Chapter 2 – continued and ended!

You should review

- What is meant by enthalpy of physical change
  - (vaporization, fusion, sublimation – all are +ve)
- Hess’ law
- Enthalpies of formation
- Enthalpies of chemical change
  - Using Hess’ law or enthalpies of formation

Table 2.4 Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{\mathrm{trs}}H$
Fusion	$\mathrm{s} \rightarrow \mathrm{l}$	$\Delta_{\mathrm{fus}}H$
Vaporization	$\mathrm{l} \rightarrow \mathrm{g}$	$\Delta_{\mathrm{vap}}H$
Sublimation	$\mathrm{s} \rightarrow \mathrm{g}$	$\Delta_{\mathrm{sub}}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{\mathrm{mix}}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{\mathrm{sol}}H$
Hydration	$\mathrm{X}^{\pm}(\mathrm{g}) \rightarrow \mathrm{X}^{\pm}(\mathrm{aq})$	$\Delta_{\mathrm{hyd}}H$
Atomization	Species(s, l, g) $\rightarrow$ atoms(g)	$\Delta_{\mathrm{at}}H$
Ionization	$\mathrm{X(g)} \rightarrow \mathrm{X}^{+}(\mathrm{g}) + \mathrm{e}^{-}(\mathrm{g})$	$\Delta_{\mathrm{ion}}H$
Electron gain	$\mathrm{X(g)} + \mathrm{e}^{-}(\mathrm{g}) \rightarrow \mathrm{X}^{-}(\mathrm{g})$	$\Delta_{\mathrm{eg}}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_{\mathrm{r}}H$
Combustion	Compounds(s, l, g) + $\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}, \mathrm{H_2O(l, g)}$	$\Delta_{\mathrm{c}}H$
Formation	Elements $\rightarrow$ compound	$\Delta_{\mathrm{f}}H$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^{\ddagger}H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH, as in ΔH_{trs}.

Table 2-4
Atkins Physical Chemistry, Eighth Edition

QUESTION

The standard enthalpy of sublimation of solid bromine is +40.1kJ.mol^{-1} and the standard enthalpy of fusion of solid bromine is 10.61kJ.mol^{-1}. The standard enthalpy of vaporization of liquid bromine is…..

1 +14.8 kJ.mol^{-1}

2 -29.5 kJ.mol^{-1}

Why????????

3 -50.7 kJ.mol^{-1}

4 +29.5 kJ.mol^{-1}

5 +50.7 kJ.mol^{-1}

Lithium metal is the only alkali metal that can react with dinitrogen breaking the N N triple bond and forming solid lithium nitride Li_3N. If the lattice energy for the formation of Li_3N,

$$3Li^{+}(g) + N^{3-}(g) \rightarrow Li_3N(s)$$

is – 4426 kJ mole^{-1}, determine ΔH_f^0 for Li_3N. Label each thermochemical step in the cycle with a description (i.e., ΔH°vaporization, etc). Looking at this diagram:

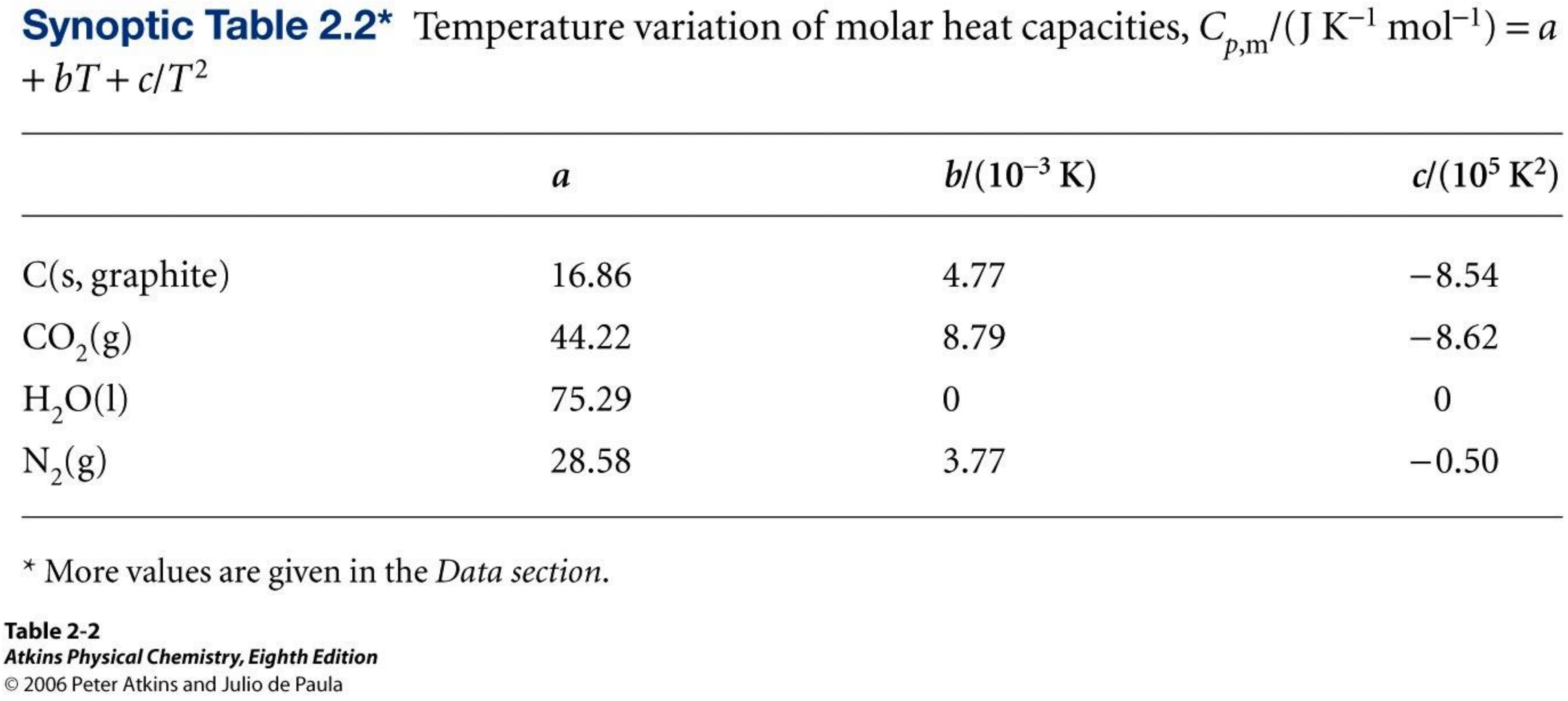
a) Why is the N_2 generally unreactive?

b) What is the major driving force for the formation of Li_3N?

Temperature dependence of Enthalpy

- If a substance is heated from T_1 to T_2 (no phase transition)

$dH = C_p dT$ $\qquad$ $H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$



Synoptic Table 2.2* Temperature variation of molar heat capacities, $C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a + bT + c/T^2$

	a	$b/(10^{-3}\ \mathrm{K})$	$c/(10^{5}\ \mathrm{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
CO_2(g)	44.22	8.79	−8.62
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77	−0.50

* More values are given in the *Data section*.

Table 2-2
Atkins Physical Chemistry, Eighth Edition

Enthalpy at constant pressure

$$\int_{H(T_1)}^{H(T_2)} \mathrm{d}H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) \mathrm{d}T$$

$$H(T_2) - H(T_1) = a(T_2 - T_1) + \tfrac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Temperature dependence of Enthalpy

- Now for a chemical reaction

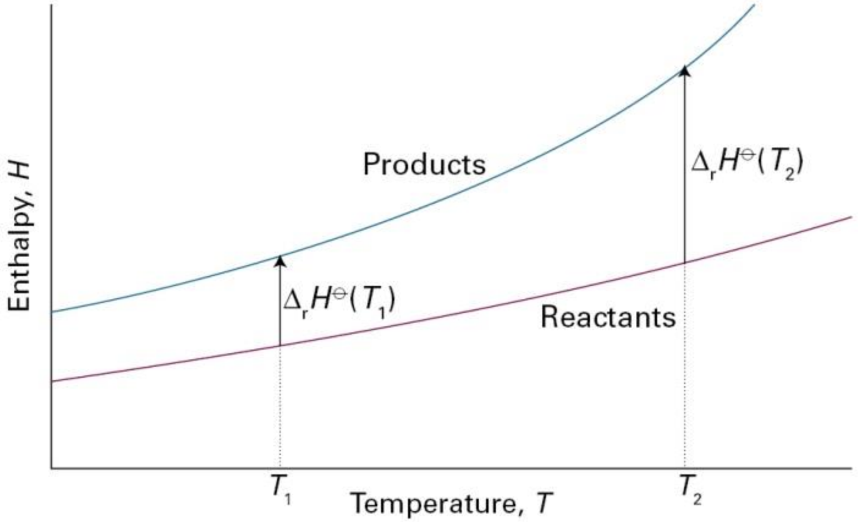


Figure 2C.2 When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

So what is the enthalpy change at T$_2$

Kirchhoff's Law

$$\Delta_{RXN} H^o(T_2) = \Delta_{RXN} H^o(T_1) + \int_{T_1}^{T_2} \Delta_{RXN} C_{pm}{}^o \, dT$$

$$\Delta_{RXN} C_{pm}{}^o = \sum\nolimits_{products} v C_{pm}{}^o - \sum\nolimits_{reactants} v C_{pm}{}^o$$

Things you can assume

$\Delta_{RXN} C_{pm}{}^o$ is independent of T (or at least it is over small ranges)

Why?

individual heat capacities can vary, but chances are the difference varies less significantly

Are gases real or ideal or what happens if the internal energy does change with a change in volume?

Let’s ask Joule....(Closed system of constant composition)

We discussed that for an ideal gas, enthalpy and internal energy are dependent on T

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

← **PERFECT**

If gases are real, its not so simple......

Changing internal energy..

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

Step 1 **Step 2**

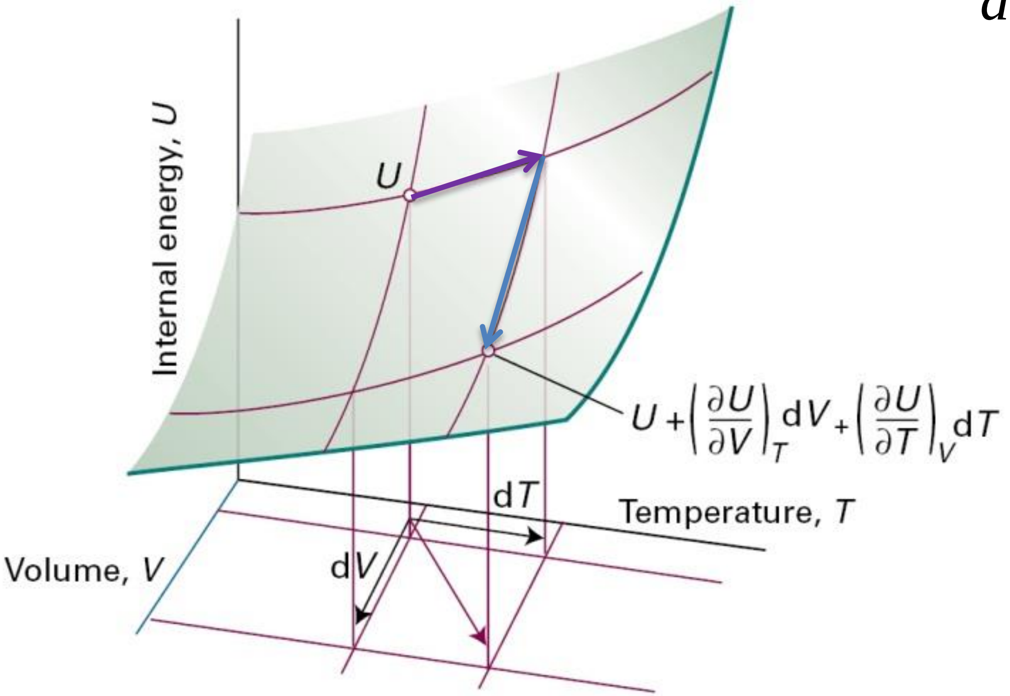


Figure 2D.2 An overall change in U, which is denoted dU, arises when both V and T are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.

Changing internal energy..

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

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

$$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T \text{(the internal pressure)}$$

$$\boxed{dU = C_V dT + \pi_T dV}$$

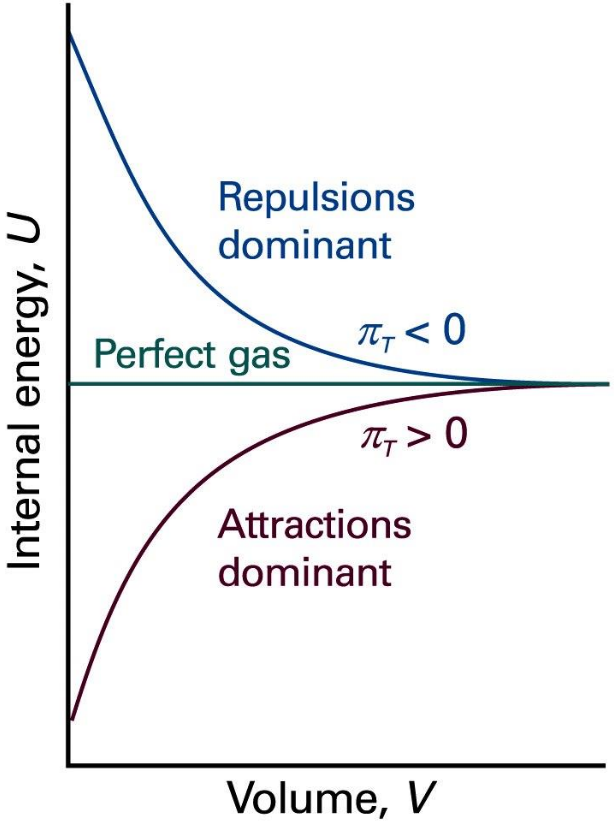


Figure 2-25
Atkins Physical Chemistry, Eighth Edition

$\pi_T = 0$ for a perfect gas
If $dU > 0$ when volume increases isothermally, attractive forces dominate, $\pi_T > 0$
If $dU < 0$ when volume increases isothermally, repulsive forces dominate, $\pi_T < 0$

Internal pressure

If you monitor the change in temperature when a gas expands into a vacuum, can you determine π_T ?

High pressure 22atm

Low pressure evacuated

No observed temperature change.

What does the mean?

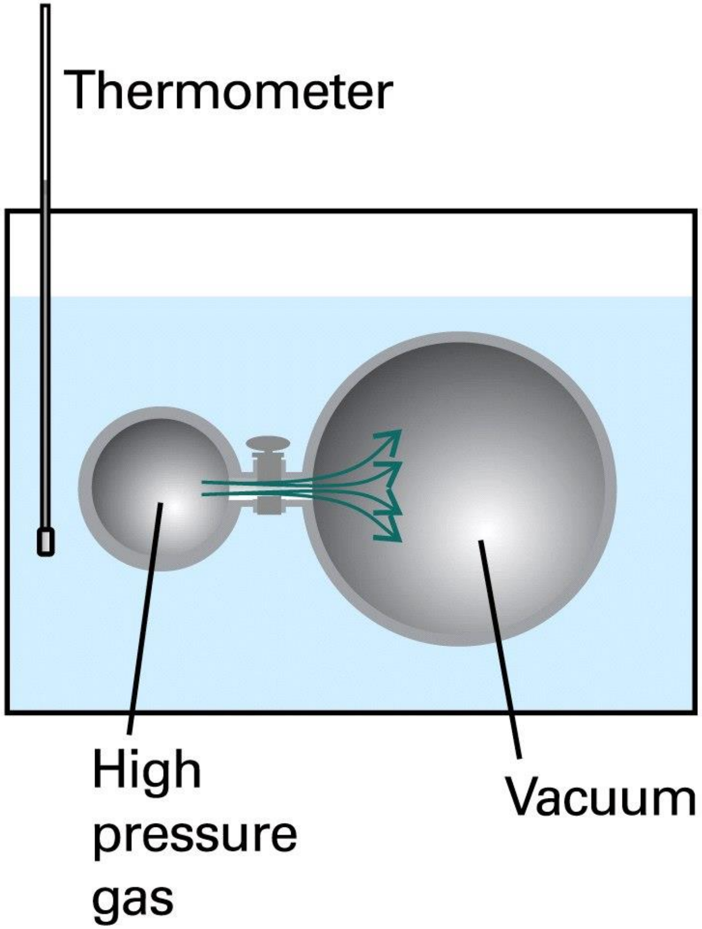


Figure 2-26
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Internal pressure

What does the mean?

No temperature change means that no heat was transferred.

No work was done by expansion into vacuum

$$w = -\int_{V_i}^{V_f} p_{ex} dV$$

$\Delta U = 0$, $\pi_T = 0$

Alternatively, it means that the apparatus was not sensitive enough.

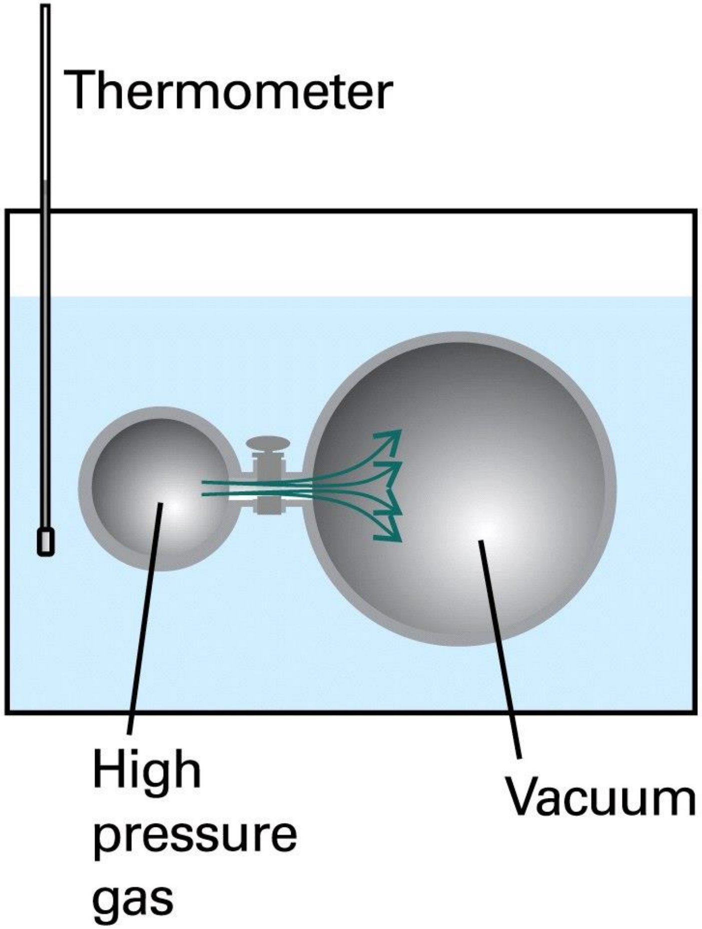


Figure 2-26
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Internal energy at constant pressure

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V\left(\frac{dT}{dT}\right)_p + \pi_T\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{dU = C_V dT + \pi_T dV}$$

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \pi_T\left(\frac{\partial V}{\partial T}\right)_p = \alpha\pi_T V + C_V$$

Does anything look familiar or possible meaningful ?

$(1/V)(dV/dT)_p$ is the expansion coefficient (i.e. the fractional change in volume per change in temperature), α

Similarily, $\kappa = -(1/V)(dV/dp)_T$ is the isothermal expansion compressibility (-ve because an increase in pressure causes a decrease in volume)

Why do you care about α

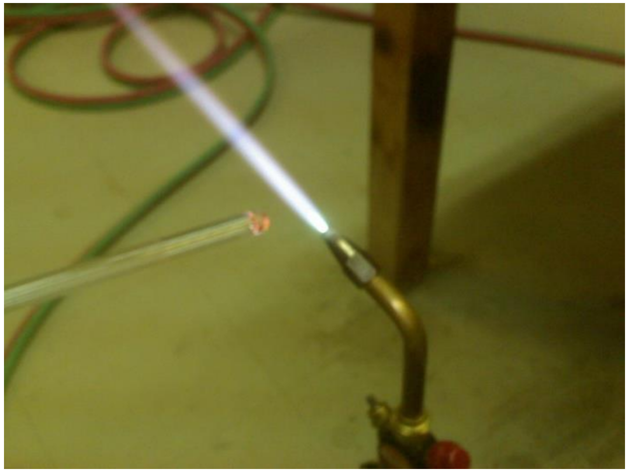
Who has a small α ?

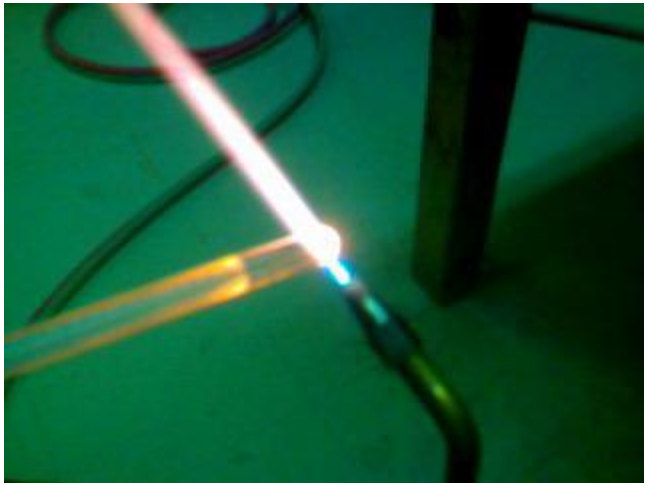
diamond $0.03 \times 10^{-4}\ \mathrm{K}^{-1}$

Who has a larger α ?

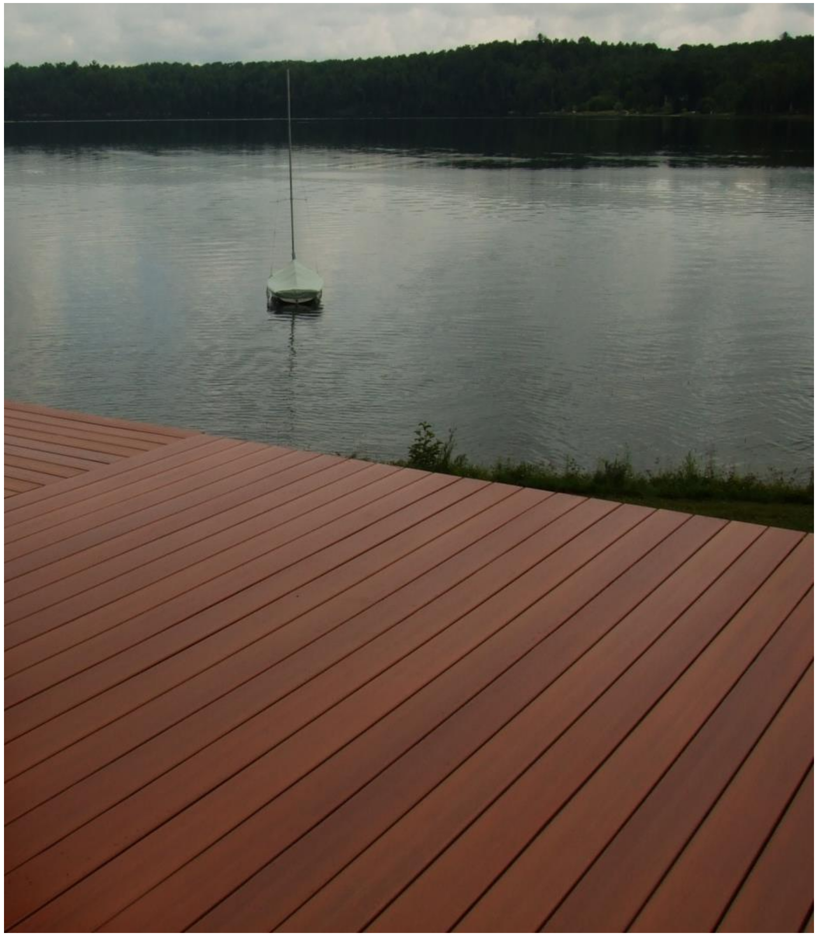
water $2.1 \times 10^{-4}\ \mathrm{K}^{-1}$

Benzene $12.4 \times 10^{-4}\ \mathrm{K}^{-1}$





http://www.materials.uoi.gr/polymers/pages-en/photoalbum.html



More interesting things about perfect gases

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

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

IDEAL

Since $V = \frac{nRT}{P}$

$$p\left(\frac{\partial V}{\partial T}\right)_p = p\left(\frac{nR}{p}\right) = nR$$

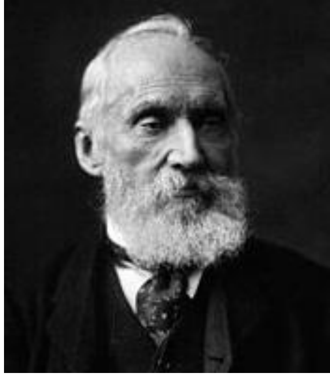
$C_p – C_V = nR$

or more generally,

$= \alpha^2 TV/\kappa_T$

IDEAL or REAL

Closed system of constant composition



$dH=-\mu C_p dp + C_p dT = 0$

where μ is the Joule Thomson coefficient,

$\mu=(\partial T/\partial p)_H$

Constant H means system is isenthalpic:

e.g. a gas expanding adiabatically through a porous barrier from one constant pressure to another

Joule Thomson Experiment

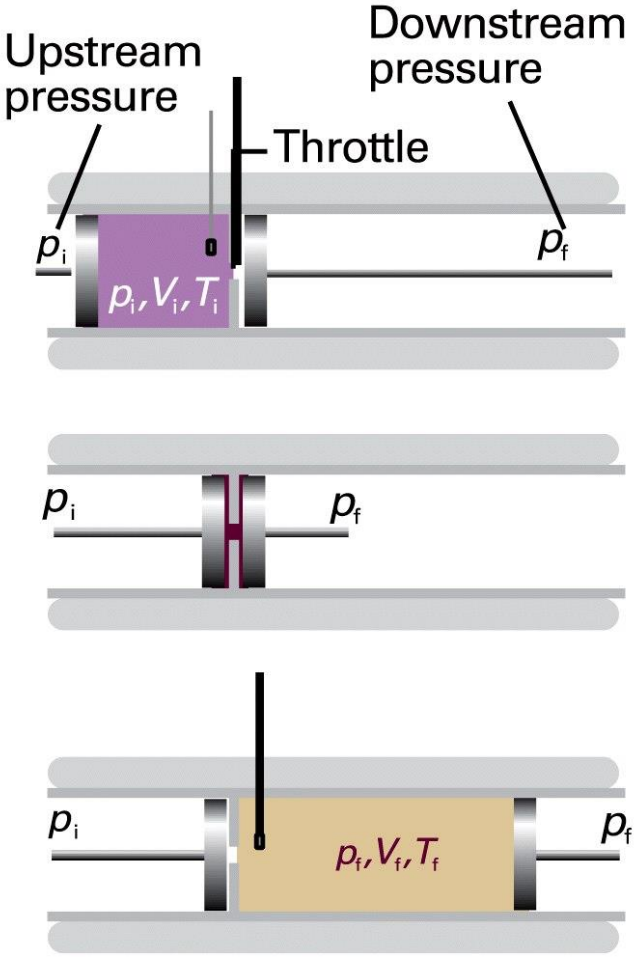


Figure 2-28
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Gas flows from high pressure cylinder to low pressure cylinder through a porous plug in an insulated pipe. Diagram at right represents this experiment. Pistons will move to maintain constant pressure on both sides of the plug.

Volume on left decreases from V_1 to 0, while volume on right increases from 0 to V_2.

System is adiabatic, so q is 0.

What is the work done by the system?

On left:

$$-\int_{V1}^{0} p_1 dV$$

$$-p_1(0-V_1)$$

$$p_1V_1$$

On right:

$$-\int_{0}^{V2} p_2 dV$$

$$-p_2(V_2-0)$$

$$-p_2V_2$$

Joule Thomson Experiment

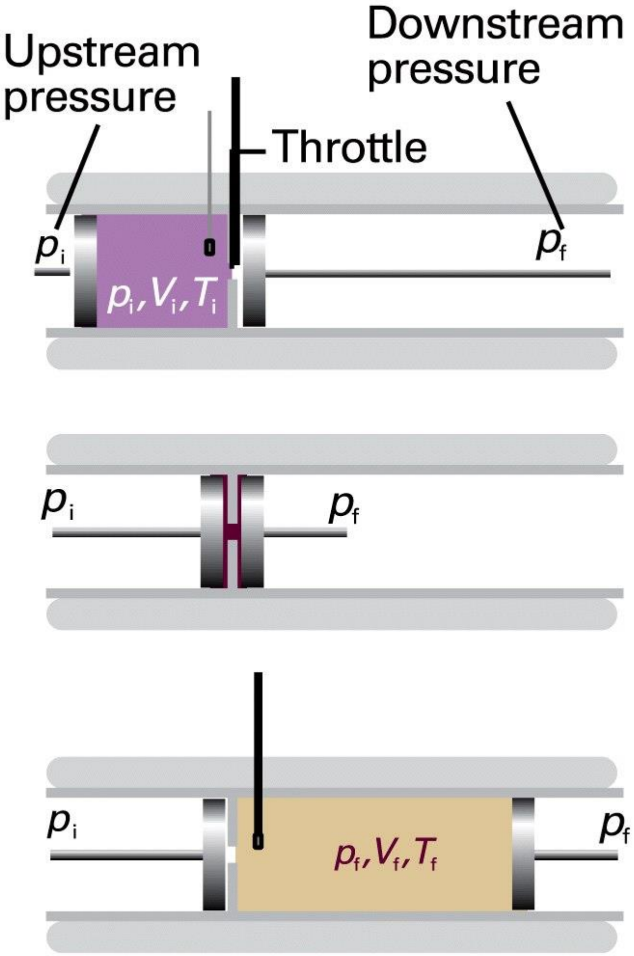


Figure 2-28
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

$$\Delta U = U_2 - U_1 = q + w$$
$$= p_1V_1 - p_2V_2$$

$$U_2 + p_2V_2 = U_1 + p_1V_1$$

$$H_2 = H_1$$

Physically, what does this mean?

If you have N_2 gas expanding out of a cylinder: $p_1 > p_2$ and $T_2 < T_1$ (so the valve on the N_2 tank will feel cold and water will condense on it…..

$$\mu = \lim_{\Delta p \to 0} \left(\frac{\Delta T}{\Delta p} \right)_H = \left(\frac{\partial T}{\partial p} \right)_H$$

Joule Thomson Experiment

$$\mu = \lim_{\Delta p \to 0} \left(\frac{\Delta T}{\Delta p} \right)_H = \left(\frac{\partial T}{\partial p} \right)_H$$

Perfect gases have $\mu_{JT} = 0$

Real gases have non zero μ_{JT}, it can be negative or positive

If μ_{JT} is positive (i.e. increase in pressure is accompanied by an increase in temperature) then the attractive part of the potential dominates,

if μ_{JT} is negative then the repulsive part of the potential dominates.

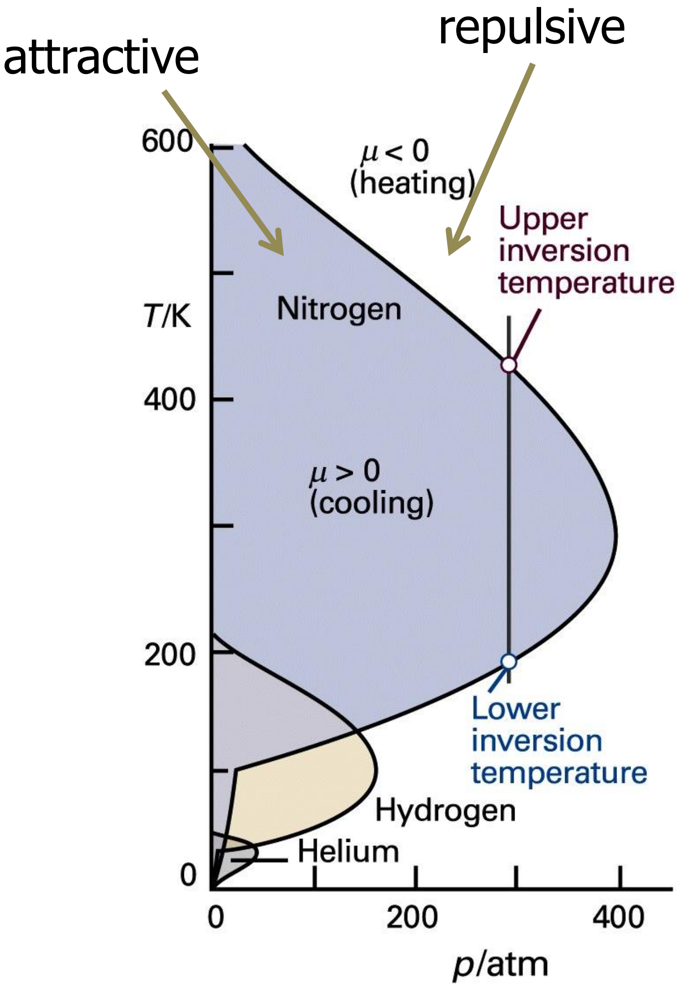


Figure 2-32
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Along the solid curves, $\mu_{JT} = 0$. To left of the curve μ_{JT} is positive and to the right, it is negative. To experience cooling of N_2 on expansion at 100 atm, the temperature must lie between ca. 100 and 550 K.

What about for hydrogen ?

Show that μ is 0 for a perfect gas

$$dH = \left(\frac{dH}{dT}\right)_P dT + \left(\frac{dH}{dP}\right)_T dP = C_p dT + \left(\frac{dH}{dP}\right)_T dP = 0$$

$$C_p\left(\frac{dT}{dp}\right)_H + \left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dp}\right)_H = 0$$

$$C_p\left(\frac{dT}{dp}\right)_H + \left(\frac{dH}{dp}\right)_T = 0$$

$$C_p\left(\frac{dT}{dp}\right)_H = -\left(\frac{dH}{dp}\right)_T$$

$$\mu_{JT} = \left(\frac{dT}{dp}\right)_H = -\frac{1}{C_P}\left(\frac{dH}{dp}\right)_T$$

Show that μ is 0 for a perfect gas

We need an expression for $(dH/dP)_T$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$substituting:$$

$$dH = \left(\frac{dH}{dT}\right)_P dT + \left(\frac{dH}{dP}\right)_T dP = C_p dT + \left(\frac{dH}{dP}\right)_T dP$$

$$dU = \left(\frac{dU}{dT}\right)_V dT + \left(\frac{dU}{dV}\right)_T dV = C_V dT + \left(\frac{dU}{dV}\right)_T dV$$

$$C_p dT + \left(\frac{dH}{dP}\right)_T dP = C_V dT + \left(\frac{dU}{dV}\right)_T dV + PdV + VdP$$

Show that μ_{JT} is 0 for a perfect gas

We need an expression for $(dH/dP)_T$

$$C_p dT + \left(\frac{dH}{dP}\right)_T dP = C_V dT + \left[\left(\frac{dU}{dV}\right)_T + P\right] dV + VdP$$

at constant T

$$\left(\frac{dH}{dP}\right)_T dP = \left[\left(\frac{dU}{dV}\right)_T + P\right] dV + VdP$$

$$\left(\frac{dH}{dP}\right)_T \left(\frac{dP}{dP}\right) = \left[\left(\frac{dU}{dV}\right)_T + P\right]\left(\frac{dV}{dP}\right)_T + V\left(\frac{dP}{dP}\right)$$

$$\left(\frac{dH}{dP}\right)_T = \left[\left(\frac{dU}{dV}\right)_T + P\right]\left(\frac{dV}{dP}\right)_T + V$$

Show that μ_{JT} is 0 for a perfect gas

Substituting the expression for $(dH/dP)_T$

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T = -\frac{1}{C_P}\left[\left(\frac{dU}{dV}\right)_T + P\right]\left(\frac{dV}{dP}\right)_T + V$$

For a perfect gas, $(dU/dV)_T = 0$ and PV=nRT, so

$$\mu_{JT} = -\frac{1}{C_P}\left\{[0+P]\left(\frac{d(nRT/P)}{dP}\right)_T + \frac{nRT}{P}\right\}$$

$$= -\frac{1}{C_P}\left\{[P]\left(-\frac{(nRT)}{P^2}\right)_T + \frac{nRT}{P}\right\}$$

$$= -\frac{1}{C_P}\left\{\left(-\frac{(nRT)}{P}\right)_T + \frac{nRT}{P}\right\} = -\frac{1}{C_P}\{0\} = 0$$

For a van der Waal's gas at the limit of zero pressure

$$\mu = -\frac{1}{C_P}\left\{\frac{2a}{RT} - b\right\}$$

Isothermal Joule-Thomson Coefficient “Modern Method”

$$\mu_T = -C_P \mu = \left(\frac{\partial H}{dp} \right)_T$$

Summary

- π internal pressure $\left(\frac{\partial U}{\partial T}\right)_V$
- α expansion coefficient $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
- κ isothermal compressibility $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$
- μ Joule Thompson coefficient $\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p}$
- μ_T Isothermal JT coefficient $\left(\frac{\partial H}{\partial P}\right)_T$