

**CHEM 5200
FALL 2018**

Lecture: Tues & Thur - 9:30 AM to 10:50 AM:
Room: CHEM 252
Instructor: Martin Schwartz
Office: Rm 272
Off. Hrs: Tu-Tr 8:30 AM - 9:30 AM + 11:00 AM - 12:00 AM
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or: <http://www.chem.unt.edu/> and navigate (→Faculty→Schwartz→Classes)

I. COURSE MATERIAL

A. Text: Physical Chemistry (9th. Edition)

Atkins and de Paula - **Optional**

Student Solutions Manual: No

Note: I have prepared Homework Problems + Solutions, which will be posted on the Course Web Site

| B. Chapter | Title | Approx. Starting Date (Week of) |
|-------------------|---|--|
| 2. | The First Law | Aug. 28 |
| 3. | The Second Law | Sept. 11 |
| 4. | Physical Transformations of Pure Substances | Oct. 2 |
| 5. | Simple Mixtures..... | Oct. 9 |
| 6. | Chemical Equilibrium | Oct. 23 |
| 21. | The Rates of Chemical Reactions | Nov. 6 |

II. HOMEWORK

Homework questions will be given in each Chapter Outline, which will be provided as part of the Chapter Handout. Solutions to the Homework will be posted on the course web site.

Homework will **not** be collected. However, you are **strongly encouraged** to work the homework, since problems and questions on the exams will be based upon homework and examples worked in class.

I will be happy to solve homework problems (as well as answer other questions) before or after class

III. EXAMS

A. GENERAL

1. There will be four (4) “hourly” exams. You will be given the complete 1 hr-20 min class period for each exam.

The tests will be primarily problems, but will include some multiple choice questions. Each hourly exam will count 100 points.

2. There will be a comprehensive final exam. The final will count 200 points.
3. Either the lowest of the four hourly exams **OR** one-half of the final exam will be **dropped** prior to computing your average.
4. All exams must be taken during the regularly scheduled times. Exams cannot be taken outside the scheduled time.
5. There will **not** be any makeup exams. A missed exam will count as your dropped test (excluding a **well documented** serious illness, requiring hospitalization).
6. If classes are cancelled by the University on the day of a scheduled exam, then the test is automatically scheduled for the next class lecture period.

B. TEST SCHEDULE**Exam # Date**

1 Thursday, Sept. 20

2 Thursday, Oct. 11

3 Thursday, Nov. 1

4 Thursday, Nov. 29

Final Exam Thursday, Dec. 13 8:00 AM - 10:00

Note: I have reserved Rm. 331 of the Chemistry Building for the tests so that we can allocate a bit more time than the class period for you to complete your tests.

IV. COURSE GRADING**A. CALCULATION OF AVERAGE**

Your average will be calculated as a percentage of 500 points. The average will be calculated after dropping the lower of either:

- a) The lowest of the four hourly exams.
- b) One-half of the final exam.

B. COURSE GRADES

(Based on average calculated to nearest 0.1% after dropped exam)

FEG = Final Exam Grade

A: Avg. \geq 90.0%

B: Avg. \geq 75.0%

C: Avg. \geq 60.0%

D (or F): Avg. $<$ 60.0%

V. NOTES

1. You should plan on bringing a Scientific Calculator to the exams.
2. By University regulations, a grade of "I" cannot be given as a substitute for a failing grade in a course.
3. Any student caught cheating on an examination will receive an "F" in the course and will be reported to the Dean of Students. In order to protect against potential cheating, I must request that students either refrain from wearing long-billed caps on test days or turn the bill towards the back.
4. There are no "extra credit" assignments in this course. Grades will be determined on the basis of examination scores, as detailed above.

THE FIRST LAW
Chapter 2 Outline

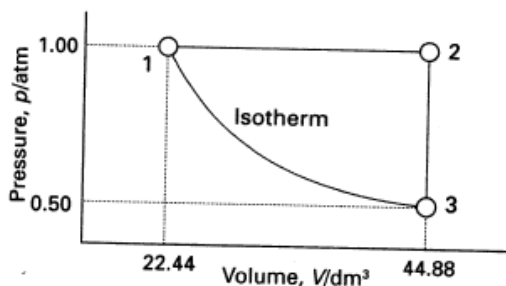
HW: Questions are below. Solutions are in separate file on the course web site.

| Sect. | Title and Comments | Required? |
|-----------------------------|--|------------------|
| 1. | Work, Heat and Energy | YES |
| 2. | The Internal Energy | YES |
| 3. | Expansion Work | YES |
| 4. | Heat Transactions | YES |
| 5. | Enthalpy We have added a section (not in text) on the calculation of heat capacities of gases. | YES |
| 6. | Adiabatic Changes | YES |
| 7. | Standard Enthalpy Changes | YES |
| 8. | Standard Enthalpies of Formation | YES |
| 9. | The Temperature Dependence of Reaction Enthalpies | YES |
| 10. | Exact and Inexact Differentials | YES |
| 11. | Changes in Internal Energy | YES |
| 12. | The Joule-Thomson Effect You are NOT responsible for interpretation of the J-T coefficient nor for the Joule-Thomson inversion temperature. | SOME |
| Further Information: | | |
| 2.1 | Adiabatic Processes | YES |
| 2.2 | The Relation Between Heat Capacities | YES |

Chapter 2 - Homework

- 2.1 Calculate the constant pressure molar heat capacity of $\text{Cl}_2(\text{g})$, assuming that (a) the molecules are rigid, and (b) the molecules can vibrate.
- 2.2 Calculate the constant pressure molar heat capacity of $\text{C}_6\text{H}_6(\text{g})$, assuming that (a) the molecules are rigid, and (b) the molecules can vibrate.
- 2.3 Calculate the constant pressure molar heat capacity of $\text{CO}_2(\text{g})$, assuming that (a) the molecules are rigid, and (b) the molecules can vibrate.
- 2.4 A sample of 1 mole of Ar is expanded isothermally at 0°C from 22.4 L to 44.8 L. Calculate q , w , ΔU and ΔH for the expansion occurring:
(a) Reversibly
(b) at constant external pressure equal to the final pressure of the gas.
(c) freely (against zero pressure)
- 2.5 A sample consisting of 1 mole of a perfect gas atoms, for which $C_{V,m} = (3/2)R$, initially at $p_1 = 1\text{ atm}$ and $T_1 = 300\text{ K}$ is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU , q and w for this process.
- 2.6 A sample of 1 mole of $\text{H}_2(\text{g})$ is condensed reversibly and isothermally to liquid water at 100°C . The standard enthalpy of vaporization of water at 100°C is 40.6 kJ/mol . Calculate w , q , ΔU and ΔH for this process.
- 2.7 A 15. g strip of magnesium ($M=24.3$) is placed in a beaker of dilute $\text{HCl}(\text{aq})$. Calculate the work involved in this reaction. The atmospheric pressure is 1.0 atm and the temperature is 23°C .
- 2.8 Solid tungsten will react with gaseous carbon monoxide to form solid tungsten hexacarbonyl according to the equation: $\text{W}(\text{s}) + 6\text{ CO}(\text{g}) \rightarrow \text{W}(\text{CO})_6(\text{s})$. What is the work involved when two moles of $\text{W}(\text{s})$ reacts with $\text{CO}(\text{g})$ to form two moles of $\text{W}(\text{CO})_6(\text{s})$ at 150°C and 1 bar pressure?
- 2.9 The constant pressure molar heat capacity of a perfect gas is given by:
 $C_{p,m} = a + bT$, $a = 20.17\text{ J/mol}\cdot\text{K}$, $b = 0.37\text{ J/mol}\cdot\text{K}^1$
Calculate q , w , ΔU and ΔH when the temperature of 1. mole of the gas is raised from 25°C to 200°C
(a) at constant pressure
(b) at constant volume
- 2.10 A sample of carbon dioxide, $\text{CO}_2(\text{g})$ ($M=44$) of mass 2.45 g at 27°C is allowed to expand reversibly and adiabatically from 500 mL to 3.0 L . The constant pressure molar heat capacity of CO_2 is $37.11\text{ J/mol}\cdot\text{K}$. What is the work involved in this expansion?

- 2.11** When 3. mol of O_2 is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the constant pressure molar heat capacity of O_2 is $29.4 \text{ J/mol}\cdot\text{K}$, calculate q , ΔU and ΔH for this process.
- 2.12** A sample consisting of 1.0 mol of a perfect gas with $C_V = 20.8 \text{ J/mol}\cdot\text{K}$ is initially at 3.25 atm and 310 K. It undergoes a reversible adiabatic expansion to a final pressure of 2.50 atm. Calculate the final volume and temperature and the work involved in this process.
- 2.13** A certain liquid has an enthalpy of vaporization, $\Delta_{\text{vap}}H^\circ = 26.0 \text{ kJ/mol}$. Calculate q , w , ΔH and ΔU when 0.50 mol is vaporized at 250 K and 750 torr.
- 2.14** The standard enthalpies of formation of ethylbenzene ($C_6H_5C_2H_5(l) = C_8H_{10}$), $CO_2(g)$, and $H_2O(l)$ are -12.5 kJ/mol , -393.5 kJ/mol and -285.8 kJ/mol , respectively. Calculate the standard enthalpy of combustion of ethylbenzene (at 25°C).
- 2.15** For a van der Waals gas, the internal pressure is: $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2}$.
For $N_2(g)$, $a = 1.35 \text{ L}^2\text{atm/mol}^2$ and $b = 0.039 \text{ L/mol}$. Calculate ΔU , q and w for the expansion of 2. moles of $N_2(g)$ from 1.0 L to 24.8 L.
- 2.16** A sample consisting of 1. mol of perfect gas atoms (for which $C_{V,m} = (3/2)R$) is taken through the cycle in the figure shown below.
(a) Determine the temperature at the points 1, 2 and 3.
(b) Calculate q , w , ΔU and ΔH for each step, and for the overall cycle.



- 2.17** A sample consisting of 1. mol of a perfect gas (for which $C_{p,m} = (7/2)R$) is initially at $T_1 = 298 \text{ K}$ and $p_1 = 1. \text{ atm}$. The gas is put through the following cycle: (a) constant volume heating to twice its initial pressure, (b) reversible adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to $p = 1. \text{ atm}$. Calculate q , w , ΔU and ΔH for each step, and for the overall cycle.

Chapter 2

The First Law

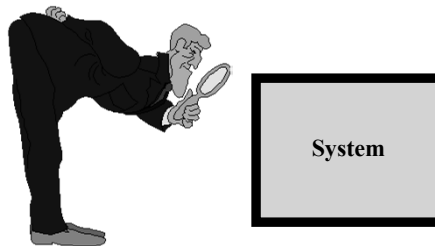
1

Definitions

SYSTEM AND SURROUNDINGS

The system is the part of the universe we are interested in.

The rest of the universe is the surroundings.



2

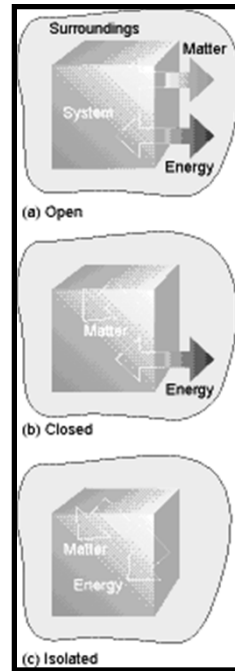
Definitions

TYPES OF SYSTEMS

Open: Exchange Matter and Energy with surroundings.

Closed: Exchange Energy (but not Matter) with surroundings.

Isolated: No exchange of Matter or Energy with surroundings.



Definitions

THE STATE OF A SYSTEM

A system is in a definite state when each of its properties has a definite value.

The state of a system is uniquely defined in terms of a few state properties that may be linked by an Equation of State

PROPERTIES

A state property (a.k.a. state function, state variable) is one which has a definite value when the state of the system is specified.

The properties of a system may be:

INTENSIVE

Do *not* depend on the quantity of matter

EXTENSIVE

Do depend on the quantity of matter

Definitions

CHANGES IN THE STATE OF A SYSTEM

Isothermal: Constant temperature
(e.g. in temperature bath)

Isobaric:* Constant pressure
(e.g. in open room)

Isochoric:* Constant volume
(e.g. in closed container)

Adiabatic: No heat transfer
(e.g. in insulated container
or explosion)

Note:* You are responsible to know the meaning of isothermal and adiabatic processes. However, I will furnish definitions of isochoric and isobaric processes as needed.

Definitions

WORK

Defined in physics as $\text{Work} = \text{Force} \times \text{Distance}$.

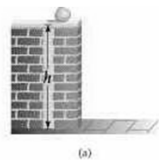
In Physical Chemistry, the principal form of work involves changes in volume of the system under a pressure (PV Work)

ENERGY

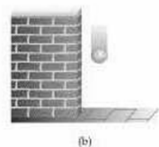
Energy is the capacity of a system to do work.

Definitions

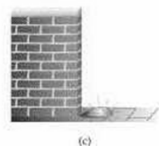
Forms of Energy / Energy Conversion



Potential Energy



Kinetic Energy



Thermal Energy

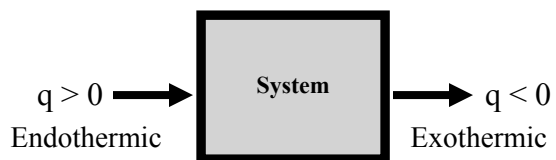
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Heat: Transfer of thermal energy.

$$q \equiv \text{Heat}$$

Heat into system: $q > 0$ Endothermic

Heat out of system: $q < 0$ Exothermic



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THE FIRST LAW OF THERMODYNAMICS

Internal Energy (U)

Internal Energy is the energy of:

- (1) Molecular Translation
- (2) Molecular Rotation
- (3) Molecular Vibration
- (4) Electronic

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elect}}$$

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The First Law: Conservation of Internal Energy

$$\Delta U = q + w$$

$q > 0$: Heat flows into system

$q < 0$: Heat flows out of system

$w > 0$: Work done **ON** system (Compression)

$w < 0$: Work done **BY** system (Expansion)

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Differential Form of the First Law

For a finite change of state from A to B the first law states:

$$\Delta U = U_B - U_A = q + w$$

For an infinitesimal change, the First Law can be rewritten as:

$$dU = dq + dw$$

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SI and Related Unites

Pressure

SI Units: 1 Pascal (Pa) \equiv 1 N/m²
1 kPa = 1000 Pa
1 bar = 1x10⁵ Pa = 100 kPa

Classic Units: 1 torr = 1 mm Hg
1 atmosphere (atm) = 760 torr

Conversion: 1 atm = 1.013x10⁵ Pa = 101.3 kPa = 1.013 bar
1 kPa = 7.50 torr

You are **not** responsible for conversion between different units of pressure. The relevant conversion factors will be furnished to you.

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Volume

Classic Unit: 1 Liter (L)

SI Units: 1 meter³ (m³)

Conversion: 1 m³ = 1,000 L

1 decimeter³ (dm³) = 1 × 10⁻³ m³ = 1.00 L

You are *not* responsible for conversion between different units of volume. The relevant conversion factors will be furnished to you.

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The Gas Constant, R

$$pV = nRT$$

SI Units: R = 8.31 J/mol

= 8.31 Pa·m³ /mol·K : Must use p in Pa and V in m³

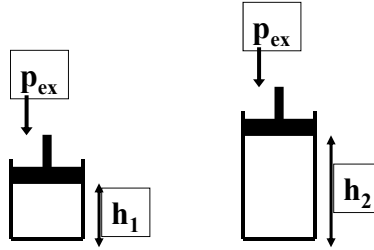
Similar: R = 8.31 kPa·L /mol·K : Must use p in kPa and V in L)

Classic: R = 0.082 L·atm /mol·K Must use p in atm and V in dm³ (L)

We will use whichever form is most suitable for the data.

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Pressure-Volume Work



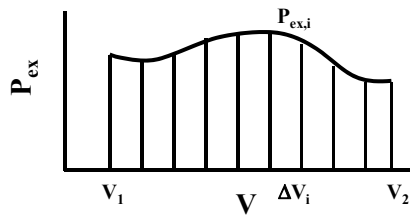
$$\begin{aligned}
 w_{\text{by}} &= F_{\text{ex}} \cdot (h_2 - h_1) = p_{\text{ex}} \cdot A \cdot (h_2 - h_1) \\
 &= p_{\text{ex}} \cdot (A \cdot h_2 - A \cdot h_1) \\
 &= p_{\text{ex}} \cdot (V_2 - V_1) \\
 &= p_{\text{ex}} \cdot \Delta V
 \end{aligned}$$

$$w = -w_{\text{by}} = -p_{\text{ex}} \cdot \Delta V$$

| | |
|------------------|--------------------|
| Expansion | Compression |
| $V_2 > V_1$ | $V_2 < V_1$ |
| $w < 0$ | $w > 0$ |

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Generalization to Variable Pressure



$$w = -\text{Area} = -\sum p_{\text{ex},i} \Delta V_i = -p_{\text{ex},1} \Delta V_1 - p_{\text{ex},2} \Delta V_2 - \dots$$

General Case: Integral

$$w = -\text{Area} = -\int_{V_1}^{V_2} p_{\text{ex}} dV$$

Special Case: $p_{\text{ex}} = \text{Constant}$

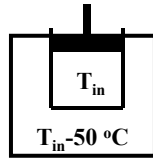
$$\int_{x_1}^{x_2} C dx = C(x_2 - x_1) \quad w = -\text{Area} = -p_{\text{ex}}(V_2 - V_1) \quad \text{i.e. we get back our original equation}$$

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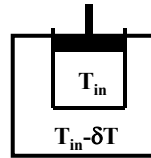
Reversible Processes

A reversible process is one that is carried out at an infinitesimal rate, and which can be reversed at any step along the way.

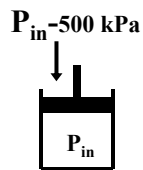
Irreversible Cooling



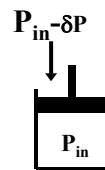
Reversible Cooling



Irreversible Expansion



Reversible Expansion



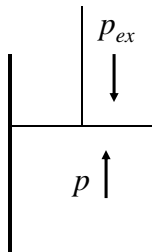
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WORK AND THE FIRST LAW

Some Examples of PV Work

Constant Pressure Expansion (or Compression)

$$w = -\int_{V_1}^{V_2} p_{ex} dV = -p_{ex}(V_2 - V_1) = -p_{ex}\Delta V$$



This process can be carried out either *reversibly* by slow heating or cooling the sample

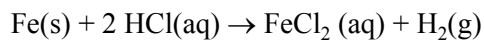
or *irreversibly* by instantaneously increasing or decreasing the pressure.

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Work in Chemical Reactions

When a reaction either produces a gaseous product or removes a gaseous reactant, then there is work accompanying the reaction.

Consider the reaction of iron with hydrochloric acid:



What is w when 111.6 g (2 mol) of Fe(s) reacts with HCl(aq) to give H₂(g) at 25 °C:

- (a) At fixed volume?
- (b) In an open beaker?

- (a) 0
- (b) -4950 J \approx -5.0 kJ

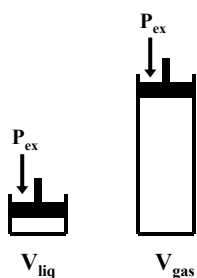
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Work in Phase Transitions

Phase transitions occur at constant pressure and temperature

$$P_{\text{ex}} = 1 \text{ atm} = 101.3 \text{ kPa}$$

$$T = T_b^\circ$$



Vaporization

$$w = -\int_{V_{\text{liq}}}^{V_{\text{gas}}} p dV$$

$$w = -p(V_{\text{gas}} - \cancel{V_{\text{liq}}}) \\ = -pV_{\text{gas}}$$

$$w = -nRT$$

$$w < 0$$

Condensation

$$w = -\int_{V_{\text{gas}}}^{V_{\text{liq}}} p dV$$

$$w = -p(\cancel{V_{\text{liq}}} - V_{\text{gas}}) \\ = +pV_{\text{gas}}$$

$$w = +nRT$$

$$w > 0$$

What is w for the condensation of 72 g (4 mol) of H₂O at 100 °C and 1 atm?

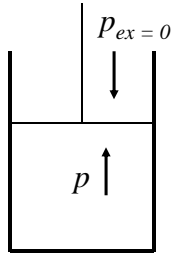
$$w = +12,400 \text{ J} = 12.4 \text{ kJ}$$

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Expansion into a vacuum

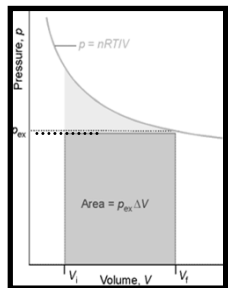
$$P_{ex} = 0$$

$$\text{Therefore: } w = -\int_{V_1}^{V_2} p_{ex} dV = 0$$



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Reversible Isothermal Expansion (or Compression)



Reversible: Therefore, $p = p_{ex} = nRT/V$.

$$dw = -pdV = -nRT/V dV$$

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV \quad \text{Because } T = \text{const.}$$

$$w = -nRT \ln(V_2 / V_1)$$

Expansion

$$V_2 > V_1$$

$$w < 0$$

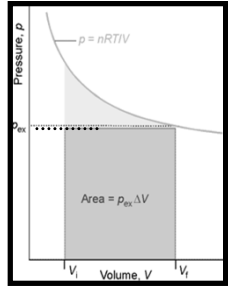
Compression

$$V_2 < V_1$$

$$w > 0$$

22

Reversible Isothermal Expansion (or Compression)



Reversible, so $p = p_{ex} = nRT/V$.

$$dw = -pdV = -nRT/V dV$$

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV \quad \text{Because } T = \text{const.}$$

$$w = -nRT \ln(V_f / V_i)$$

Note that the work for a *reversible, isothermal* expansion is the negative of the **total** curve (yellow + green).

This is greater than the negative work for an *irreversible, isothermal* expansion, which is the yellow portion of the area.

This is general. You can get more work from a reversible process than an irreversible process.

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Example: 2 mol of He is expanded isothermally at 22°C (295 K) from 22 L to 31.7 L.

Calculate w for (a) a reversible isothermal expansion

(b) irreversible isothermal expansion at $P = P_{fin}$

$$\begin{aligned} R &= 8.31 \text{ J/mol}\cdot\text{K} \\ &= 8.31 \text{ kPa}\cdot\text{L/mol}\cdot\text{K} \\ &= 0.082 \text{ L}\cdot\text{atm/mol}\cdot\text{K} \\ 1 \text{ kPa}\cdot\text{L} &= 1 \text{ J} \end{aligned}$$

Reversible isothermal expansion

$$w = -nRT \ln(V_f / V_i) = -(2 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(295 \text{ K}) \ln(31.7 / 22.0)$$

$$w = -1790 \text{ J} \approx -1.8 \text{ kJ}$$

Irreversible isothermal expansion in which the external pressure is suddenly dropped to the final pressure.

$$P_{ex} = P_{fin} = (2 \text{ mol})(8.31 \text{ kPa}\cdot\text{L/mol}\cdot\text{K})(295 \text{ K}) / 31.7 \text{ L} = 154.7 \text{ kPa}$$

$$w = -P_{ex} \Delta V = -154.7 \text{ kPa}(31.7 \text{ L} - 22.0 \text{ L}) = -1500 \text{ kPa}\cdot\text{L} = -1500 \text{ J} = -1.5 \text{ kJ}$$

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Example: 2 mol of He is expanded isothermally at 22°C (295 K)
from 22 L to 31.7 L.

Calculate w for (a) a reversible isothermal expansion

(b) irreversible isothermal expansion at $P = P_{\text{fin}}$

$$\begin{aligned}R &= 8.31 \text{ J/mol-K} \\ &= 0.082 \text{ L-atm/mol-K} \\ 1 \text{ L-atm} &= 101 \text{ J}\end{aligned}$$

Alternate Units:

Irreversible isothermal expansion in which the external pressure is suddenly dropped to the final pressure.

$$P_{\text{ext}} = P_{\text{fin}} = (2 \text{ mol})(0.082 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})(295 \text{ K}) / 31.7 \text{ L} = 1.53 \text{ atm}$$

$$w = -P_{\text{ext}} \Delta V = -1.53 \text{ atm}(31.7 \text{ L} - 22.0 \text{ L}) = -14.8 \text{ L} \cdot \text{atm}$$

$$w = -14.8 \text{ L} \cdot \text{atm} \cdot 101 \text{ J} / 1 \text{ L} \cdot \text{atm} = -1500 \text{ J} = -1.5 \text{ kJ}$$

Get same result using L-atm.

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WORK, HEAT AND THE FIRST LAW

Expansion/compression work is called " pV work" and in this context the First Law (differential form) becomes

$$dU = dq + dw = dq - pdV$$

Constant Volume: $dV = 0$

$$dU = dq_V$$

$$\text{so } q_V = \Delta U = U_2 - U_1$$

The heat exchanged with the surroundings by a constant-volume system is equal to the change of internal energy of the system.

It is **VERY** useful to have a state function (U) whose change is equal to the heat.

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WORK, HEAT AND THE FIRST LAW

Expansion/compression work is called " pV work" and in this context the First Law becomes

$$dU = dq + dw = dq - pdV$$

Constant Pressure

$$dU = dq_p - pdV$$

$$\text{so } dq_p = dU + pdV \quad \text{or} \quad q_p = \Delta U + p \Delta V \neq \Delta U$$

Bummer!!

Unfortunately, the heat exchanged with the system is **NOT** equal to the change in the State Function, U .

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ENTHALPY

Constant Pressure

$$dq_p = dU + pdV \quad \text{or} \quad q_p = \Delta U + p \Delta V \neq \Delta U$$

It would be convenient to have a State Function, whose change is equal to the heat under constant pressure conditions. Let's invent one!!

Enthalpy: Define $H \equiv U + pV$

$$\text{In general: } \Delta H = \Delta U + \Delta pV$$

Constant Pressure: $\Delta pV = p\Delta V$ (Not true in general)

$$\Delta H = \Delta U + p\Delta V = q_p$$

$p = \text{Constant:}$ $q_p = \Delta H \quad \text{and} \quad dq_p = dH$

28

Relating Enthalpy and Internal Energy Changes

Calcium Carbonate (CaCO_3) has two crystalline solid state forms,

CaCO_3 (calcite) \rightarrow CaCO_3 (aragonite)

ΔU for the conversion of one mole of calcite to aragonite is +0.21 kJ

Calculate ΔH for this conversion at 1 bar (1×10^5 Pa).

$$p\Delta V = (1 \times 10^5 \text{ Pa})(34 \text{ cm}^3 - 37 \text{ cm}^3) \frac{10^{-6} \text{ m}^3}{1 \text{ cm}^3}$$

$$p\Delta V = -0.3 \text{ Pa} \cdot \text{m}^3 = -0.3 \text{ J} = -3.0 \times 10^{-4} \text{ kJ}$$

$$V_m(\text{calcite}) = 37 \text{ cm}^3/\text{mol}$$

$$V_m(\text{aragonite}) = 34 \text{ cm}^3/\text{mol}$$

$$1 \text{ J} = 1 \text{ Pa} \cdot \text{m}^3$$

$$1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

$$\Delta H = \Delta U + \Delta pV = \Delta U + p\Delta V = 0.21 \text{ kJ} - 3.0 \times 10^{-4} \text{ kJ} = 0.21 \text{ kJ}$$

Conclusion: In reactions involving only liquids and solids, the difference between ΔU and ΔH is negligible

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Relating Enthalpy and Internal Energy Changes

For the combustion of methane: $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$,

$\Delta H = -890.0$ kJ at 25 °C. Calculate ΔU for this reaction at 25 °C.

One can ignore the volumes of liquids or solids when calculating differences between ΔU and ΔH for a reaction.

$$\Delta pV = (pV_{\text{Prod}}) - (pV_{\text{Rct}}) = n_{\text{Prod}}(\text{gas})RT - n_{\text{Rct}}(\text{gas})RT$$

$$= RT [n_{\text{Prod}}(\text{gas}) - n_{\text{Rct}}(\text{gas})] = RT [1 - 3]$$

$$= -2 \text{ mol}(8.31 \text{ J} / \text{mol} \cdot \text{K})(298 \text{ K}) = -4950 \text{ J} \approx -5.0 \text{ kJ}$$

$$\Delta U = \Delta H - \Delta pV = -890.0 \text{ kJ} - (-5.0 \text{ kJ}) = -885.0 \text{ kJ}$$

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Heat Capacities

The heat capacity, C , of any system is the amount of heat required To raise the temperature of the system by 1 K (= 1 °C).

Define: $C = \frac{dq}{dT}$

Constant Volume: $q_v = \Delta U$ and $dq_v = dU$

$$C_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T} \right)_v$$

Constant Pressure: $q_p = \Delta H$ and $dq_p = dH$

$$C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T} \right)_p$$

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Molar Heat Capacities

The heat capacity of a material is an **extensive** property.

It is more useful to tabulate Molar Heat Capacities, $C_{V,m}$ and $C_{P,m}$

Constant Volume: $C_v = \left(\frac{\partial U}{\partial T} \right)_v$

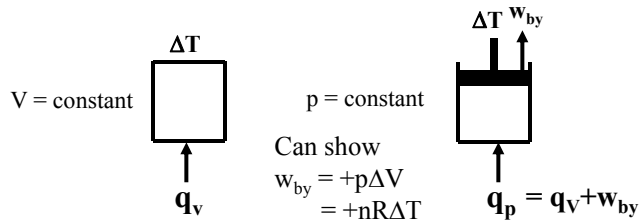
$$C_{V,m} = C_v/n$$

Constant Pressure: $C_p = \left(\frac{\partial H}{\partial T} \right)_p$

$$C_{p,m} = C_p/n$$

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The Relation Between $C_{p,m}$ and $C_{v,m}$



$$q_p = q_v + nR \Delta T$$

$$q_p / \Delta T = q_v / \Delta T + nR \Delta T / \Delta T$$

$$C_p = C_v + nR$$

$$C_p / n = C_v / n + nR / n$$

$$C_{p,m} = C_{v,m} + R$$

or $C_{p,m} - C_{v,m} = R$

Above relation is valid for Perfect Gases.

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The Calculation of Heat Capacities of Gases

Statistical Mechanics and the Molecular Kinetic Theory of Gases can be used to compute the heat capacities of gas phase molecules.

This material is *not* discussed in any significant detail in the text. However, don't worry. It's Easy!!

Equipartition of Energy

Translation: The Translational Molar Internal Energy is:

$$U_m(\text{trans}) = 1/2 RT \text{ per translational degree of freedom.}$$

Rotation: The Rotational Molar Internal Energy is:

$$U_m(\text{rot}) = 1/2 RT \text{ per rotational degree of freedom.}$$

Vibration: The Vibrational Molar Internal Energy is:

$$U_m(\text{vib}) = 1 RT \text{ per vibrational degree of freedom.}$$

Vibrational contributions are twice as high because each vibration has both kinetic and potential energy.

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Note: $H_m = U_m + pV = U_m + RT$

Monatomic Gases (e.g. Ar): 3 translations

$$U_m = U_m(\text{trans}) = 3(1/2 RT) = 3/2 RT$$

$$H_m = U_m + RT = 5/2 RT$$

$$C_{p,m} = \left(\frac{\partial H_m}{\partial T} \right)_p = 5/2 R = 5/2 (8.31 J/mol \cdot K) = 20.8 J/mol \cdot K$$

$$C_{p,m}(\text{exp}) = 20.8 J/mol \cdot K \text{ for Ar [and other monatomic gases]}$$

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Diatomic Gases (e.g. O₂): 3 translations + 2 rotations + 1 vibration

$$U_m(\text{trans}) = 3(1/2 RT) = 3/2 RT$$

$$U_m(\text{rot}) = 2(1/2 RT) = 1 RT$$

$$U_m(\text{vib}) = 1(1 RT) = 1 RT$$

$$U_m(\text{rigid}) = U_m(\text{trans}) + U_m(\text{rot}) = 5/2 RT^{**}$$

$$H_m(\text{rigid}) = U_m(\text{rigid}) + RT = 7/2 RT$$

$$\begin{aligned} C_{p,m}(\text{rigid}) &= \left(\frac{\partial H_m(\text{rigid})}{\partial T} \right)_p = 7/2 R \\ &= (7/2)(8.31 J/mol \cdot K) = 29.1 J/mol \cdot K \end{aligned}$$

At low to moderate temperatures, vibrations do not contribute the full amount of Internal Energy predicted by Equipartition of Energy.

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Diatomic Gases (e.g. O₂): 3 translations + 2 rotations + 1 vibration

$$U_m(\text{trans}) = 3(1/2 RT) = 3/2 RT$$

$$U_m(\text{rot}) = 2(1/2 RT) = 1 RT$$

$$U_m(\text{vib}) = 1(1 RT) = 1 RT$$

$$U_m(\text{vibrating}) = U_m(\text{trans}) + U_m(\text{rot}) + U_m(\text{vib}) = 7/2 RT^{**}$$

$$H_m(\text{vibrating}) = U_m(\text{vibrating}) + RT = 9/2 RT$$

$$C_{p,m}(\text{vibrating}) = \left(\frac{\partial H_m(\text{vibrating})}{\partial T} \right)_P = 9/2 R$$

$$= (9/2)(8.31 J / mol \cdot K) = 37.4 J / mol \cdot K$$

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Diatomic Gases (e.g. O₂): 3 translations + 2 rotations + 1 vibration

$$C_{p,m}(\text{rigid}) = 7/2 R = 29.1 J / mol \cdot K$$

$$C_{p,m}(\text{vibrating}) = 9/2 R = 37.4 J / mol \cdot K$$

Experimental O₂(g) heat capacities

| t | C _{p,m} | |
|-------|------------------|---------------------------------------|
| 25 °C | 29.1 J/mol-K | ← Very small vibrational contribution |
| 500 | 31.1 | |
| 1000 | 34.9 | |
| 1500 | 36.6 | ← Large vibrational contribution |
| 2000 | 37.8 | ← Small Electronic contribution |

Note: Statistical Mechanics formulas can be used to calculate the vibrational contribution to C_{p,m} very accurately.

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Non-Linear Polyatomic Gases (e.g. NH₃): 3 translations +
 3 rotations +
 3N-6 vibrations
 (N = No. Atoms)

NH₃: 3 translations + 3 rotations + 6 vibrations

In Class: $C_{p,m}(\text{rigid}) = 4 R = 33.2 \text{ J/mol-K}$
 $C_{p,m}(\text{vibrating}) = 10 R = 83.1 \text{ J/mol-K}$

Experimental NH₃(g) heat capacities

| t | C_{p,m} |
|----------|--|
| 25 °C | 35.6 J/mol-K ← Small vibrational contribution |
| 1000 | 63.0 |
| 2000 | 75.2 |
| 3000 | 79.7 ← Large vibrational contribution |

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Linear Polyatomic Gases (e.g. HC≡CH): 3 translations +
 2 rotations +
 3N-5 vibrations
 (N = No. Atoms)

HC≡CH: 3 translations + 2 rotations + 7 vibrations

Homework: Show $C_{p,m}(\text{rigid}) = 7/2 R = 29.1 \text{ J/mol-K}$
 Show $C_{p,m}(\text{vibrating}) = 21/2 R = 87.3 \text{ J/mol-K}$

Experimental HC≡CH(g) heat capacities

| t | C_{p,m} |
|----------|---|
| 25 °C | 35.6 J/mol-K ← Relatively small vibrational contribution |
| 1000 | 73.2 |
| 2000 | 82.9 ← Large vibrational contribution |

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The Variation of Internal Energy (U) with Temperature

We recently showed that: $C_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_v$

Therefore, at **constant volume**, one has: $dU = C_v dT = nC_{v,m} dT$

or:
$$\Delta U = U(T_2) - U(T_1) = \int_{T_1}^{T_2} nC_{v,m} dT$$

Over small temperature ranges, for which $C_{v,m} \approx \text{Constant}$, this expression simplifies to: $\Delta U = nC_{v,m}(T_2 - T_1) = nC_{v,m}\Delta T$

However, over extended ranges of temperature, and for accurate results, one must use the temperature dependent heat capacities and integrate over the temperature range to calculate ΔU upon heating (or cooling)

Note: The above expression is valid only if **V is constant**. If the volume changes (e.g. at constant pressure), then there is an additional term. This will be addressed at the end of the chapter.

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The Variation of Enthalpy (H) with Temperature

We recently showed that: $C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p$

Therefore, at **constant pressure**, one has: $dH = C_p dT = nC_{p,m} dT$

or:
$$\Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} nC_{p,m} dT$$

Over small temperature ranges, for which $C_{p,m} \approx \text{Constant}$, this expression simplifies to: $\Delta H = nC_{p,m}(T_2 - T_1) = nC_{p,m}\Delta T$

However, over extended ranges of temperature, and for accurate results, one must use the temperature dependent heat capacities and integrate over the temperature range to calculate ΔH upon heating (or cooling)

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One common functional form to characterize temperature dependent heat capacities is: $C_{p,m} = a + bT + \frac{c}{T^2}$

a, b and c are empirical constants determined for a given gas by fitting the equation to experimental data of $C_{p,m}$ vs. temperature.

Determine the change in enthalpy upon heating 1 mole of $\text{CO}_2(\text{g})$ from 100 °C to 400 °C.

$$\Delta H = H(673 \text{ K}) - H(373 \text{ K}) = +13,620 \text{ J} \\ \approx +13.6 \text{ kJ}$$

For $\text{CO}_2(\text{g})$,

$$a = 44.22 \text{ J/mol-K}$$

$$b = 8.79 \times 10^{-3} \text{ J/mol-K}^2$$

$$c = -8.62 \times 10^5 \text{ J/mol-K}^3$$

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Adiabatic Expansion (and Compression) of a Perfect Gas

Preliminary: Variation of U with temperature for a Perfect Gas

In principle, changes in the Internal Energy (ΔU) of a substance will occur with changes in temperature or with changes in volume.

In fact, we will learn in a little while that the "total differential" for an infinitesimal change, dU is given by:

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

It can be proven that for a Perfect Gas, which has no intermolecular attractions or repulsions, the Internal Energy will be unchanged by changes in volume if the temperature is constant; i.e.

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \text{for a Perfect Gas}$$

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$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for a Perfect Gas}$$

Therefore, one has: $dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT = nC_{V,m} dT$

independent of whether the volume (pressure) is changing.

Thus, if the gas is changing from T_1 to T_2 , the Internal Energy change is:

$$\Delta U = \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} nC_{V,m} dT = nC_{V,m} (T_2 - T_1)$$

if $C_{V,m} = \text{Constant}$

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Adiabatic Expansions (and Compressions) of a Perfect Gas

Adiabatic: There is no heat exchange between system and surroundings;
i.e. $q = 0$ (or $dq = 0$)

For isothermal expansions (or compressions) from State 1 to State 2, the pressure and volume are related by: $p_2 V_2 = p_1 V_1$

We shall develop equivalent expressions relating the variables of State 1 (p_1, V_1, T_1) and State 2 (p_2, V_2, T_2).

The First Law (applied to Perfect Gases) may be written:

$$dU = dq + dw$$

$$nC_{V,m} dT = dq - pdV$$

$$nC_{V,m} dT = 0 - pdV \quad \text{for an adiabatic process}$$

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$nC_{V,m}dT = 0 - p dV$ for an adiabatic process

$$nC_{V,m}dT = -\frac{nRT}{V}dV$$

$$\frac{dT}{T} = -\frac{R}{C_{V,m}} \frac{dV}{V} \quad \text{separating variables}$$

$$\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_{V,m}} \int_{V_1}^{V_2} \frac{dV}{V} \quad \text{assuming } C_{V,m} = \text{constant}$$

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_{V,m}} \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_{V,m}}} = \ln\left(\frac{V_1}{V_2}\right)^{+\frac{R}{C_{V,m}}}$$

$$\boxed{\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}}}$$

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$$\boxed{\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}}}$$

An alternative form relates p_2 and V_2 to p_1 and V_1

$$\left(\frac{p_2 V_2 / nR}{p_1 V_1 / nR}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}} \rightarrow \frac{p_2 V_2}{p_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}} \rightarrow \frac{p_2}{p_1} = \frac{V_1}{V_2} \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}}$$

$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{1 + \frac{R}{C_{V,m}}}$$

This can be simplified further.

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$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{1 + \frac{R}{C_{V,m}}}$$

This can be simplified further.

$$1 + \frac{R}{C_{V,m}} = \frac{C_{V,m} + R}{C_{V,m}} = \frac{C_{p,m}}{C_{V,m}} = \gamma \quad \gamma \equiv C_{p,m} / C_{V,m}$$

Therefore: $\frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^\gamma$

This latter formula is often written: $p_2 V_2^\gamma = p_1 V_1^\gamma$

This form is analogous to the isothermal expansion expression:

$$p_2 V_2 = p_1 V_1$$

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$$\left(\frac{T_2}{T_1} \right) = \left(\frac{V_1}{V_2} \right)^{\frac{R}{C_{V,m}}} \quad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^\gamma$$

Consider 80 g of O₂(g) [M=32] originally at 2,000 kPa and 8 L.

This gas is expanded reversibly and adiabatically to a final volume of 16 L

Calculate q, w and ΔU (in kJ) for this expansion. $R = 8.31 \text{ kPa}\cdot\text{L}/\text{mol}\cdot\text{K}$
 $= 8.31 \text{ J}/\text{mol}\cdot\text{K}$

$$T_1 = 770 \text{ K}$$

$$T_2 = 584 \text{ K}$$

$$C_{p,m} = (7/2)R$$

$$q = 0$$

$$w = \Delta U = -9660 \text{ J} = -9.7 \text{ kJ}$$

If a perfect gas is compressed reversibly and adiabatically, what are the signs of q, w and ΔU?

$$q = 0$$

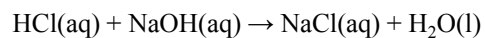
$$w = \Delta U > 0$$

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THERMOCHEMISTRY

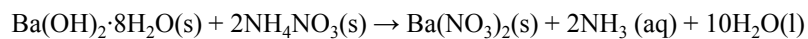
Thermochemistry is the quantitative study of the heat produced by a given chemical reaction.

If we perform this reaction:



We will note that the vessel gets hot.

Alternatively, if we perform the following reaction in a beaker:



We will observe the spontaneous formation of ice on the outside of the vessel as the temperature of the system decreases rapidly.

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NOTE:

A large percentage of reactions are performed at constant pressure, in which case: $q_p = \Delta H$

Therefore, the terms "Heat of Reaction" and "Enthalpy of Reaction" are often used interchangeably.

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We don't (can't) measure a chemical's enthalpy. What we measure is the change in enthalpy that occurs during a transformation.

In order to report enthalpy changes, ΔH , for a given transformation it is useful to discuss changes between substances in their standard states, we then use ΔH° to represent the standard change in enthalpy.

The standard state of a substance at a specified temperature is its pure form at 1 bar.

For example, the standard state of

Oxygen at 298.15 K is $O_2(g)$

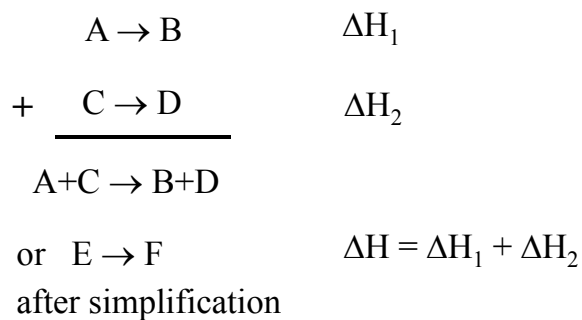
Ethanol at 298 K is $C_2H_5OH(l)$

Carbon at 298.15 K is $C(\text{graphite})$

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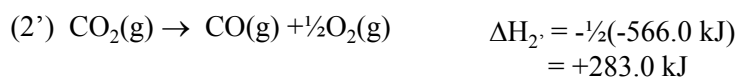
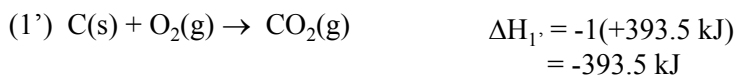
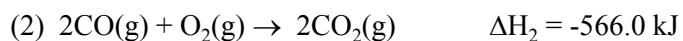
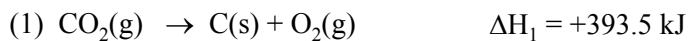
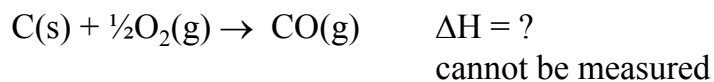
HESS'S LAW

If a reaction occurs in a series of steps, one adds the ΔH 's for the individual steps to obtain the overall ΔH of the reaction.

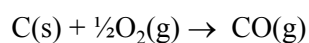
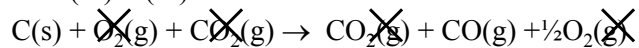


Hess's Law can be utilized to calculate ΔH for a reaction whose enthalpy change has not been measured.

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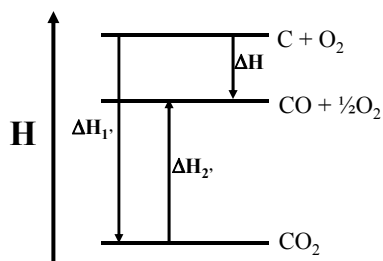
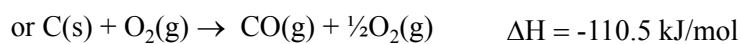
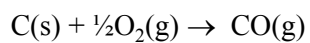
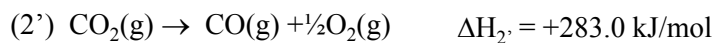
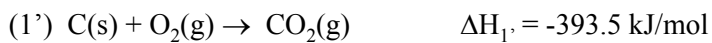


Add (1') + (2')



$$\Delta\text{H} = \Delta\text{H}_{1'} + \Delta\text{H}_{2'} = -393.5 + (+283.0) = -110.5 \text{ kJ}$$

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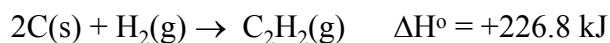
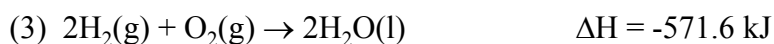
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Hess's Law Example

Determine the enthalpy change for the formation of acetylene,



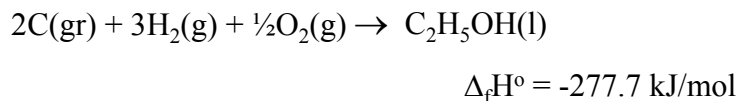
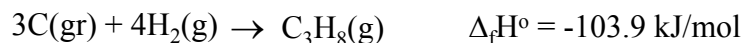
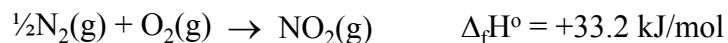
from the thermochemical equations below.



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ENTHALPIES OF FORMATION

The Enthalpy of Formation (aka Heat of Formation), $\Delta_f\text{H}^\circ$, of a compound is defined as the enthalpy of the reaction creating one mole of the compound from the elements in their standard states.

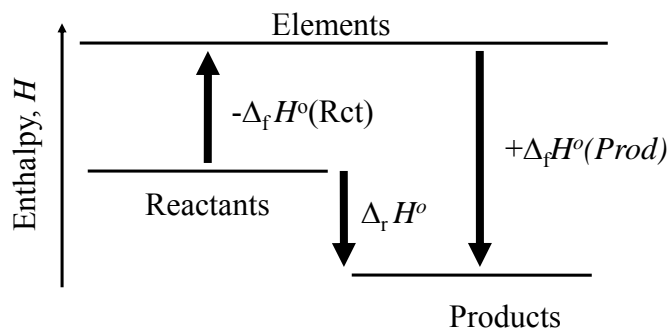


As we shall see, the enthalpy change for a reaction, $\Delta_r\text{H}^\circ$, can be calculated if one knows the enthalpies of formation of all reactants and products.

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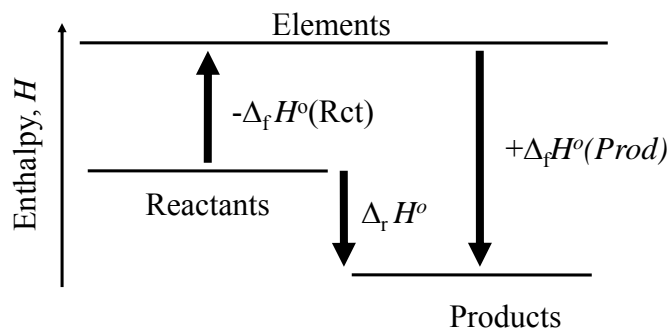
ENTHALPIES OF FORMATION

Taking Hess's law to its logical conclusion suggests that we may consider a reaction as proceeding by first breaking the reactants up into their elements and then forming the products from those elements.



Note: If a reactant or product is an element in its standard state, its enthalpy of formation is zero.

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$$\Delta_r H^\circ = \Delta_f H^\circ(\text{Prod}) - \Delta_f H^\circ(\text{Rct})$$

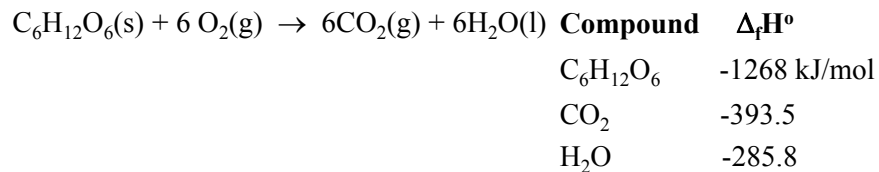
$$\Delta_r H^\circ = \sum_{\text{Prod}} \nu_P \Delta_f H^\circ(P_i) - \sum_{\text{Rct}} \nu_R \Delta_f H^\circ(R_i)$$

Example: $A + 3 B \rightarrow 2 C + D$

$$\Delta_r H^\circ = [2\Delta_f H(C) + \Delta_f H(D)] - [\Delta_f H(A) + 3\Delta_f H(B)]$$

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Use the data in the table to calculate ΔH° for the reaction



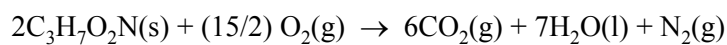
$$\Delta_r H^\circ = [6\Delta_f H(\text{CO}_2) + 6\Delta_f H(\text{H}_2\text{O})] - [\Delta_f H(\text{C}_6\text{H}_{12}\text{O}_6) + 6\Delta_f H(\text{O}_2)]$$

$$\Delta_r H^\circ = [6(-393.5) + 6(-285.8)] - [(-1268) + 6(0)]$$

$$\Delta_r H^\circ = -2808 \text{ kJ}$$

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Homework: The reaction for the combustion of L-alanine is:



$$\Delta H^\circ = -3236 \text{ kJ}$$

| Use the data in the table to calculate the enthalpy of formation of L-alanine | Compound | $\Delta_f H^\circ$ |
|---|----------------------|--------------------|
| | CO_2 | -393.5 |
| | H_2O | -285.8 |

$$\text{Answer: } \Delta_f H^\circ(\text{C}_3\text{H}_7\text{O}_2\text{N}) = -562.8 \text{ kJ/mol}$$

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The Temperature Dependence of Reaction Enthalpies

Note: I will discuss this briefly. However, you are not responsible for any calculations.

When the enthalpy change of a reaction, $\Delta_r H$, is measured using either Hess's Law or Enthalpies of Formation, the results are generally for the reaction occurring at Room Temperature (298 K).

If you need to know $\Delta_r H$ at some other temperature (at the same pressure), it can be calculated using Kirchoff's Law if one knows the heat capacities of both reactants and products of the reaction.

Kirchoff's Law $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ Slope = C_p

We showed earlier that: $\longrightarrow dH = \left(\frac{\partial H}{\partial T}\right)_p dT = C_p dT$

Therefore: $H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$

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$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$$

If one has a reaction, $R \rightarrow P$, the above equation can be applied to both reactants and products to get:

$$\Delta_r H(T_2) - \Delta_r H(T_1) = \int_{T_1}^{T_2} \Delta_r C_p dT \longrightarrow \Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT$$

$$\text{where: } \Delta_r C_p = C_p(P) - C_p(R) = \sum_{\text{Prod}} \nu_{P_i} C_{p,m}(P_i) - \sum_{\text{Ret}} \nu_{R_i} C_{p,m}(R_i)$$

Note: If the heat capacities of reactants and products can be taken as approximately constant, then Kirchoff's Law simplifies to:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \Delta_r C_p (T_2 - T_1)$$

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$$\Delta_r H(T_2) = \Delta_r H(T_1) + \Delta_r C_p (T_2 - T_1)$$

Consider the combustion of hydrogen: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

For this reaction at 298 K (=25 °C), the reaction enthalpy is:

$$\Delta_r H(298 \text{ K}) = -571.6 \text{ kJ} \quad 25 \text{ }^\circ\text{C}$$

Calculate the reaction enthalpy at 373 K (=100 °C).

$$\Delta_r C_p = +54.0 \text{ J/mol}\cdot\text{K}$$

$$\Delta_r H(373 \text{ K}) = -567.6 \text{ kJ} \quad 100 \text{ }^\circ\text{C}$$

| Species | $C_{p,m}$ |
|--------------------------------|--------------|
| $\text{H}_2(\text{g})$ | 33.6 J/mol-K |
| $\text{O}_2(\text{g})$ | 29.4 |
| $\text{H}_2\text{O}(\text{l})$ | 75.3 |

Notice that the change in $\Delta_r H$ is pretty small over the 75 °C range from 25 °C to 100 °C.

As noted above, you are not responsible for this calculation.

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Mathematics and the First Law

In the following section, will we learn:

1. State Functions and Exact Differentials
2. Partial Derivatives and The Total Differential
3. How mathematics can be used to simplify Physical Chemistry

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State Functions and Exact Differentials

A State Function is one whose change is independent of how one proceeds from an initial state to a final state.

Internal Energy (U) is a State Function.

The differential of a State Function is an Exact Differential

$$\Delta U = \int_{init}^{fin} dU = U_{fin} - U_{init}$$

We say that the integral of an exact differential is independent of the path

Note: The cyclic integral of an exact differential is zero

$$\Delta U = \oint dU = \int_{init}^{init} dU = 0$$

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Work and Heat are NOT State Functions.

Therefore, their differentials are inexact differentials

i.e. their integrals are dependent on path.

$$w = \int_{init, Path}^{fin} dw$$

We CANNOT write: $\Delta w = \int_{init}^{fin} dw = w_{fin} - w_{init}$

Similarly: $q = \int_{init, Path}^{fin} dq$

We CANNOT write: $\Delta q = \int_{init}^{fin} dq = q_{fin} - q_{init}$

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The Total Differential

One Independent Variable

Consider a function, $z = z(x)$

For a finite change, Δx , one can approximate Δz as: $\Delta z \approx \left(\frac{dz}{dx}\right) \Delta x$

For an infinitesimal change, dx , one can write dz exactly as: $dz = \left(\frac{dz}{dx}\right) dx$

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Two Independent Variables

Consider a function of two independent variables, $z = z(x,y)$

If one changes x , holding y constant, then the change in z is:

$$dz_x = \left(\frac{\partial z}{\partial x}\right)_y dx$$

If one changes y , holding x constant, then the change in z is:

$$dz_y = \left(\frac{\partial z}{\partial y}\right)_x dy$$

The total change, dz , is given by the sum of these two changes.

$$dz = dz_x + dz_y = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

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$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

As an example from thermodynamics, one generally writes that the internal energy is a function of volume and temperature, $U=U(V,T)$,

The total differential, dU is written as:

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

\uparrow \uparrow
 dU due to change in V dU due to change in T

Analogously, if one considers $H = H(p,T)$, the total differential, dH , is:

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT$$

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More than Two Independent Variables

There can be more than two independent variables.

For example: $p = p(n, V, T)$

$$dp = \left(\frac{\partial p}{\partial n} \right)_{V,T} dn + \left(\frac{\partial p}{\partial V} \right)_{n,T} dV + \left(\frac{\partial p}{\partial T} \right)_{n,V} dT$$

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An Example of the Utility of the Total Differential

Thermal Expansion Coefficient: $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

Isothermal Compressibility: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$

These two coefficients are very useful, and have been tabulated for thousands of materials.

If one wishes to know the effect of temperature on the pressure exerted by a substance on a constant volume container, the following coefficient would be very valuable. $\left(\frac{\partial p}{\partial T} \right)_V$

Then the increase in pressure accompanying a rise in temperature could be calculated by:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{\partial P}{\partial T} \right)_V dT \approx \left(\frac{\partial P}{\partial T} \right)_V [T_2 - T_1]$$

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Then the increase in pressure accompanying a rise in temperature could be calculated by:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{\partial P}{\partial T} \right)_V dT \approx \left(\frac{\partial P}{\partial T} \right)_V [T_2 - T_1]$$

Unfortunately, one can look high and low and never find an experimental measurement of this important quantity.

Fortunately, it is not necessary to measure this quantity directly because it can be calculated from tabulated values of α and κ_T for a substance.

It can be shown *in class* that, starting with the total differential for $V = V(p,T)$:

$$\left(\frac{\partial p}{\partial T} \right)_V = -\frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = \frac{\alpha}{\kappa_T} \quad \text{where} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

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The thermal expansion coefficient of liquid mercury is: $\alpha = 1.8 \times 10^{-6} \text{ K}^{-1}$

The isothermal compressibility of liquid mercury is: $\kappa_T = 4.0 \times 10^{-7} \text{ bar}^{-1}$

The inside of a glass capillary tube can tolerate a pressure of 10 bar without exploding.

If a capillary is filled with liquid mercury at 25 °C and 1 bar, what will be the pressure inside the capillary tube if it is heated to 29 °C;
i.e. will the capillary tube explode?

$$(\partial p / \partial T)_V = 4.5 \text{ bar/K}$$

$$\Delta P = 18 \text{ bar}$$

$$P_{\text{fin}} = 1 + 18 = 19 \text{ bar}$$

Kaboom!!

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Changes in Internal Energy

Earlier in the chapter (in section on Adiabatic Expansions) we showed that:

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad \left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \text{for a Perfect Gas}$$

$$\text{Therefore, one has: } dU = \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT = nC_{V,m} dT$$

independent of whether the volume (pressure) is changing.

However, the assumption that U is independent of volume, $(\partial U / \partial V)_T = 0$, is **not** valid for any material other than a Perfect Gas.

In general, one must consider changes in **both** V and T when determining changes in the internal energy, ΔU .

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In general, one must consider changes in **both** V and T when determining changes in the Internal Energy, ΔU .

Starting with: $U = U(V, T)$

We can write the total differential:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

The Constant Volume Heat Capacity, C_V , is: $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

We can also define the Internal Pressure, π_T , as: $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$

$$\text{Therefore: } dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = \pi_T dV + C_V dT$$

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$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = \pi_T dV + C_V dT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

If both the volume and temperature change during a process, ΔU can be calculated from:

$$\Delta U = \int_{V_1}^{V_2} \pi_T dV + \int_{T_1}^{T_2} C_V dT$$

For $\text{NH}_3(\text{g})$ at 298 K and 1 bar, $\pi_{T,m} = 0.84 \text{ kPa/mol}$ and $C_{V,m} = 27.3 \text{ J/mol}\cdot\text{K}$

Calculate the change in Molar Internal Energy, ΔU_m , when NH_3 is heated from 298 K to 300 K and simultaneously compressed from 1.0 L to 0.6 L.

$$1 \text{ kPa}\cdot\text{L} = 1 \text{ J}$$

$$\begin{aligned} \Delta U &= \pi_{T,m}(V_2 - V_1) + C_{V,m}(T_2 - T_1) \\ &= 0.84 \text{ kPa} / \text{mol}(0.6 \text{ L} - 1.0 \text{ L}) + 27.3 \text{ J/mol} \cdot \text{K}(300 \text{ K} - 298 \text{ K}) \\ &= -0.34 \text{ kPa} \cdot \text{L} / \text{mol} + 54.6 \text{ J} / \text{mol} = 54.3 \text{ J} / \text{mol} \end{aligned}$$

Note that for a gas at moderate pressure, changes in internal energy resulting from a change in T are greater than those resulting from a change in V.

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The sign of π_T is a very useful measure of whether repulsive or attractive forces are dominating the intermolecular interactions of a system under a given set of conditions.

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$$

Repulsions Dominant

$$\pi_T < 0$$

and for a volume increase:

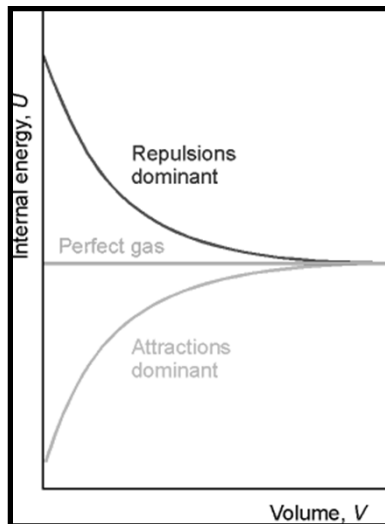
$$\Delta U = \int_{V_1}^{V_2} \pi_T dV < 0$$

Attractions Dominant

$$\pi_T > 0$$

and for a volume increase:

$$\Delta U = \int_{V_1}^{V_2} \pi_T dV > 0$$



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Example Calculations

The Internal Pressure, π_T , can be related to state variables of a material.

We will learn (in Chapter 3), that one can derive:

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

(A) Show (in class) that for a Perfect Gas, $\pi_T = 0$ $pV = nRT$

(B) Show (in class) that for a van der Waals Gas, $\pi_T = a(n/V)^2$

$$\left(p + a \left[\frac{n}{V} \right]^2 \right) (V - nb) = nRT$$

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Changes in Internal Energy at constant Pressure

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = \pi_T dV + C_V dT$$

In a **constant volume** experiment, the rate at which U changes with temperature is given by:

$$dU = \pi_T dV + C_V dT \xrightarrow[\text{Hold V constant}]{\text{Divide by } dT} \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

Let's assume, instead, that the temperature is varied in a **constant pressure** experiment.

$$dU = \pi_T dV + C_V dT \xrightarrow[\text{Hold P constant}]{\text{Divide by } dT} \left(\frac{\partial U}{\partial T}\right)_P = \pi_T \left(\frac{\partial V}{\partial T}\right)_P + C_V$$

We can recast this in terms of the thermal expansion coefficient:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \longrightarrow \left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$

$$\text{Thus, we have: } \left(\frac{\partial U}{\partial T}\right)_P = \alpha\pi_T V + C_V$$

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$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_P = \alpha\pi_T V + C_V \quad \text{and} \quad \Delta U &= \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_P dT = \int_{T_1}^{T_2} (\alpha\pi_T V + C_V) dT \\ &= \int_{T_1}^{T_2} \alpha\pi_T V dT + \int_{T_1}^{T_2} C_V dT \end{aligned}$$

- (1) If attractive forces dominate, $\pi_T > 0$, and ΔU is higher for the same temperature rise at constant pressure than at constant volume.
- (2) If repulsive forces dominate, $\pi_T < 0$, and ΔU is lower for the same temperature rise at constant pressure than at constant volume.
- (3) For a Perfect Gas, with no attractive or repulsive forces, $\pi_T = 0$, and ΔU is the same independent of whether the temperature rise is at constant pressure or constant volume.

These trends make sense!!

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Note: The Joule Experiment

As outlined in the text (Sect. 2.11 B), James Joule thought that he could determine the Internal Pressure, π_T , by measuring the temperature change when a gas expands into a vacuum.

Unfortunately, his measurement apparatus was not sufficiently accurate to measure this quantity.

However, he later developed another experiment (the Joule-Thomson Experiment) that can be used to measure deviations of real gases from ideality (the Joule-Thomson Coefficient) [coming up shortly]

You are *not* responsible for the Joule Experiment.

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The Relation Between C_p and C_v

Early in the Chapter, we presented the relation: $C_p - C_v = nR$

Actually, there is a general relationship which can be derived for $C_p - C_v$ for any material. For a Perfect Gas, it reduces to the above equation.

The derivation is presented in "Further Information 2.2" in the text, although it requires a relationship for π_T which will be derived in Chapter 3. We will use the following equation (deferring its derivation until the next chapter).

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - P$$

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The Relation Between C_p and C_v

Let's start with the definition: $C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$

We show **in class** that, using the standard relation between H and U, one has:

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v + p \left(\frac{\partial V}{\partial T}\right)_p$$

Using the total differential for U(V,T) to compute $(\partial U/\partial T)_p$, we show **in class** that:

$$C_p - C_v = \left[p + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_p$$

We then use **in class** the relation, $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p$ to show that:

$$C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_p$$

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The Relation Between C_p and C_v

$$C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_p$$

The above equation is easily usable, as is, to determine $C_p - C_v$, if one knows the Equation of State of the substance.

However, it is convenient to recast the equation in terms of the Thermal Expansion Coefficient, α , and Isothermal Compressibility, κ_T .

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad \text{and} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad \text{using} \quad \left(\frac{\partial p}{\partial T}\right)_v = \frac{\alpha}{\kappa_T}$$

Therefore, we obtain **in class**: $C_p - C_v = TV \frac{\alpha^2}{\kappa_T}$

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$$C_p - C_V = TV \frac{\alpha^2}{\kappa_T} \quad \text{where } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{and} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Let's apply this equation to a Perfect Gas.

Let's show *in class* that for a Perfect Gas,

1. $\alpha = 1/T$
2. $\kappa_T = 1/p$
3. $C_p - C_V = nR$ and $C_{p,m} - C_{V,m} = R$

As discussed earlier in the chapter, the reason that $C_p > C_V$ for a Perfect Gas is that extra heat is required to replace the energy lost by the gas in pushing aside the atmosphere.

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$$C_p - C_V = TV \frac{\alpha^2}{\kappa_T} \quad \text{where } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{and} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Because the volume of a liquid changes very little with a rise in temperature, it is tempting to assume that $C_p = C_V$ for a liquid (or solid).

Let's apply this formula to $H_2O(l)$ at 25 °C.

$$\begin{aligned}
 C_{p,m} - C_{V,m} &= TV_m \frac{\alpha^2}{\kappa_T} & C_{p,m} &= 75.3 \text{ J/mol-K} \\
 &= (298 \text{ K})(0.018 \text{ L/mol}) \frac{(2.1 \times 10^{-4} \text{ K}^{-1})^2}{4.9 \times 10^{-5} \text{ bar}^{-1}} & V_m &= 0.018 \text{ L/mol} \\
 &= 4.8 \times 10^{-3} \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \cdot \frac{100 \text{ J}}{1 \text{ L} \cdot \text{bar}} \approx 0.5 \text{ J/mol} \cdot \text{K} & \alpha &= 2.1 \times 10^{-4} \text{ K}^{-1} \\
 & & \kappa_T &= 4.9 \times 10^{-5} \text{ bar}^{-1} \\
 & & & 1 \text{ L} \cdot \text{bar} = 100 \text{ J}
 \end{aligned}$$

$$C_{V,m} = C_{p,m} - 0.5 \text{ J/mol-K} = 75.3 \text{ J/mol-K} - 0.5 \text{ J/mol-K} = 74.8 \text{ J/mol-K}$$

In some liquids, $C_{p,m}$ and $C_{V,m}$ can differ by as much as 30%.

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HOMEWORK

In the last section, we proved that an expression for $C_p - C_V$ is:

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p$$

There is an alternative expression for $C_p - C_V$:

Use: (1) $H = U + pV$
(2) The total differential for $H(p,T)$
to derive the following equation for $C_p - C_V$:

$$C_p - C_V = \left[V - \left(\frac{\partial H}{\partial p} \right)_T \right] \left(\frac{\partial p}{\partial T} \right)_V$$

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$$C_p - C_V = \left[V - \left(\frac{\partial H}{\partial p} \right)_T \right] \left(\frac{\partial p}{\partial T} \right)_V$$

In the last section, we noted that the material in Chapter 3 will permit us to develop the following expression for $(\partial U/\partial V)_T$:

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

The material in Chapter 3 will also permit us to develop the following expression for $(\partial H/\partial p)_T$:

$$\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p$$

It is easy to show that for a gas obeying the Perfect Gas equation, $(\partial H/\partial p)_T = 0$, in which case $C_p - C_V = nR$.

However, for a real gas or a condensed phase material, $(\partial H/\partial p)_T \neq 0$.

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The Dependence of H (Enthalpy) on p and T

In general, one must consider changes in **both** p and T when determining changes in the Enthalpy, ΔH .

Starting with: $H = H(p,T)$

We can write the total differential:

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

The Constant Pressure Heat Capacity, C_p , is: $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$\text{Therefore: } dH = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT$$

As noted in the last section, $(\partial H/\partial p)_T = 0$ for a Perfect Gas, in which case the first term vanishes, and H is a function of temperature only.

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$$\text{Therefore: } dH = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT$$

As noted in the last section, $(\partial H/\partial p)_T = 0$ for a Perfect Gas, in which case the first term vanishes, and H is a function of temperature only.

However, in a real gas or condensed phase material, $(\partial H/\partial p)_T \neq 0$, and the Enthalpy is a function of both pressure and temperature.

The value of $(\partial H/\partial p)_T$ for a non-ideal material can be related to an experimental quantity called the Joule-Thomson Coefficient (μ)

You are NOT responsible for the following material on the Joule-Thomson Coefficient

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The Joule-Thomson Coefficient

Following the failure of his initial experiment to measure deviations of gases from ideality, James Joule teamed with William Thomson (Lord Kelvin) to devise a rather sophisticated experiment in which a gas is expanded from high pressure to low pressure through an insulated throttling valve, and the change in temperature is measured.

It can be proven that this expansion occurs at constant enthalpy (H) [e.g. Justification 2.3 in the text].

From change in temperature (ΔT) divided by the change in pressure (Δp), one obtains a quantity, now termed the Joule-Thomson Coefficient (μ):

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \quad \text{One expects that } \mu = 0 \text{ for a Perfect Gas}$$

It can be proven (you are not responsible for the proof) that:

$$\left(\frac{\partial H}{\partial p} \right)_T = -\mu C_p$$

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Using $\left(\frac{\partial H}{\partial p} \right)_T = -\mu C_p$ and $\left(\frac{\partial H}{\partial T} \right)_p = C_p$

One can write: $dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT = -\mu C_p dp + C_p dT$

Thus, if one has experimental values for the Joule-Thomson Coefficient and Constant Pressure Heat Capacity of a substance, then the dependence of H on pressure and temperature can be determined.

If Pressure is varied from p_1 to p_2 and Temperature is varied from T_1 to T_2 : $\Delta H = \int_{p_1}^{p_2} -\mu C_p dp + \int_{T_1}^{T_2} C_p dT$

\uparrow
 Variation in H due to change in Pressure
 \uparrow
 Variation in H due to change in Temperature

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