

Chemistry 163B Winter 2020

Lectures 2-3 Heat and Work


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Lectures 2-3

Heat and Work

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Menu: for TODAY(s)




- Heat (q), Work (w) and the First Law of Thermodynamics $\Delta U = q + w$
- 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

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




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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

$$\oint df = 0$$

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a few "FACTS OF (thermodynamic) LIFE" 


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

initial state $\xrightarrow{\text{red arrow}}$ 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 \Rightarrow exact differential, there is underlying STATE FUNCTION

- if change is path dependent \Rightarrow inexact differential, no underlying property of the state of system

more in Lecture #5 (math !!) 

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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. δq and δw

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

- **U** is symbol for **INTERNAL ENERGY** of a system
- $\Delta U = q + w$; $dU = dq + dw + \sum_i dn_i$ dn_i=0 closed system, ignore for now
- $\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$ (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

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

- $\frac{dq}{dT} = C$ heat capacity [$J K^{-1}$] extensive
- the amount (transfer) of heat required to raise substance 1K
- $\frac{dq}{dT} = n\bar{C}$ 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 $\bar{C}_P = \frac{5}{2}R$

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

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

change of energy by heat transfer


$$dq = C dT = n\bar{C} dT \quad (C \text{ is extensive, } \bar{C} \text{ is intensive})$$

$$q = \int_{\text{path}} dq = \int_{\text{path}} n\bar{C} dT$$

\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



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heat only transfer; thermal equilibrium (also zeroth law; E&R p11)_[4th]

initial

T_1, n_1, \bar{C}_1

T_2, n_2, \bar{C}_2

vacuum

$dq_1 = n_1 \bar{C}_1 dT_1$ $dq_2 = n_2 \bar{C}_2 dT_2$
 assume \bar{C} 's independent of T

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

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

final

T_f, n_1, \bar{C}_1

T_f, n_2, \bar{C}_2

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

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

change of energy by work done ON system

energy into system

$$dw = d w_{PV} + d w_{\text{other}}$$

e.g. electrical, gravitational, etc.

derive in a moment.

$$d w_{PV} = -P_{\text{ext}} dV$$

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

$w > 0 \Rightarrow$ 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" $P_{\text{ext}} = \text{const}$
- 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

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

$w_{\text{surr}}^* = \text{work done ON SURROUNDINGS}$

pressure = force/area
 $P = F/A ; F = P \times A$

$\Delta V = A \times \Delta h$

$w_{\text{surr}}^* = \text{Force} \times \text{Distance}$

$w_{\text{surr}}^* = F \times \Delta h$

$w_{\text{surr}}^* = P \times A \times \Delta h$

$w_{\text{surr}}^* = P \times \Delta V = P\Delta V$

want $w = \text{work ON SYSTEM}$
 $w = -P\Delta V$
 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 (ideal gas, previous class)
- isothermal, $\Delta T=0$,
 - $\Delta U=0=q+w$ (ideal gas)
 - $q=-w$
- adiabatic: $q=0, \Delta U=w$ (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)

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work of expansion ideal gas (3 conditions)

$P = 10 \text{ atm}$
 1 mol
 $T = T_{\text{initial}}$
 $V_i = RT_i / 10 \text{ atm}$

$P = 1 \text{ atm}$
 1 mol
 $T = T_{\text{final}}$
 $V_f = RT_f / 1 \text{ atm}$

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

why ??

- understanding of thermodynamic conditions
- how to calculate $w = -\int P dv$
- compare w_{rev} vs w_{irrev}
- AND lots of 'rewards' on HW and EXAMS

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system is gas inside piston; weights are surrounding

$P = 10 \text{ atm}$ isothermal $\Delta T=0$ $P_{\text{ext}} = 1 \text{ atm}$

expansion

heat

isothermal 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)
- E for ideal gas depends only on T
- isothermal ideal gas $\Delta T=0 \Rightarrow \Delta U=0$ since $w < 0$; $q = -w > 0$; heat absorbed by system

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system is gas inside piston; weights are surrounding

adiabatic $q=0$

$P = 10 \text{ atm}$ expansion $P_{\text{ext}} = 1 \text{ atm}$

adiabatic 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); $\Delta V_{\text{sys}} > 0$; $w_{\text{sys}} = -P_{\text{ext}} \Delta V_{\text{sys}} < 0$
- work (<0) is done BY SYSTEM ON SURROUNDINGS (1 atm weight lifted)
- $w < 0$; $q=0$ (adiabatic); $E_{\text{sys}} (=U_{\text{sys}}) < 0$;
- energy (potential) of surroundings increases \Rightarrow energy of system decreases \Rightarrow gas cools $\Delta T < 0$

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Pressure-Volume work reversible expansion

$P = 10 \text{ atm}$ isothermal $\Delta T=0$ reversible $P_{\text{ext}} = 10 \text{ atm} \rightarrow 1 \text{ atm}$

expansion

$\Delta T=0$ heat

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

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

change of energy by work done ON system

$$d w = d w_{pv} + d w_{other}$$

$$d w = -P_{ext} dV + d w_{other}$$

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

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.	$-\int_{V_1}^{V_2} P_{ext} dV$	$\text{Pa m}^3 = \text{J}$
Spring stretching and compression	Force (F), distance (x) The spring is the system.	$w = \int_{x_1}^{x_2} F \cdot dx$	$\text{N m} = \text{J}$
Bubble expansion and contraction	Surface tension (γ), surface area (σ) The content of the bubble is the system.	$w = -\int_{\sigma_1}^{\sigma_2} \gamma d\sigma$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$
Current passes through conductor	Electrical potential difference (ϕ), electrical charge (Q) The conductor is the system.	$w = \int_{Q_1}^{Q_2} \phi \cdot dQ$	$\text{V C} = \text{J}$
Done lifting a weight against gravity (weight is surroundings)	Mass (m), position (h)	$W = -\int_{h_1}^{h_2} m g dh$	$\text{kg m}^2 \text{s}^{-2} = \text{J}$

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

isothermal $\Delta T = 0$

expansion

1 mole
300K
10 atm
 V_1

1 mole
300K
1 atm
 V_2

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

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

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

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

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

isothermal $\Delta T = 0$

expansion

1 mole
300K
10 atm
 V_1

1 mole
300K
1 atm
 V_2

$$w = -\int_{V_1}^{V_2} P_{ext} dV$$

$$PV = nRT$$

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

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

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

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

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

(- sign implies net work done ON surrounding)

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

isothermal

expansion

1 mole
300K
10 atm
 V_1

1 mole
300K
1 atm
 V_2

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

irrev
 $w_{sys} = -2244 \text{ kJ}$
 $w_{surr} = +2244 \text{ kJ}$

rev
 $w_{surr} \text{ ? } < w_{surr}$

irrev
 w_{surr}

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

$P_{ext} = \frac{nRT}{V}$

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

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

$w_{sur} = \text{Area under } P_{ext}-V \text{ curve}$

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

$P_{ext} = 10 \text{ atm} \rightarrow 1 \text{ atm}$

isothermal $\Delta T = 0$

expansion

$w = - \int_{V_1}^{V_2} P_{ext} dV$ $P_{ext} = P_{int} = \frac{nRT}{V}$

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

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

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

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

(more work done ON surroundings by reversible than irreversible; $w_{irr} = -2.244 \text{ kJ}$)

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

$P = 10 \text{ atm}$ $P_{ext} = 1 \text{ atm}$

adiabatic $q=0$

expansion

adiabatic expansion against constant pressure (irreversible)

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

$\Delta U = nC_V \Delta T = \frac{3}{2} nR(T_2 - T_1)$

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

brr! $T_2 = 192 \text{ K}$ $w = -1.347 \text{ J} = -1.347 \text{ kJ}$ **no q in, less work done than isothermal (-2.244 kJ)**

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molecular correlates of heat and work for ideal gas

- total energy:** sum of [number of particles in energy level (v) \times energy of that level (ϵ_i)]
 $E = \sum_n V_n \epsilon_n$
- heat only (no work):** redistributes particles among levels
 $q > 0 \Rightarrow$ more particles to higher energy levels
 $q < 0 \Rightarrow$ more particles to lower energy levels
- P-V work only (adiabatic)**
particle in 3D cube: CHEM 163A DON'T FRET
 $\epsilon_n \approx \frac{3h^2}{8mV^{2/3}} n^2$ where n is an integer (1, 2, ...)

larger volume ($w < 0$) \Rightarrow energy levels lower and get more closely spaced
 smaller volume ($w > 0$) \Rightarrow energy levels higher and less closely spaced

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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'; 0.3 K

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

- energy levels same spacing: $\Delta V = 0$, $w = 0$ (no change in size of box)
- greater number of atoms in higher energy levels: $q > 0$ raises U ;
- $\Delta U > 0$ ($\Delta E > 0$)

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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

Arrows show how energy of each level decreases as length of box increases.

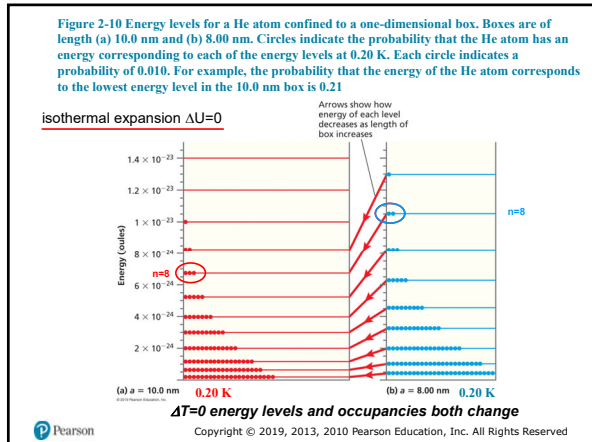
- for **reversible adiabatic expansion** (no heat in) populations in levels do not change
- does total energy $E = \sum_n n_i \epsilon_i$ and thus temperature increase or decrease ??

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Menu: for TODAY(s)

- ✓ Heat (q), Work (w) and the First Law of Thermodynamics $\Delta U = q + w$
- ✓ 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

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End of

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