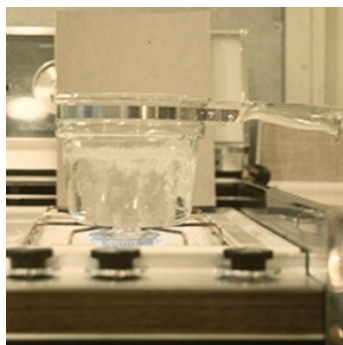


Chemistry BC3252y: Part III

Applications of the First Law



1

Heat capacity: Concept and history

Add heat q to an object: temperature rises: $\Delta T > 0$

The **heat capacity** of the object determines how fast the temperature rises.

Extensive property : think of boiling water. A large cooking pot comes to a boil more slowly than a small one.

Also depends on the substance.

Historic definition: $C = q/\Delta T$

Historically, $C_{\text{water}} = 1$ calorie/gram-degree heat capacity per gram called “**specific heat**”.

One calorie of heat warms one gram of water by one degree.

2

Heat capacity: modern version

ΔT differs when q is added at **constant V** or **constant p**.

Modern definitions:

$$C_v \equiv (\partial U / \partial T)_v$$

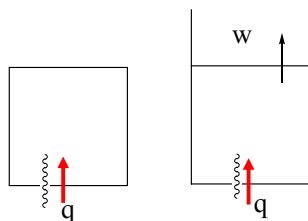
$$C_p \equiv (\partial H / \partial T)_p$$

Consequences:

If V is constant, $dq = dU = C_v dT$

If p is constant, $dq = dH = C_p dT$

$C_v < C_p$: see diagram (more later)



When V is constant, no work is done, so ΔU is larger, ΔT is larger, so C is smaller

3

Heat capacities

$$C_v \equiv (\partial U / \partial T)_v \text{ and } C_p \equiv (\partial H / \partial T)_p$$

When V and C_v are both **constant** $\Delta U = C_v \Delta T$

Both U and C_v are **extensive**: $U/n = U_m$, $C_v/n = C_{v,m}$

some books use overbar to indicate molar: \bar{U} instead of U_m

$$\Delta U_m = C_{v,m} \Delta T \text{ or } \Delta U = C_v \Delta T = n C_{v,m} \Delta T$$

C_v has units J/K while $C_{v,m}$ has units J/K-mole

Similarly for H:

if p and C_p are both **constant**, $\Delta H = C_p \Delta T = n C_{p,m} \Delta T$

If ΔT is large, so C's are not constant (they vary with T):

$$\text{then } \Delta U = n \int C_{v,m} dT \text{ and } \Delta H = n \int C_{p,m} dT$$

4

The Relationship between C_p and C_v for an ideal gas

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial(pV)}{\partial T}\right)_p \quad \text{so} \quad C_p = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p$$

For an ideal gas

$$1) V = nRT/p \quad \text{so} \quad (\partial V/\partial T)_p = nR/p \\ \rightarrow p(\partial V/\partial T)_p = nR$$

$$2) \text{ If } U = U(T) \text{ only, then } (\partial U/\partial T)_p = (\partial U/\partial T)_v = C_v$$

Thus, for an ideal gas

$$C_p = C_v + nR \quad \text{or} \quad C_{p,m} = C_{v,m} + R$$

5

Calorimetry



If $dV = 0$ (pressure changes)
 $q = \Delta U$ (bomb calorimeter)

If $dp = 0$ (volume changes) $q = \Delta H$

Calorimeters typically well insulated, so $q_{\text{tot}} = 0$.

The heat given off by the reaction warms the contents of the calorimeter. Measure ΔT

6

Calorimetry

$$q_{\text{tot}} = 0$$

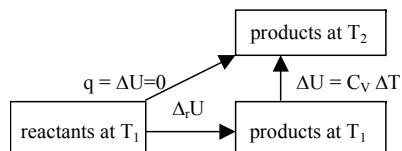
$$q_{\text{tot}} = q_{\text{rxn}} + q_{\text{thermal}} = \Delta_r U + C_v \Delta T = 0$$

C_v is the heat capacity of both the calorimeter (container, stirrer, etc.) and contents = products.

$$C_{v,\text{tot}} = n_{\text{products}} C_{v,m}(\text{products}) + C_{v,\text{cal}}$$

$C_{v,\text{cal}}$ determined by calibration (combustion of benzoic acid often used)

But is $C_{v,\text{cal}} = C_{v,\text{tot}}$? Sometimes almost so.



7

Calorimetry: terms in $C_{\text{total}} = C_{\text{cal}} + C_{\text{contents}}$

Depending on the design of a calorimeter, one or the other of the contributions to C_{tot} may be negligible.

For large calorimeters, it is often true that

$$C_{\text{cal}} \gg C_{\text{contents}} \quad \text{so} \quad C_{\text{tot}} = C_{\text{cal}}$$

For a styrofoam cup calorimeter,

$$C_{\text{contents}} \gg C_{\text{cal}} \quad \text{so} \quad C_{\text{tot}} = C_{\text{contents}}$$

In some cases, neither is negligible, so both must be included in the calculation.

You must consider both, unless told otherwise.



8

Atkins 8th Ed: Problem 2.8 (7th 2.13)

A 0.727 g sample of the sugar ribose (C₅H₁₀O₅) was placed in a **bomb** calorimeter and burned in an excess of oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid gave a temperature rise of 1.940 K.

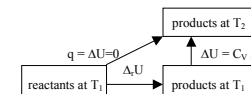
What are $\Delta_{\text{comb}}U_{\text{m}}^{\circ}$ and $\Delta_{\text{comb}}H_{\text{m}}^{\circ}$ for ribose?

$$\Delta_{\text{comb}}U_{\text{m}}^{\circ}(\text{benzoic acid}) = -3251 \text{ kJ/mole.}$$

| substance | Molar mass (g/mole) | mass (g) | moles |
|--------------|---------------------|----------|-----------|
| benzoic acid | 122.12 | 0.825 | 0.0067556 |
| ribose | 150.13 | 0.727 | 0.0048427 |

9

Atkins Problem 2.13 (2), continued



In a **bomb** calorimeter, V is constant, so $q = \Delta U$

$$q_{\text{tot}} = 0 = q_{\text{rxn}} + q_{\text{heating}} = q_{\text{rxn}} + C_{V,\text{tot}} \Delta T$$

Find $C_{V,\text{tot}}$: use the known $\Delta_{\text{r}}U_{\text{m}}$ for benzoic acid (pay close attention to moles):

$$\begin{aligned} q_{\text{rxn}} &= n \Delta_{\text{r}}U_{\text{m}} \\ &= (0.0067556 \text{ mole})(-3251 \text{ kJ/mole}) \\ &= -21.962 \text{ kJ} \end{aligned}$$

$$\begin{aligned} C_{V,\text{tot}} &= -q_{\text{rxn}}/\Delta T \\ &= -(-21.962 \text{ kJ})/(1.940 \text{ K}) \\ &= 11.3209 \text{ kJ/K} = 11320 \text{ J/K.} \end{aligned}$$

10

In the solutions manual, Atkins assumes that C_V is the same for benzoic acid and ribose combustions. Why?



Combustion of 0.825 g benzoic acid yields
7(0.0067556 mole) of CO₂(g) and
3(0.0067556 mole) of liquid water.

What is $C_V(\text{products})$?

$$C_{V,\text{m}}[\text{CO}_2\text{(g)}] = 28.8 \text{ J/K-mole}$$

$$C_{V,\text{m}}[\text{H}_2\text{O(l)}] = 75.3 \text{ J/K-mole.}$$

$$\begin{aligned} C_{V,\text{products}} &= (0.0067556 \text{ mole})[7(28.8) + 3(75.3)] \\ &= 2.888 \text{ J/K} \quad (\ll C_{\text{cal}} = 11320 \text{ J/K})! \end{aligned}$$

Conclusion: for **this** calorimeter, $C_{V,\text{tot}} = C_{V,\text{cal}}$

But if not explicitly stated, this must be demonstrated.

11

[Prob.2.13, cont.] Now for the combustion of Ribose
 $\text{C}_5\text{H}_{10}\text{O}_5\text{(s)} + 5 \text{ O}_2\text{(g)} \rightarrow 5 \text{ CO}_2\text{(g)} + 5 \text{ H}_2\text{O(l)}$

Find $\Delta_{\text{r}}U_{\text{m}}$ based on the now *known* $C_{V,\text{tot}} = C_{V,\text{cal}}$:

$$\begin{aligned} \Delta_{\text{r}}U &= q_{\text{rxn}} = -C_{V,\text{tot}} \Delta T \\ &= -(11.320 \text{ kJ/K})(0.910 \text{ K}) = -10.302 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{r}}U_{\text{m}} &= \Delta_{\text{r}}U/n = (-10.302 \text{ kJ})/(0.0048427 \text{ moles}) \\ &= -2127.4 \rightarrow -2130 \text{ kJ/mole} \end{aligned}$$

What is $\Delta_{\text{r}}H_{\text{m}}^{\circ}$? $\Delta_{\text{r}}H_{\text{m}}^{\circ} = \Delta_{\text{r}}U_{\text{m}} + RT\Delta_{\text{r}}n_{\text{gas}}$

$$\text{But } \Delta_{\text{r}}n_{\text{gas}} = 0 \rightarrow \Delta_{\text{r}}H_{\text{m}}^{\circ} = -2130 \text{ kJ/mole}$$

Pay close attention to moles in such problems!

keeping careful track of units (J/mole vs J) is often helpful.

12

Example 2: Ammonium nitrate



Used in commercial cold packs.

Dissolving $\text{NH}_4\text{NO}_3(\text{s})$ in water is **endothermic**:



The pack gets **cold**: heat is drawn from the water as the reaction proceeds.

If one mole of ammonium nitrate is dissolved in one liter of water at 25.0°C and one atm., the temperature of the solution falls to 16.2°C . What is $\Delta_r H^\circ$?

Assume constant pressure, and make the approximation that the heat capacity and density of the **solution** are the same as of **pure water** at 25°C :

$$C_{p,m} = 75.291 \text{ J/K-mole and } \rho = 0.99705 \text{ g/mL.}$$

$$\Delta T = 16.2^\circ\text{C} - 25.0^\circ\text{C} = -8.8^\circ\text{C} = -8.8 \text{ K}$$

13



Water: $1 \text{ L} = 1000 \text{ mL}$

$$= (997.05 \text{ g}) / (18.015 \text{ g/mole})$$

$$= 55.344 \text{ moles of water in one L}$$

$$C_p = (55.344 \text{ mole})(75.291 \text{ J/K-mole})$$

$$= 4167 \text{ J/K}$$

$$q_{\text{tot}} = 0 = q_{\text{rxn}} + q_{\text{thermal}} = \Delta_r H^\circ + C_p \Delta T$$

$$\Delta_r H^\circ = -C_p \Delta T = -(-8.8 \text{ K})(4167 \text{ J/K})$$

$$= 36.67 \rightarrow 37 \text{ kJ/mole}$$

14

Defining $\Delta_f H^\circ$ for ions

All solutions are electrically neutral:

moles of + charge = moles of - charge

Cannot study cations or anions alone.

But with one arbitrary choice, define $\Delta_f H^\circ$ for ions:

let $\Delta_f H^\circ(\text{H}^+ \text{ at exactly } 1.00 \text{ M}) \equiv 0$.

Then for a 1 M solution of HCl

$$\Delta_f H^\circ(\text{solution}) = \Delta_f H^\circ(\text{H}^+) + \Delta_f H^\circ(\text{Cl}^-) = \Delta_f H^\circ(\text{Cl}^-)$$

then from $\Delta_f H^\circ(\text{Cl}^-)$, find $\Delta_f H^\circ$ (other cations)

Tables often include $\Delta_f H^\circ$ (ions at 1.00 M)

15

Modern Calorimetry methods

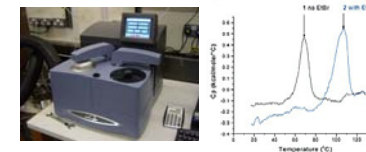
Faster, much smaller samples

Differential Scanning Calorimetry

(Atkins p 46-47)

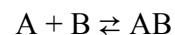
two samples simultaneously

get C_p vs. T curves, integrate $\rightarrow \Delta H$



Isothermal Titration Calorimetry

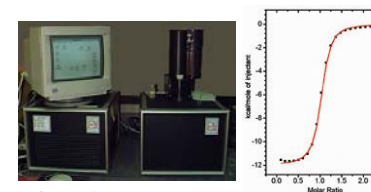
to study binding processes



measure q to keep $\Delta T = 0$

as B is injected

works for K_B 's from about 10^2 to $\sim 10^9 \text{ M}^{-1}$



16

Adiabatic processes



Definition: **adiabatic** means $dq = 0$

This can be effected with good insulation.

If $dq = 0$, then $dU = dw$ or $\Delta U = w$ (first law).

If a process is reversible, then $p = p_{ex}$

So for a **reversible adiabatic expansion**

$$dU = -pdV$$

Expansion: $dV > 0$, so $w < 0$, so $\Delta U < 0$, so $\Delta T < 0$:
the gas cools. **p, V, and T all change**

17

Reversible adiabatic expansion/compression of an ideal gas

Reversible adiabatic expansion: $dU = -pdV$

Ideal gas: $dU = C_v dT$ and $p = nRT/V$

Substituting: $C_v dT = -(nRT) dV/V$

Separate variables: $(C_v/nR) dT/T = -dV/V$

If C_v is constant (true if the range of T is small),
integration gives

$$\frac{C_v}{nR} \ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right) = +\ln\left(\frac{V_1}{V_2}\right)$$

18

Reversible adiabatic expansion/compression of an ideal gas: Two useful results

If C_v is constant, $(C_v/nR) \ln(T_2/T_1) = \ln(V_1/V_2)$

$$(C_v/nR) \ln T_2 - (C_v/nR) \ln T_1 = \ln V_1 - \ln V_2$$

Put all terms relating to state 2 on left, 1 on right:

$$(C_v/nR) \ln T_2 + \ln V_2 = (C_v/nR) \ln T_1 + \ln V_1$$

log properties: $a \ln x = \ln x^a$ and $\ln x + \ln y = \ln(xy)$

$$\ln T_2^{(C_v/nR)} + \ln V_2 = \ln T_1^{(C_v/nR)} + \ln V_1$$

$$\ln(T_2^{(C_v/nR)} V_2) = \ln(T_1^{(C_v/nR)} V_1)$$

$$(T_2^{(C_v/nR)} V_2) = (T_1^{(C_v/nR)} V_1)$$

Result 1: **$VT^{(C_v/nR)}$ is constant!**

19

Reversible adiabatic expansion/compression of an ideal gas: Result 2

Start with $VT^{(C_v/nR)}$ is constant

$$V_1 T_1^{(C_v/nR)} = V_2 T_2^{(C_v/nR)}$$

$$(V_1/V_2) = (T_2/T_1)^{(C_v/nR)}$$

$$(V_1/V_2)^{(nR/C_v)} = (T_2/T_1) = (p_2 V_2 / p_1 V_1)$$

$$(V_1/V_2)^{(nR/C_v)} = (p_2/p_1) (V_2/V_1)$$

$$(V_1/V_2)^{[(nR/C_v) + 1]} = (p_2/p_1)$$

$$\text{But } nR/C_v + 1 = (nR + C_v)/C_v = C_p/C_v \equiv \gamma$$

$$\text{So } p_1 V_1^\gamma = p_2 V_2^\gamma$$

Result 2: **pV^γ is constant**

20

Reversible adiabatic expansion/compression of an ideal gas

(1) $\mathbf{VT}^{C_v/nR}$ is constant

(2) \mathbf{PV}^γ is constant,
where $\gamma = C_p/C_v$

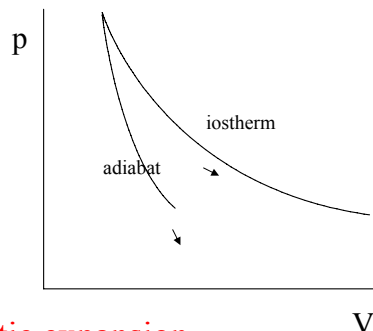
$$V_2 = V_1(p_1/p_2)^{1/\gamma}$$

Since $\gamma > 1$, as p increases,
 V falls **faster** than isothermally

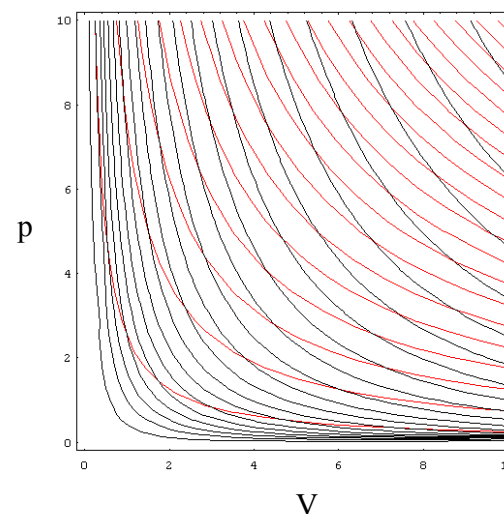
An ideal gas cools upon adiabatic expansion

Why? it is **doing work**, and $q = 0$, so energy U falls!

In plots of $p(V)$, **adiabats** are steeper than **isotherms**



21



Red = isotherms
 $\Delta T = 0$
 $pV = k$
(*hyperbolas*)

Black = adiabats
 $dq = 0$
 $pV^\gamma = k$
(*steeper!*)

22

Heat capacities of gases

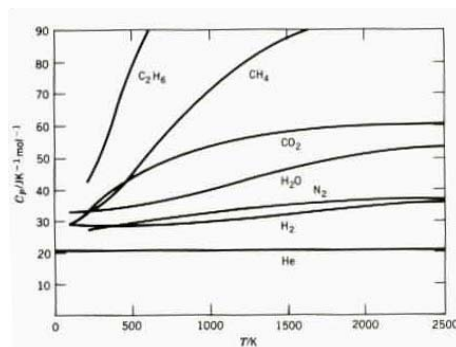
C_v and C_p vs. T :

Small and **constant**
for He (and other
monatomic gases)

Larger, with slow
increase in T , for
diatomics

Larger, steeper for
polyatomics

Why?



23

Molecular interpretation of heat capacity

Degrees of freedom: $3N$ ($N = \#$ atoms)

Translation: 3

Rotation: 2 (if linear) or 3 (if non-linear)

Vibration: the rest: $(3N-5)$ if linear, or else $(3N-6)$

Classical **law of equipartition of energy:**

in a system at thermal equilibrium (at temperature T)
each mode contains $\frac{1}{2} RT$ of **kinetic energy** per mole

(at 25°C , $\frac{1}{2} RT = 1.24 \text{ kJ/mole} = 104 \text{ cm}^{-1}$)

Thermal equilibrium means that energy is distributed evenly across the system.

24

Molecular interpretation of heat capacity
Classical equipartition of energy

$\frac{1}{2} RT$ of kinetic energy per mode per mole, $C_v \equiv (\partial U/\partial T)_V$

Translation: $U_{\text{trans}} = (3/2) RT$, $C_{V,\text{trans}} = (3/2) R$

Rotation: if **linear:** $U_{\text{rot}} = RT$ $C_{V,\text{rot}} = (2/2) R = R$

if **non-linear** $U_{\text{rot}} = (3/2) RT$, $C_{V,\text{rot}} = (3/2) R$

Vibration: both kinetic and potential energy

on average, kinetic = potential, so RT per mode:

linear: $U_{\text{vib}} = (3N - 5) RT$, $C_{V,\text{vib}} = (3N - 5) R$

non linear: $U_{\text{vib}} = (3N - 6) RT$ $C_{V,\text{vib}} = (3N - 6) R$

25

Classical equipartition of energy:
 does it work for monatomic gases?

Monatomic gases: $C_{V,m} = (3/2) R = 12.5 \text{ J/mol-K}$

Theory also predicts no dependence on temperature.

Experimental data:

| t°C | 0 | 100 | 200 | 500 | 1200 | 2000 |
|--------------------------------------|------|------|------|------|------|------|
| $C_{v,m}(\text{Ar}) \text{ J/mol-K}$ | 12.5 | 12.5 | 12.5 | 12.5 | 12.6 | 12.6 |

Yes! Theory works well:

values are correct, and C_V is constant.

$C_{p,m} = C_{V,m} + R$, $\gamma = (C_p/C_V) = 5/3 = 1.667$

26

Classical equipartition of energy:
 Does this work for **diatomic** gases?

Diatomic gases: $C_{V,m}/R = (3/2) + 1 + 1 = (7/2)$

Theory says $C_{V,m} = (7/2) R = 29.1 \text{ J-mol}^{-1}\text{K}^{-1}$

Experimental data:

| $C_{v,m} \text{ J/mol-K}$ | 0°C | 100°C | 200°C | 500°C | 1200°C | 2000°C | γ |
|---------------------------------|------|-------|-------|-------|--------|--------|----------|
| H_2 | 20.4 | 20.6 | 21.1 | 21.6 | 23.7 | 26.3 | 1.41 |
| Cl_2 | 24.9 | 26.4 | 28.0 | 28.9 | 29.7 | 30.1 | 1.36 |
| $\text{N}_2, \text{CO and O}_2$ | 20.9 | 21.1 | 21.5 | 22.0 | 24.1 | 26.4 | 1.40 |

No! C_V values *increase*, and they are too small at 25°C.

Many are closer to $(5/2) R = 20.8 \text{ J-mol}^{-1}\text{K}^{-1}$

Why? **Quantum mechanics!**

27

Polyatomics

CO₂(g): linear (2 rotations, 4 vibrations)

Classical: $C_V = (3/2)R + R + 4 R = 6.5 R$

$C_{p,m}$ (classical) = $7.5R = 62.4 \text{ J/K-mole}$

experiment: $C_{p,m} = 37.11 \text{ J/K-mole}$ at 25°C
 (and increases considerably with T)

CH₄(g): non-linear (3 rotations, 9 vibrations)

Classical: $C_V = (3/2)R + (3/2) R + 9R = 12 R$

$C_{p,m}$ (classical) = $13R = 108.1 \text{ J/K-mole}$

experiment: $C_{p,m} = 35.31 \text{ J/K-mole}$ at 25°C
 (also increases considerably with T)

Classical equations overestimate C's badly!

28

Comparing molecules with $N = 5$
 If classical: $C_{p,m} = 108 \text{ J/K-mole}$

| | CH ₄ | CH ₃ Cl | CH ₂ Cl ₂ | CF ₄ | CCl ₄ |
|---|-----------------|--------------------|---------------------------------|-----------------|------------------|
| Molar mass | 16 | 51 | 85 | 88 | 154 |
| $C_{p,m} (\text{J}\cdot\text{mol}^{-1}\text{K}^{-1})$ | 35.1 | 41.0 | 51.5 | 61.1 | 83.3 |

Quantum effects: Energy is **quantized**:

values are not continuous, but **discrete**.

If the gap between adjacent quantum states is larger than the thermal energy, then that mode cannot absorb thermal energy.

Vibrational energy gaps are often much larger than $\frac{1}{2}RT$.

(rotational gaps, except for H₂, are smaller than $\frac{1}{2}RT$)

Quantum effects are greater for lighter particles, as above

As T increases, more modes can absorb, so C's increase

29

Estimating gas heat capacities at 25°C

Approximation: assume translation and rotation are classical, but ~20% of vibration thermally excited.

C₆H₆(g): (N=12; 3 rotations, 30 vibrations)

$$C_{V,m} = (3/2)R + (3/2)R + (30/5)R = 9R$$

$$\text{estimate: } C_{p,m} = C_{V,m} + R = 10R = 83 \text{ J/K-mole}$$

$$\text{experiment: } C_{p,m} = 98.3 \text{ J/K-mole}$$

SF₆(g): (N= 21; 3 rotations, 15 vibrations)

$$C_{V,m} = (3/2)R + (3/2)R + (15/5)R = 6R$$

$$\text{estimate: } C_{p,m} = 7R = 58 \text{ J/K-mole}$$

$$\text{experiment: } C_{p,m} = 97.28 \text{ J/K-mole}$$

Method rough, at best. QM needed for precise work.

30

Heat Capacities of Solids

Heavier solid elements have C_p values that are quite similar at 25°C

Law of Dulong and Petit (1819):

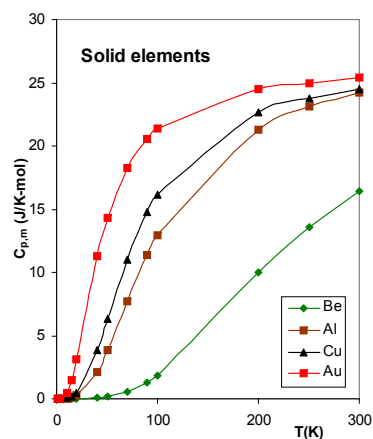
molar heat capacities $C_{p,m}$ of most solid elements are $\sim 25 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ ($\sim 3R$)

$p\Delta V$ is small so

$$C_{p,m} \approx C_{V,m} = 3R$$

(vibrations in three directions)

| Substance | $C_{p,m} (\text{J/K-mole})$ |
|-----------|-----------------------------|
| Cu(s) | 24.44 |
| Al(s) | 24.35 |
| Au(s) | 25.42 |



31

Heat Capacities of Liquids

No convenient generalizations!

Water. One calorie first defined as energy absorbed when 1 gram of water is warmed by 1°C.

$$\text{So } C = q/\Delta T = 1 \text{ calorie/gram-deg}$$

Specific heat (= heat capacity **per gram**)
 for water = 1.00 cal/g-deg

$$C_{p,m} = (18 \text{ g/mole})(1 \text{ cal/g-K}) = 18 \text{ cal/mole-K}$$

$$C_{p,m} = (18 \text{ cal/mole-K})(4.184 \text{ J/cal}) = 75 \text{ J/K-mole}$$

This is at 25°C; $C_{p,m}$ depends (a bit) on T.

32

T dependence of ΔH (or ΔU)

If $dp = 0$, $dH = C_p dT$

$$\Delta H = H(\text{at } T_2) - H(\text{at } T_1)$$

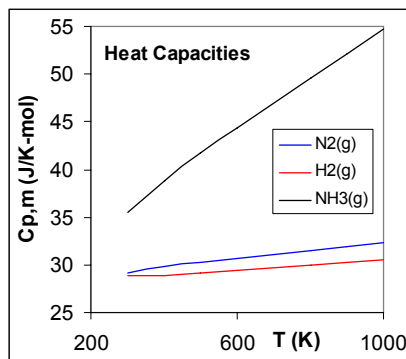
$$\Delta H = n \int_{T_1}^{T_2} C_{p,m} dT$$

If ΔT is large, assuming constant C_v or C_p is not valid!

Various fits: for example

$$C_{p,m} = a + bT + c/T^2$$

Parameters are fit for a specific range of temperatures.



33

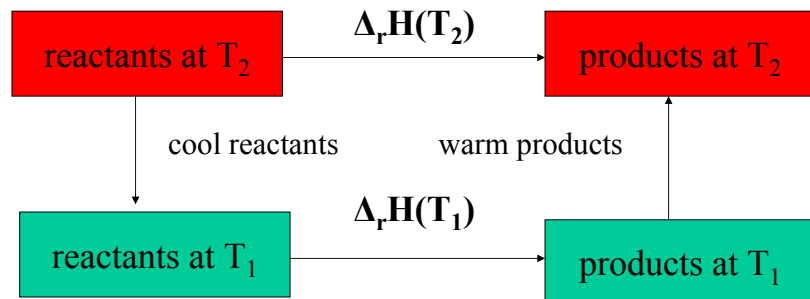
Calculating ΔH when T changes

For a single substance with $C_{p,m} = a + bT + c/T^2$

$$\begin{aligned} \Delta H &= n \int_{T_1}^{T_2} C_{p,m} dT = n \int_{T_1}^{T_2} (a + bT + c/T^2) dT \\ &= n \left[\int_{T_1}^{T_2} a dT + \int_{T_1}^{T_2} bT dT + \int_{T_1}^{T_2} (c/T^2) dT \right] \\ &= n \left[aT \Big|_{T_1}^{T_2} + \frac{b}{2} T^2 \Big|_{T_1}^{T_2} - \frac{c}{T} \Big|_{T_1}^{T_2} \right] \\ &= n \left[a(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) - c \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \end{aligned}$$

34

Calculating $\Delta_r H$ away from 25°C



T_1 is usually 25°C, since $\Delta_r H$ is known there

35

Calculating $\Delta_r H^\circ$ away from 25°C

Imagine the following path:

1. Cool the **reactants** from T_2 to T_1 :
 $\Delta H^\circ = \int C_p(\text{reactants}) dT$ (limits: T_2 to T_1)
2. Carry out the reaction at T_1 : $\Delta H^\circ = \Delta_r H^\circ(T_1)$
3. Warm the **products** from T_1 to T_2 :
 $\Delta H^\circ = \int C_p(\text{products}) dT$ (limits: T_1 to T_2)

$$\Delta_r H^\circ(T_2) = \int_{T_2}^{T_1} C_p^{\text{rea}} dT + \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_p^{\text{pro}} dT$$

36

$$\Delta_r H^\circ(T_2) = \int_{T_2}^{T_1} C_p^{\text{rea}} dT + \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_p^{\text{pro}} dT$$

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_p^{\text{pro}} dT - \int_{T_1}^{T_2} C_p^{\text{rea}} dT$$

If the reaction is $\alpha A + \beta B \rightarrow \gamma C$, then

$$\Delta_r C_{p,m} = \gamma C_{p,m}(C) - \alpha C_{p,m}(A) - \beta C_{p,m}(B).$$

$$\Delta_r H_m^\circ(T_2) = \Delta_r H_m^\circ(T_1) + \int \Delta_r C_{p,m} dT$$

Equivalent statement: $(\partial \Delta_r H^\circ / \partial T)_p = \Delta_r C_p$

If $\Delta_r C_{p,m}$ is constant

$$\Delta_r H_m^\circ(T_2) = \Delta_r H_m^\circ(T_1) + \Delta_r C_{p,m} \Delta T \quad \text{Kirchoff's Law}$$

Even when H of substances change, there is often cancellation, making $\Delta_r C_p$ small.

$\Delta_r H_m^\circ(T_2)$ and $\Delta_r H_m^\circ(T_1)$ are often not very different.

37

Calculating $\Delta_r H^\circ$ away from 25C:

example: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

| molecule | a (J/K-mole) | b (J/K ² -mole) | c (J-K/mole) |
|---------------------|--------------|----------------------------|-------------------------|
| N ₂ (g) | 28.58 | 3.77 x 10 ⁻³ | -0.50 x 10 ⁵ |
| H ₂ (g) | 27.28 | 3.26 x 10 ⁻³ | 0.50 x 10 ⁵ |
| NH ₃ (g) | 29.75 | 25.1 x 10 ⁻³ | -1.55 x 10 ⁵ |

$$C_{p,m} = a + bT + c/T^2$$

$$\Delta_r a = 2(29.75) - 3(27.28) - 28.58 = -50.92$$

$$\Delta_r b = [2(25.1) - 3(3.26) - 3.77] \times 10^{-3} = 36.65 \times 10^{-3}$$

$$\Delta_r c = [2(-1.55) - 3(0.5) - (-0.5)] \times 10^5 = -4.10 \times 10^5$$

$$\Delta_r H^\circ = -92.22 \text{ kJ/mole at } 25^\circ\text{C}$$

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) - 50.92(T_2 - T_1)$$

$$+ \frac{1}{2}(36.65 \times 10^{-3})(T_2^2 - T_1^2) - (-4.1 \times 10^5)(1/T_2 - 1/T_1)$$

$$\Delta_r H^\circ \text{ at } 500 \text{ K} = -100.10 \text{ kJ/mole}$$

38

Calculating $\Delta_r H^\circ$ away from 25C:

example: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

| molecule | a (J/K-mole) | b (J/K ² -mole) | c (J-K/mole) |
|---------------------|--------------|----------------------------|-------------------------|
| N ₂ (g) | 28.58 | 3.77 x 10 ⁻³ | -0.50 x 10 ⁵ |
| H ₂ (g) | 27.28 | 3.26 x 10 ⁻³ | 0.50 x 10 ⁵ |
| NH ₃ (g) | 29.75 | 25.1 x 10 ⁻³ | -1.55 x 10 ⁵ |

Using $C_{p,m} = a + bT + c/T^2$

$$\Delta_r H^\circ \text{ at } 500 \text{ K} = -100.10 \text{ kJ/mole}$$

Calculating C_p 's at 25°C from above (29.14, 28.81, 35.97)

and treating $\Delta_r C_p$ as constant gives

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

$$= -92.22 + (-44.605 \text{ J/K-mole})(1 \text{ kJ}/1000 \text{ J})(\Delta T)$$

$$= -101.22 \text{ kJ/mole}$$

Conclusion: $C_p(T)$ needed only for very precise results.

39

The effect of pressure on U and H for real gases

Experiment (first done by James Joule):

gas expands **adiabatically** into a vacuum.

$$q = 0, w = 0 \rightarrow \Delta U = 0.$$

Measure ΔT of gas:

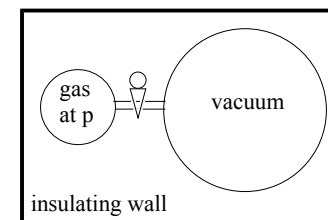
Joule observed $\Delta T = 0$

(true for ideal gases)

(Modern results see small $\Delta T < 0$)

Small drop in T for all real gases

$$(\partial T / \partial p)_U \geq 0 \text{ and } (\partial T / \partial V)_U \leq 0 \text{ (equal for ideal)}$$



40

Isothermal version of experiment

The gas expands **isothermally** into a vacuum.

If no heat were supplied T , would fall for a real gas.

The bath supplies heat, keeping T constant: $q > 0$

$w = 0$ so $\Delta U > 0$. Pressure falls: $\Delta p < 0$,

so $(\partial U/\partial p)_T < 0$ for real gases (zero for ideal)

Alternatively $\Delta V > 0$, so $(\partial U/\partial V)_T > 0$ for real gases.

Why? Attractive forces.

U is lower when molecules are closer together.

41

Relating $(\partial T/\partial V)_U$ and $(\partial U/\partial V)_T$

From above: $(\partial T/\partial V)_U \leq 0$ and $(\partial U/\partial V)_T \geq 0$

Could we derive one from the other mathematically?

$$dU = (\partial U/\partial T)_V dT + (\partial U/\partial V)_T dV$$

If U is constant, $0 = C_V dT + (\partial U/\partial V)_T dV$

Divide by dV (with U constant):

$$(\partial U/\partial V)_T = -C_V (\partial T/\partial V)_U$$

Since C_V is positive,

$$(\partial T/\partial V)_U \leq 0 \text{ implies } (\partial U/\partial V)_T \geq 0$$

42

The Joule-Thomson experiment (1852)

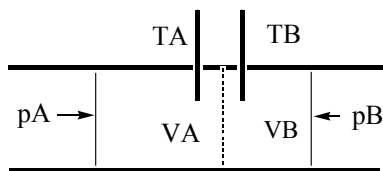
Gas starts to left of porous (clay) plug (--), at (p_A, V_A, T_A)

Adiabatic: $q = 0$.

Holding $p_B < p_A$

(with both constant), gas flows through plug.

Measure V_B, T_B after all gas is through.



Observation (at 25°C):
 most gases cool
 (H_2 and He heat up!)

43

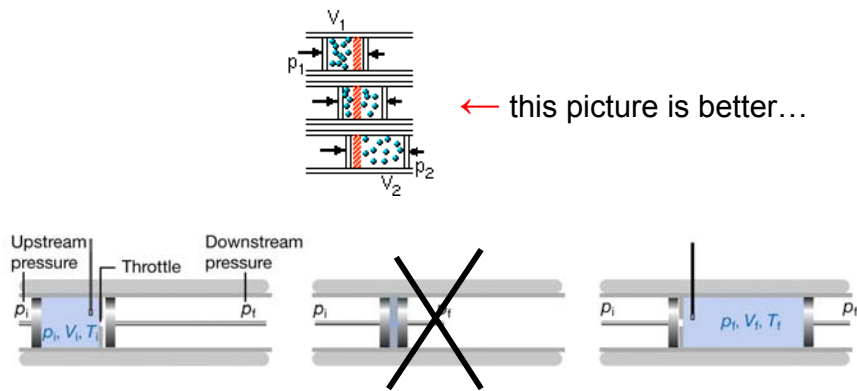
Joule-Thomson Apparatus

“Kompressionspumpe von J.P. Joule, die zur Untersuchung der Abkühlung durch adiabatische Expansion von ausströmenden Gasen (Joule-Thomson-Effekt) verwendet wurde (1852)”



<http://ehf.uni-oldenburg.de/histodid/joulethomson.html>

44



Joule Thomson Expansion
figure 3.10 from Atkins 7/E (2.28 8th)
middle picture makes little sense

The Joule-Thomson experiment

$$w = -p_A(0 - V_A) - p_B(V_B - 0) = p_A V_A - p_B V_B$$

$$\text{Since } q = 0, \text{ then } \Delta U = w = p_A V_A - p_B V_B$$

$$U_B - U_A = p_A V_A - p_B V_B$$

$$\rightarrow U_A + p_A V_A = U_B + p_B V_B$$

thus **H is constant**: isenthalpic expansion.

Define the Joule-Thomson coefficient

$$\mu_{JT} \equiv (\partial T / \partial p)_H$$

Most real gases **cool** upon JT expansion at room temperature: when $\Delta p < 0$, $\Delta T < 0$, so $\mu_{JT} > 0$

But some (H₂, He) heat up!

46

Joule-Thomson coefficient $\mu_{JT} \equiv (\partial T / \partial p)_H$

$$dH = (\partial H / \partial T)_p dT + (\partial H / \partial p)_T dp$$

If $dH = 0$,

$$0 = C_p dT + (\partial H / \partial p)_T dp$$

Divide through by dp (H is constant):

$$0 = C_p (\partial T / \partial p)_H + (\partial H / \partial p)_T$$

$$(\partial H / \partial p)_T = -C_p \mu_{JT}$$

μ_{JT} is zero for ideal gases.

For real gases, μ_{JT} is related to the pressure dependence of enthalpy: $H(p)$.

47

$$\mu_{JT} \equiv (\partial T / \partial p)_H = -(\partial H / \partial p)_T / C_p$$

How does H vary with p?

$$H \equiv U + pV$$

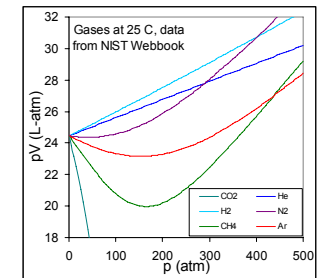
$$(\partial H / \partial p)_T = (\partial U / \partial p)_T + [\partial(pV) / \partial p]_T$$

Joule expt says $(\partial U / \partial p)_T < 0$ for real gases

What about $[\partial(pV) / \partial p]_T$?

look at slopes of pV vs. p at 1 atm:

+ or - ; depends on substance and T
usually - at lower T, always + at high T
 $\mu_{JT} > 0$ at lower T (JT expansion cools)
 < 0 at higher T (JT expansion warms)



At some intermediate T, terms cancel:

$\mu_{JT} = 0$ at the JT inversion temperature (which depends on p)

48