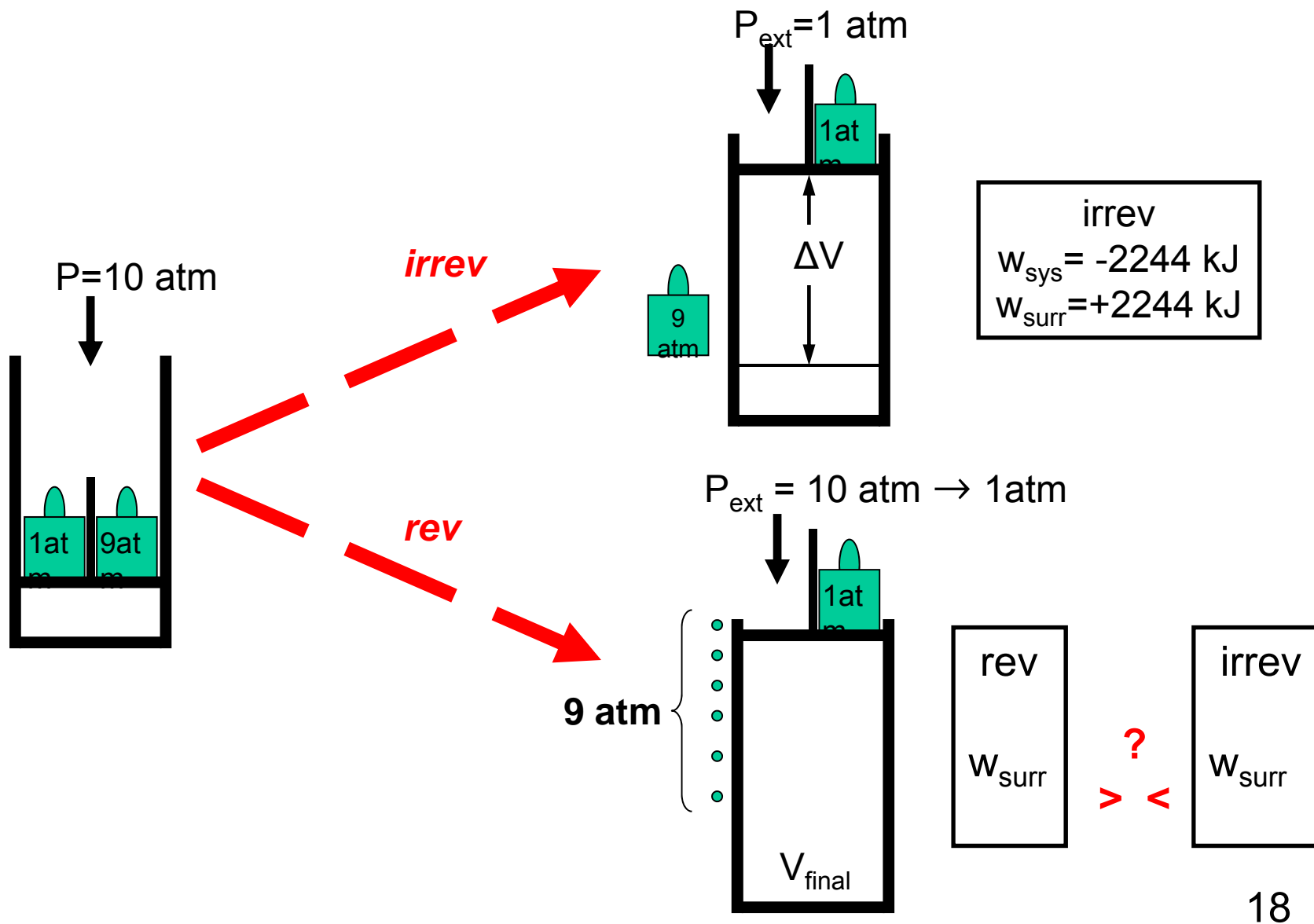
$$w = -2244 \text{ J} = -2.244 \text{ kJ}$$

(- sign implies net work done ON surrounding)

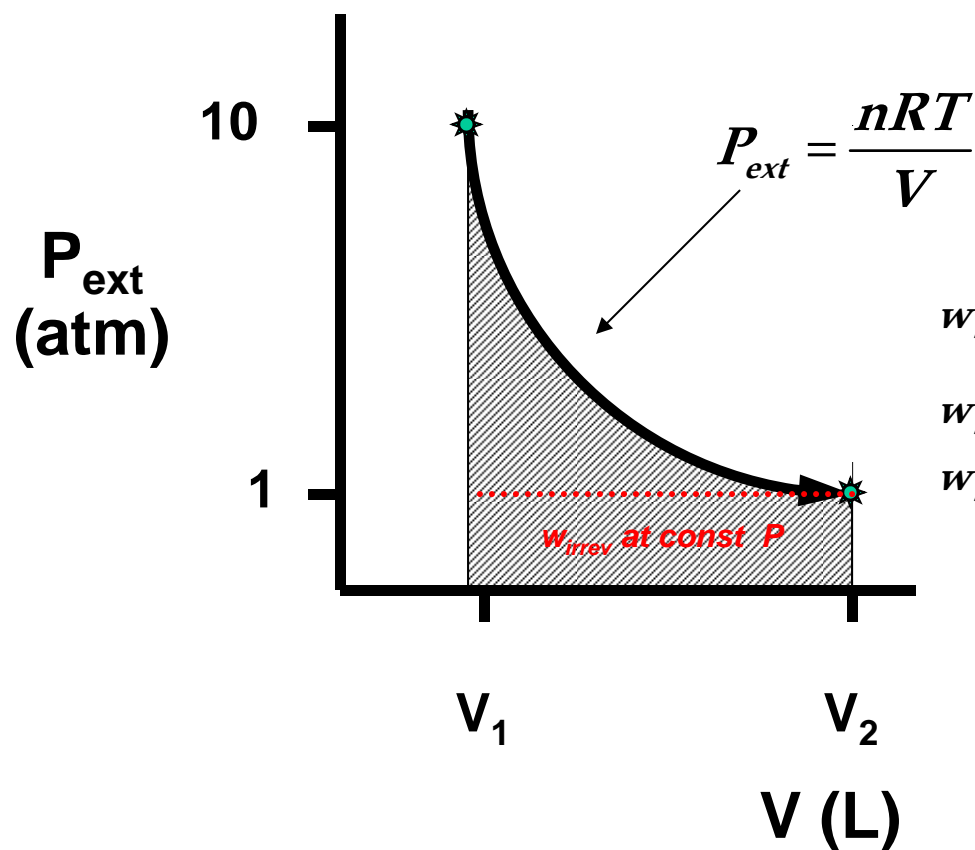
Pressure-Volume work reversible isothermal expansion; $P_{\text{ext}} = P_{\text{int}}$



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



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

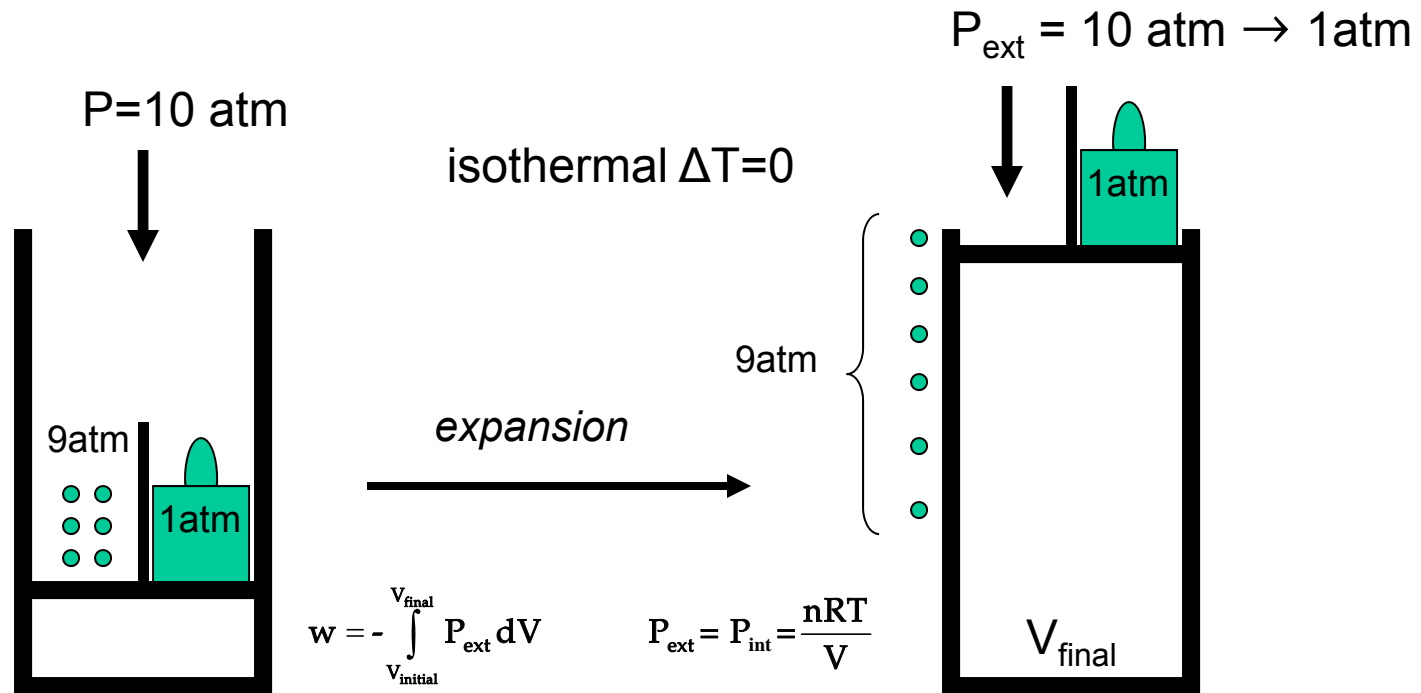


$$W_{system} = \int_{initial}^{final} -P_{ext} dV$$

$$W_{system} = -\text{Area under } P_{ext} - V \text{ curve}$$

$$W_{surr} = \text{Area under } P_{ext} - V \text{ curve}$$

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



1 mole
300K
10 atm
 V_1

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

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

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

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

$$w = -5743 \text{ J} = -5.743 \text{ kJ}$$

(more work done ON surroundings

by reversible than irreversible; $w_{irrev} = -2.244 \text{ kJ}$)

V_{final}
1 mole
300K
1 atm
 V_2

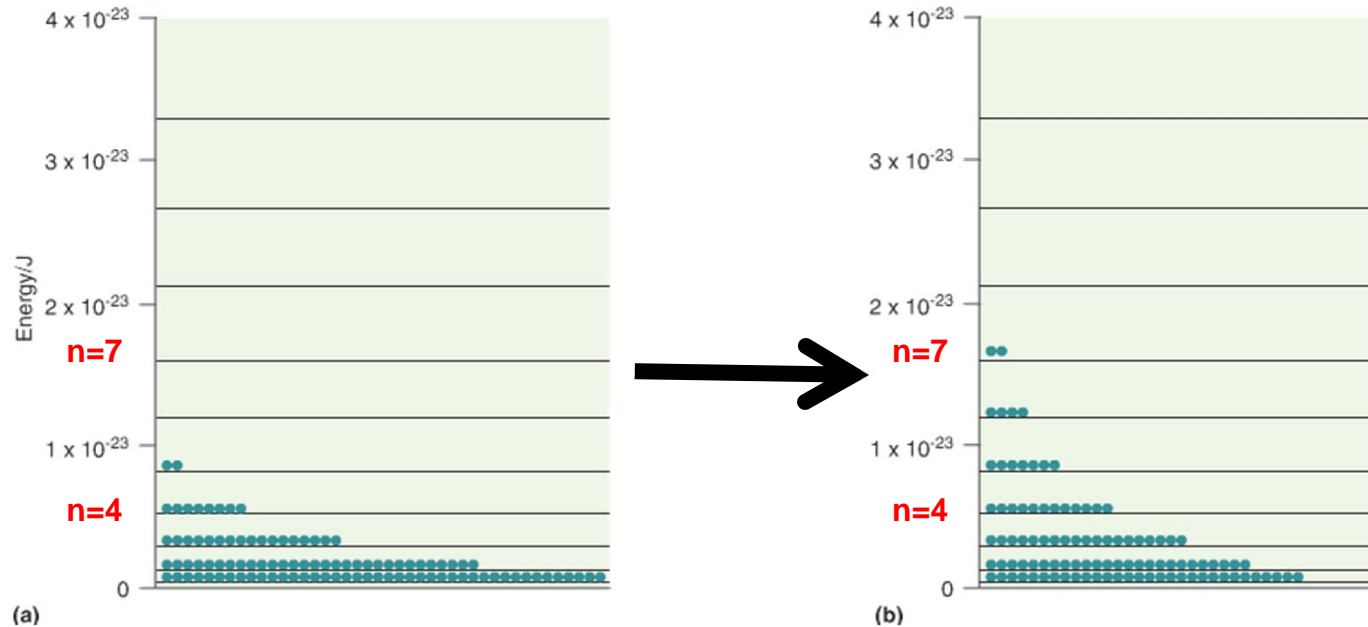
*molecular picture of heat and work:
constant volume heating (E&R p 23-24)*

He gas in 5 nm 'box'; **0.2 K**

He gas in 5 nm 'box'; **0.4K**

FIGURE 2.6

Energy levels are shown for the 5.0 nm box. The circles indicate the probability that a He atom has an energy corresponding to each of the energy levels at (a) 0.20 K and (b) 0.40 K.



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. $\Delta U > 0$

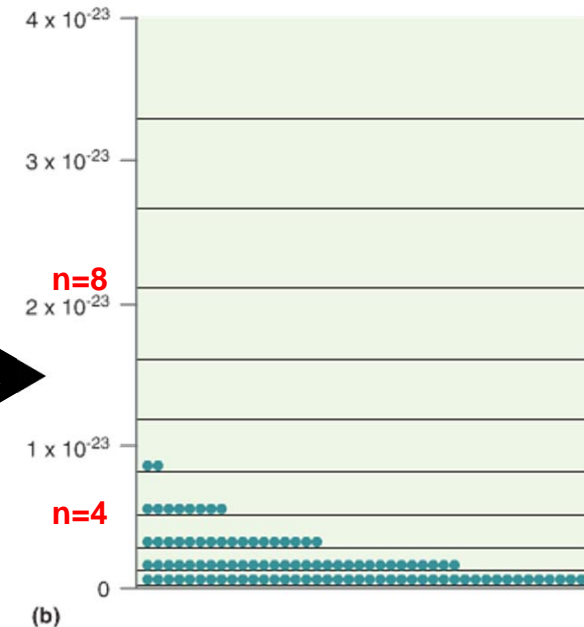
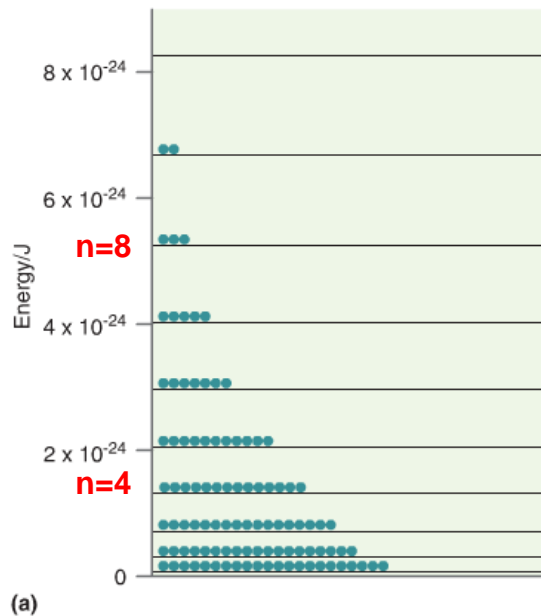
molecular picture of heat and work: isothermal compression (E&R p 23-24)

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

He gas in **5 nm** 'box', 0.2K

FIGURE 2.5

Energy levels are shown for the box of length (a) 10. nm, and (b) 5.0 nm. The circles indicate the probability that the He atom has an energy corresponding to each of the energy levels at 0.2 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 Figure 2.5a is 0.22. Note the different scales for energy in each graph.



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. $\Delta U = 0$

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



better make it a triple