L E C T U R E

3

CY11001
Spring 2018

- Energy, Heat, and Work

Lecture Slides @

http://10.57.2.100/moodle/login/index.php

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Energy

$$E = K + V + U$$

- *K* and *V* are the macroscopic (not molecular) kinetic and potential energies of the body, together represent the mechanical energy

- *U* is the internal energy of the body (due to molecular motions and intermolecular interactions)

Internal Energy, *U,* is the total energy within a system. (*E=U,* as *K=V=*0)

- Extensive property
- $U_m=U/n$ (molar internal energy)
- It is a state function, independent of path
- dU is a perfect (exact) differential
- For cyclic process $\oint dU = 0$

Heat

- Heat is that which is transferred between a system and surrounding by virtue of a *temperature difference only.*

- Heat is not a state function (path dependent).

- Heat can be transferred reversibly or irreversibly. A reversible transfer of heat requires the *temperature difference* between two bodies be *infinitesimal*.

Work:

- **expansion work,** work of expansion (or compression)
- **non-expansion / additional work**: any other work

Expansion Work:

General expression of work (**reversible process**):

p_{ex} = external pressure
A = piston area
dz = displacement
$dV = A\,dz$ = volume change for the gas

External pressure, p_{ex}

dz $dV = A\,dz$

Area, A Pressure, p

Figure 2-6
Atkins Physical Chemistry, Eighth Edition
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Work is required to move an object a distance dz against an opposing force F. Total work done,

$$w = -\int F\,dz = -\int (p_{ex}A)dz = -\int_{V_i}^{V_f} p_{ex}\,dV = -\int_{V_i}^{V_f} p\,dV$$

→ Only for reversible process
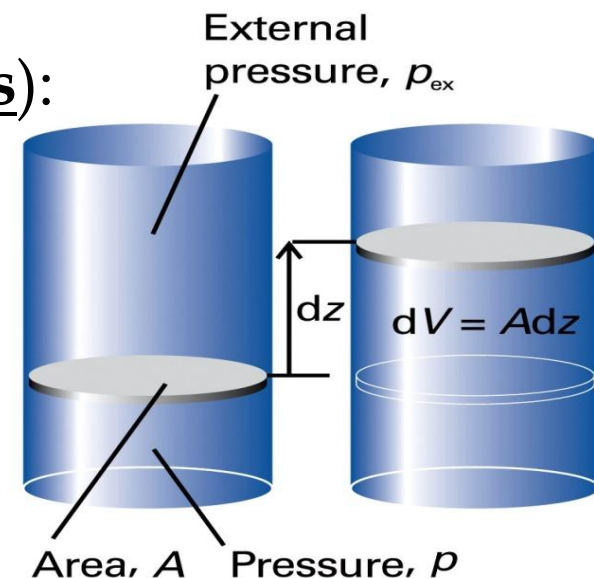
$$dV = \text{change in the volume of the system}$$

Expansion against *constant* pressure

Chemical example: expansion of a gas formed in a chemical reaction in a container that can expand

$$w = -\int_{V_i}^{V_f} p_{ex}dV = -p_{ex}(V_f - V_i) = -p_{ex}\Delta V$$

Expansion against constant final pressure:

$$w = -p_f(V_f - V_i)$$

Free expansion:
Expansion against zero opposing force
$$w = 0$$

Expansion, i.e., $V_f > V_i$, $w < 0$ (work done by the system on surrounding)
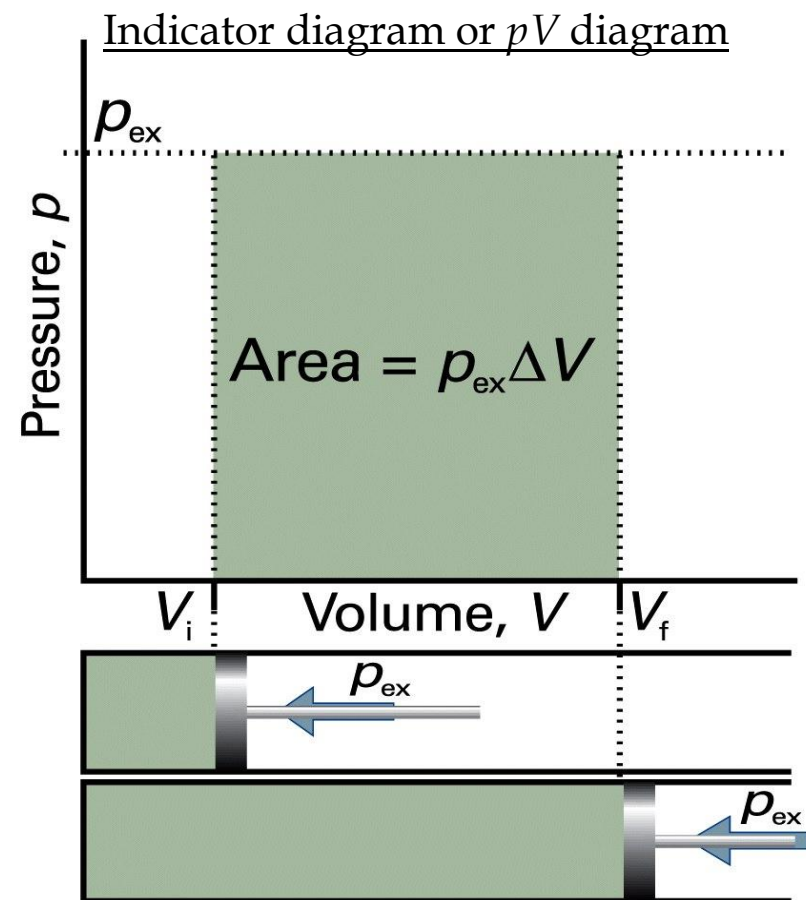
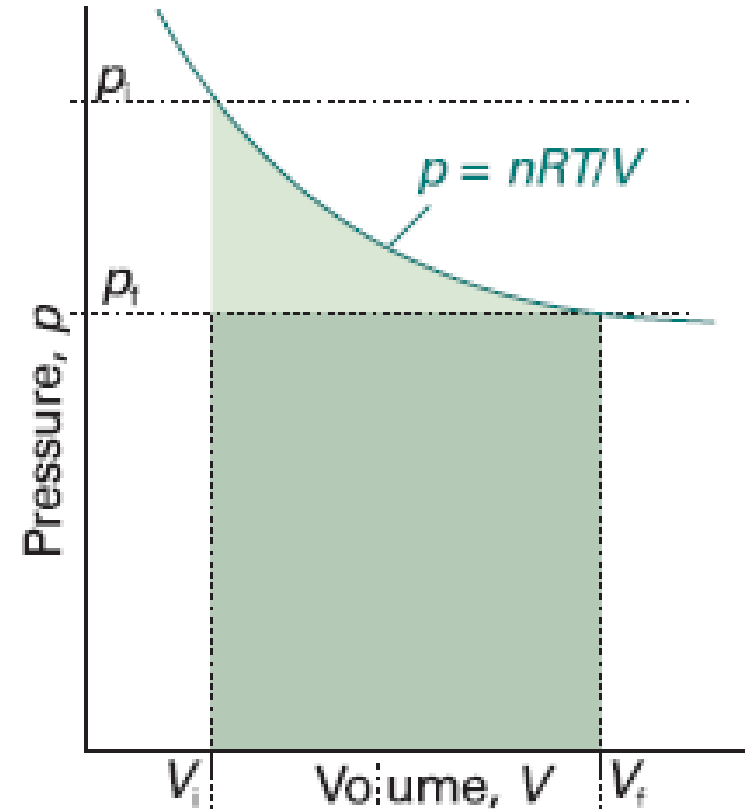*Compression*, i.e., $V_f < V_i$, $w > 0$ (work done on the system by surrounding)

Indicator diagram or *pV* diagram

Area $= p_{ex}\Delta V$

Figure 2-7
Atkins Physical Chemistry, Eighth Edition
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Isothermal expansion (ideal gas):

Reversible

$$w = -\int_{V_i}^{V_f} pdV = -nRT\int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

- At higher T, work done is more for same expansion of volume.

$p = nRT/V$

Work against constant final pressure

Irreversible $\quad w = -p_f(V_f - V_i) = -p_f\Delta V$

$$|w_{\text{rev}}| > |w_{\text{irrev}}|$$ Maximum work is obtained when expansion is reversible.

Adiabatic Reversible Process for ideal gas, (C_V independent of Temp)

$$dU = dw + dq = dw$$

For ideal gas, $C_V dT = -p dV$

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \ln \frac{T_2}{T_1} = nR \ln \frac{V_1}{V_2}$$

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^{nR} = \left(\frac{V_1}{V_2}\right)^{C_p - C_V}$$
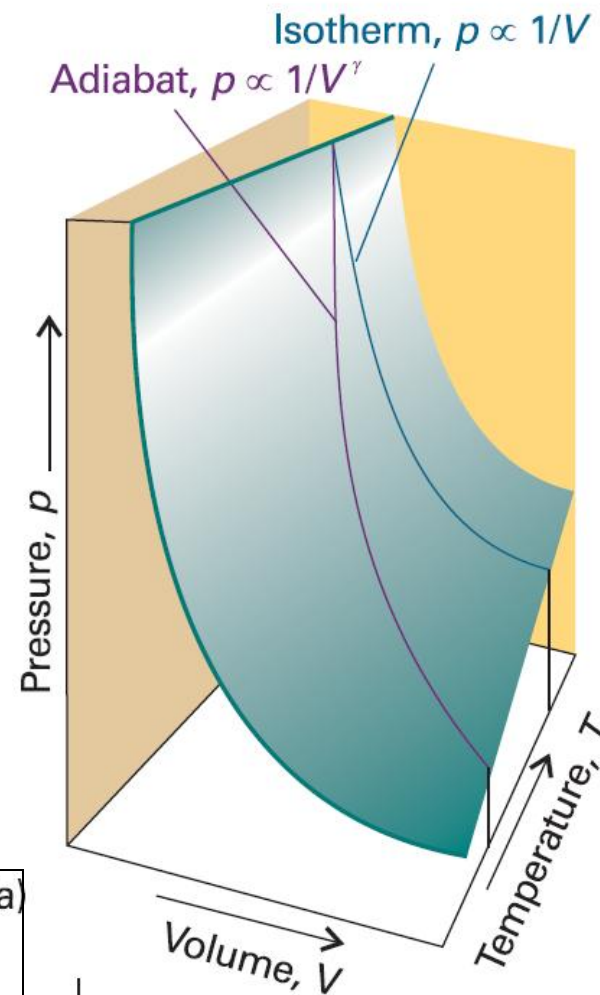
$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \text{where} \quad \gamma = \frac{C_{p,m}}{C_{V,m}}$$

$$TV^{\gamma-1} = \text{constant}$$

$$PV^{\gamma} = \text{constant}$$

$$VT^{c} = \text{constant}$$

$$T^{\gamma} P^{1-\gamma} = \text{constant}$$

Isotherm, $p \propto 1/V$

Adiabat, $p \propto 1/V^{\gamma}$

Pressure, p

Volume, V

Temperature, T

(a)

Note: $C_V = n\, C_{V,m}$

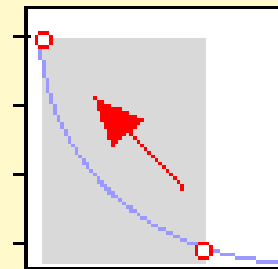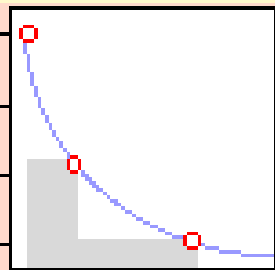2.24L, 10 atm ⟵⟶ 22.4 L, 1 atm

Expansion **Compression**

1 stage
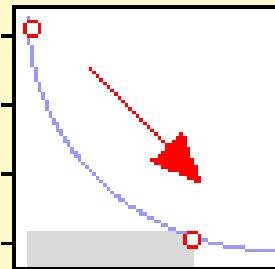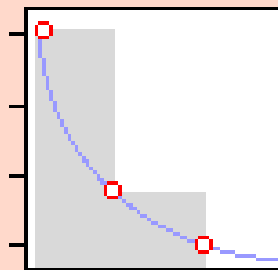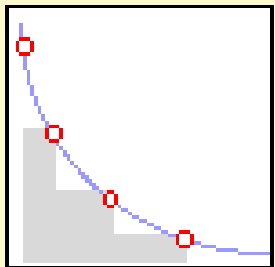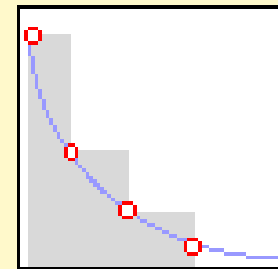
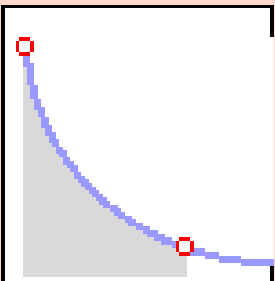−20 L-atm   +202 L-atm

2 stages

−28 L-atm   +119 L-atm

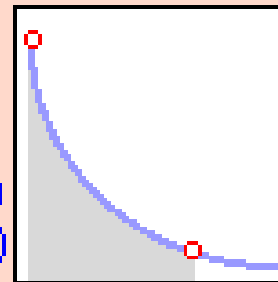3 stages

−33 L-atm   +85 L-atm

infinite stages
(reversible)

−52 L-atm   +52 L-atm
(maximum work) (minimum work)

P   P

V   V

$|w_{rev}(\text{compression})| = |w_{rev}(\text{expansion})|$

Work is path dependent:

Ideal gas, closed system, reversible process

<u>Calculate w_f and w_b</u>

- $10\ \text{Pa}, 1\text{m}^3, T \xrightarrow{\text{isothermal}} 1\ \text{Pa}, 10\ \text{m}^3, T$

- $10\ \text{Pa}, 1\text{m}^3, T \xrightarrow{\text{isochoric}} 1\ \text{Pa}, 1\text{m}^3, T_2 \xrightarrow{\text{isobaric}} 1\ \text{Pa}, 10\ \text{m}^3, T$

- $10\ \text{Pa}, 1\text{m}^3, T \xrightarrow{\text{isobaric}} 10\ \text{Pa}, 10\ \text{m}^3, T_3 \xrightarrow{\text{isochoric}} 1\ \text{Pa}, 10\ \text{m}^3, T$

> w_{rev} depends on the path used to go from 1 to 2, and w_{rev} can have *any* positive or negative value for a given change of state
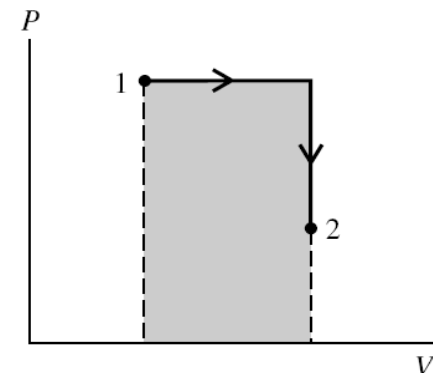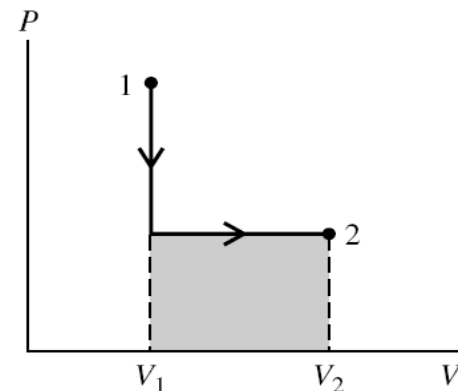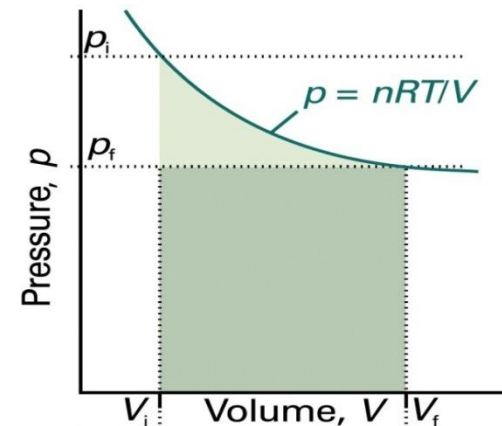
Homework

Work

$$w = -\int p_{ex}dV = -p_{ex}\Delta V$$
$$= 0 \text{ (at } 0\ p_{ex}, \text{ free expansion)}$$

Irreversible

Reversible

$$w = -p\Delta V$$

$$w = 0$$

rev, at constant V
(ex: bomb caloriemeter)

rev, at constant p
(ex: const p heating; phase change)

vdW gas, rev

$$w = -\int\left(\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right)dV$$

$$w = -\int p\ dV$$

Ideal gas, rev

$$w = -\int\frac{nRT}{V}dV$$

vdW gas, rev
isothermal

$$w = -nRT\ln\frac{V_2 - nb}{V_1 - nb} + an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

Homework: derive it!

adiabatic reversible

Ideal gas
Isothermal reversible

$$w = -\int pdV = \int C_V dT$$

$$w = -nRT\ln\frac{V_f}{V_i}$$