

Chemistry 163B Winter 2013

Lectures 2-3 Heat and Work

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Heat and Work

heat capacity (E&R section 2.4)

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

the amount of heat requires to raise substance 1K

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

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

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transfers of energy: HEAT and work

change of energy by heat transfer

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

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

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

$q > 0 \Rightarrow$ 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 p4)

initial

T_1, n_1, \bar{C}_1

T_2, n_2, \bar{C}_2

vacuum

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

assume \bar{C} 's independent of T

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

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

final

T_f, n_1, \bar{C}_1

T_f, n_2, \bar{C}_2

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transfers of energy: heat and WORK

change of energy by work done ON system

$$dw = dw_{PV} + dw_{\text{other}}$$

$$dw_{PV} = -P_{\text{ext}}dV$$

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

$w > 0 \Rightarrow$ 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_{surr}^* = work done ON SURROUNDINGS

$P = \frac{F}{A}$
 $\Delta V = A \times \Delta h$
 $w_{\text{surr}}^* = \text{Force} \times \text{Distance}$
 $w_{\text{surr}}^* = F \times \Delta h$
 $w_{\text{surr}}^* = P \times A \times \Delta h$
 $w_{\text{surr}}^* = P \times \Delta V$
 $w = -P\Delta V$ to be consistent with work done ON system

(a) Initial state (b) Final state

ideal gas and energy, heat, work

- 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
 - $U = (3/2) n RT$
 - $C_V = (3/2) n R$
 - $C_P = (5/2) n R$

system is gas inside piston; weights are surrounding

isothermal $\Delta T=0$

expansion

adiabatic $q=0$

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

system is gas inside piston; weights are surrounding

isothermal $\Delta T=0$

expansion

adiabatic $q=0$

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

isothermal $\Delta T=0$ reversible

expansion

adiabatic $q=0$

adiabatic expansion against constant pressure

- 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 [p. 10]_{2nd})

change of energy by work done ON system

$$\delta w = \delta w_{PV} + \delta w_{\text{other}}$$

$$\delta w = -P_{\text{ext}} dV + \delta w_{\text{other}}$$

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

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int_{V_i}^{V_f} P_{\text{external}} dV$	$\text{Pa m}^3 = \text{J}$
Stretching	Force (F), length (l)	$w = \int_{l_i}^{l_f} F \cdot dl$	$\text{N m} = \text{J}$
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)	$w = \int_{Q_i}^{Q_f} \phi \cdot dQ$	$\text{V C} = \text{J}$

Done lifting a weight against gravity (weight is surroundings)

Mass (m), position (h)

$$w = -\int_{h_i}^{h_f} m g dh$$

$\text{kg m}^2 \text{s}^{-2} = \text{J}$

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

1 mole
300K
10 atm
 V_1

expansion

1 mole
300K
1 atm
 V_2

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

$w_{system} = \int_{initial}^{final} -P_{ext} dV$
 $w_{system} = -\text{Area under } P_{ext} - V \text{ curve}$
 $w_{surr} = \text{Area under } P_{ext} - V \text{ curve}$

all ΔV against $P_{ext} = 1 \text{ atm}$

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

1 mole
300K
10 atm
 V_1

expansion

1 mole
300K
1 atm
 V_2

$w = -\int_{V_1}^{V_2} P_{ext} dV$
 $w = -1 \text{ atm} (V_2 - V_1)$
 $PV = nRT$
 $V_1 = \frac{300K R (1 \text{ mol})}{10 \text{ atm}}$
 $V_2 = \frac{300K R (1 \text{ mol})}{1 \text{ atm}}$
 $w = -(300 \text{ K-mol})(1 \text{ atm}) R \left(\frac{1}{1 \text{ atm}} - \frac{1}{10 \text{ atm}} \right)$
 $w = -2244 \text{ J} = -2.244 \text{ kJ}$
 (- sign implies net work done ON surrounding)

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

1 mole
300K
10 atm
 V_1

expansion

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 irrev
 $w_{sun} > < w_{surr}$

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

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

$w_{system} = \int_{initial}^{final} -P_{ext} dV$
 $w_{system} = -\text{Area under } P_{ext} - V \text{ curve}$
 $w_{surr} = \text{Area under } P_{ext} - V \text{ curve}$

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

isothermal $\Delta T=0$

expansion

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

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

1mole 300K 10 atm V_1 1mole 300K 1 atm V_2

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

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

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

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*molecular picture of heat and work:
constant volume heating (E&R p 24; 3rd ed only)*

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. $\Delta U > 0$

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*molecular picture of heat and work:
isothermal compression (E&R p 24; 3rd ed only)*

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^{-14} J vs 10^{-21} J)
2. greater number of atoms in relatively lower energy levels: $q < 0$, lowers U ;
3. $\Delta U = 0$

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