

PRE-U REVISION NOTES

THERMAL PHYSICS (II): IDEAL GASES, FIRST & SECOND LAWS OF THERMODYNAMICS, HEAT ENGINES, KINETIC THEORY, BOLTZMANN STATISTICS, PLANCK RADIATION DISTRIBUTION

MACROSCOPIC

(REAL ENGINES ON HUMAN SCALE)
Treat gases, liquids as a continuum i.e. ignore molecular properties

MICROSCOPIC

(Molecular, atomic scale)

Comprehend **macro** properties such as heat, pressure, temperature, radiation diffusion, entropy from **averages** of molecular interactions

And link to 'ideal gas' model

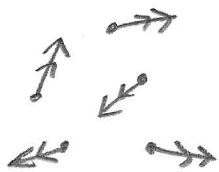
Temperature is a measure of the mean **kinetic energy** of molecules in random motion. The internal energy of an **ideal gas** is

$$U \propto T$$

Energy / s Absolute temperature in kelvin



Ideal gas

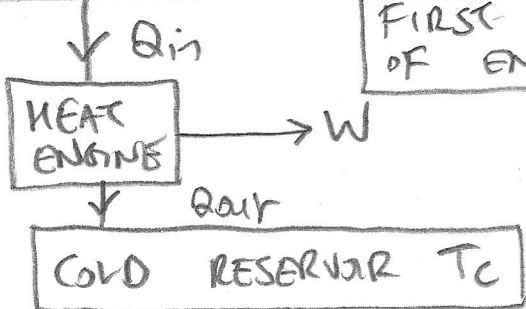


- * molecules are point-like objects that are in random motion and collide elastically
- * Mean-free path between molecular collisions \gg molecular size
- * molecules move so fast that can ignore intermolecular forces, so $U =$ kinetic energy and no potential energy due to electric and magnetic fields is not all!

A HEAT ENGINE

is a system which converts **some** of the flow of energy from **HOT** to **COLD** reservoirs into useful **work**. A reservoir is a body large enough to not change temperature when heat is added or subtracted.

HOT RESERVOIR T_H



FIRST LAW OF THERMODYNAMICS - CONSERVATION OF ENERGY

$$Q_{in} = Q_{out} + W$$

Heat input to engine Heat output of engine Work done by engine

SECOND LAW OF THERMODYNAMICS - TOTAL ENTROPY OF THE UNIVERSE CANNOT DECREASE FOR ANY CHANGE

Entropy change S $\boxed{dS = \frac{dQ}{T}}$

So for the heat engine, since T_H and T_C don't change when heat added/subtracted

$\boxed{\Delta S_H = -Q_{in}/T_H}$

$\boxed{\Delta S_C = Q_{out}/T_C}$

$\boxed{\Delta S_{total} = \Delta S_H + \Delta S_C}$

and

2nd law $\Rightarrow \boxed{\Delta S_{total} \geq 0}$

$-\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \geq 0$

New form 1st law

$\boxed{Q_{in} = Q_{out} + W}$

$\therefore Q_{out} = Q_{in} - W$

$\frac{Q_{in} - W}{T_C} - \frac{Q_{in}}{T_H} \geq 0$

$Q_{in} \left(\frac{1}{T_C} - \frac{1}{T_H} \right) \geq \frac{W}{T_C}$

$\boxed{\frac{W}{Q_{in}} \leq 1 - \frac{T_C}{T_H}}$

Define heat engine

efficiency $\eta = \frac{\text{work done}}{\text{heat input}}$

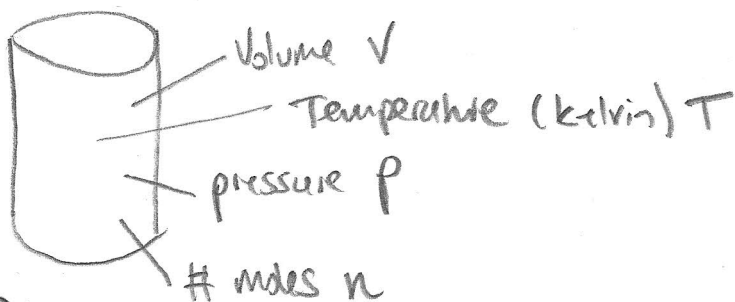
ie $\boxed{\eta = \frac{W}{Q_{in}}}$

Hence

$\boxed{\eta \leq 1 - \frac{T_C}{T_H}}$

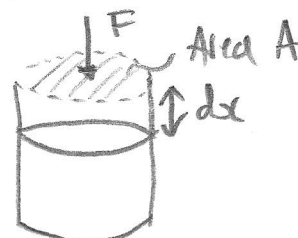
So maximum efficiency of a heat engine is $1 - \frac{T_C}{T_H}$

IDEAL GASES - EQUATION OF STATE, WORK, INTERNAL ENERGY



$\boxed{PV = nRT}$

ideal gas equation



work done compressing a gas is

$\boxed{dW = F dx}$

Now pressure acting on the gas is p and $F = pA$.

change in volume $dV = -Adx$:

so $dW = pA \times \frac{-dV}{A}$

or $dW = -pdV$

So for gases: 1st law is

$du = dQ - pdV$

change in internal energy

Heat added

Work done on gas

Internal energy of ideal gas

$U = \frac{1}{2} \alpha nRT$

moles

molar gas constant

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

α # "degrees of freedom" of molecular motion (e.g. $\alpha=3$ if only x, y, z translation. $\uparrow \uparrow \Rightarrow$ other modes eg vibration (same possible)).

so since $pV = nRT$

$\Rightarrow U = \frac{1}{2} \alpha pV$

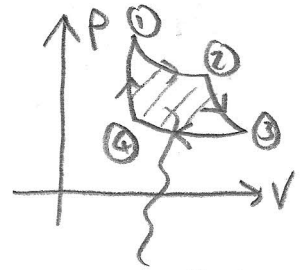
involving ideal gases

HEAT ENGINES

{ i.e. petrol, diesel, steam... }

can be analysed as a cyclical process in p, V space

Work done by gas is $\int_{\text{cycle}} (-dw) \Rightarrow \oint pdV = W$



$W = \oint pdV$

Heat inputs Q_{in} and outputs Q_{out} at various

stages of cycle

Special cases: #1 constant volume (ISOCORIC) process

$dV=0 \therefore$ 1st law $du = dQ$

$du = \frac{1}{2} \alpha nRdT$

$dQ = C_V dT$

C_V is constant volume heat capacity

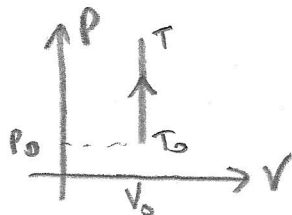
$\therefore C_V = \frac{1}{2} \alpha nR$

if M is the molar mass/kg

$C_V = \frac{1}{2} \alpha \frac{R}{M}$

the constant volume specific heat capacity

so $\Delta Q = C_V M \Delta T$



Ideal gas eqn

$p_0 V_0 = nRT_0$

$p V_0 = nRT$

$\frac{p}{p_0} = \frac{T}{T_0}$

#2: Constant pressure (ISOBARIC) process

C_p is constant pressure heat capacity

$$dU = \frac{1}{2} n R dT \quad \boxed{dQ = C_p dT}$$

From $pV = nRT$ and $dW = -pdV$
 Since $p = \text{constant}$ $pdV = nRdT \Rightarrow \boxed{dW = -nRdT}$

So from 1st law: $dU = dQ + dW \Rightarrow \frac{1}{2} n R dT = C_p dT - nRdT$

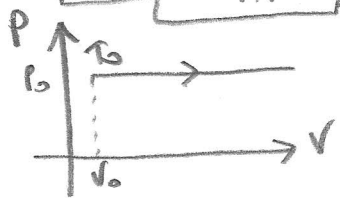
$\therefore C_p = \frac{1}{2} n R + nR$ or $\boxed{C_p = C_v + nR}$ Mayer relationship

$$\boxed{\Delta Q = m c_p \Delta T}$$

$$\boxed{\Delta W = -p \Delta V}$$

$$\boxed{C_p = \frac{C_p}{nM}}$$

← specific heat capacity



$$P_0 V_0 = nRT_0$$

$$P_0 V = nRT$$

$$\boxed{\frac{V}{V_0} = \frac{T}{T_0}}$$

#3: Constant temperature (ISOTHERMAL) process

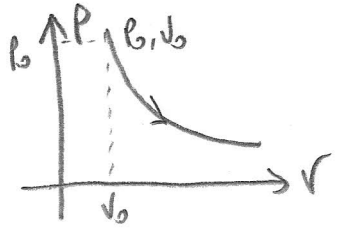
$dU = 0$ since $dT = 0$ 1st law $dQ = pdV$

$\therefore dQ = \frac{nRT}{V} dV \Rightarrow \Delta Q = nRT \int_{V_0}^V \frac{1}{V} dV$
 $\Rightarrow \boxed{\Delta Q = nRT \ln \frac{V}{V_0}}$ ← Heat supplied to gas.

$\Delta U = \Delta Q + \Delta W$ so work done on gas $\boxed{\Delta W = -nRT \ln \left(\frac{V}{V_0}\right)}$

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

$$P_0 = \frac{nRT}{V_0}$$



$$\boxed{\frac{P}{P_0} = \frac{V_0}{V}}$$

ie $\boxed{PV = \text{constant}}$
 (Boyle's law)

#4: NO HEAT EXCHANGED (ADIABATIC OR ISENTROPIC) PROCESS

$dQ = 0$ \therefore first law: $dU = -pdV$ [$U = \frac{1}{2} \alpha nRT$
 $PV = nRT$]

$U = \frac{1}{2} \alpha PV$ $\therefore dU = \frac{1}{2} \alpha (pdV + Vdp)$

So $\frac{1}{2} \alpha (pdV + Vdp) = -pdV$

$pdV (\frac{1}{2} \alpha + 1) = -\frac{1}{2} \alpha Vdp$

$(1 + \frac{2}{\alpha}) \frac{dV}{V} = -\frac{dp}{p}$

$(1 + \frac{2}{\alpha}) \int \frac{dV}{V} = -\int \frac{dp}{p}$

$(1 + \frac{2}{\alpha}) \ln V = -\ln p + \text{const}$

$\ln V^{1 + \frac{2}{\alpha}} = \ln p^{-1} + \text{const}$

$V^{1 + \frac{2}{\alpha}} = \frac{\text{Another const}}{p}$

[$e^{\ln p^{-1} + \text{const}} = \frac{1}{p} e^{\text{const}}$]

So $PV^{1 + \frac{2}{\alpha}} = \text{constant}$.

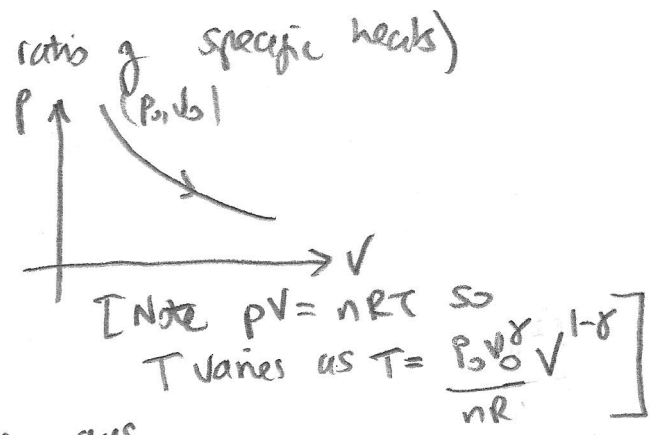
Now from Isochoric & Isobaric processes $C_p = \frac{1}{2} \alpha nR + nR$
 $C_v = \frac{1}{2} \alpha nR$

So $\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{\alpha}$

(not this is also $\gamma = \frac{C_p}{C_v}$ i.e. ratio of specific heats)

$PV^\gamma = \text{constant}$

$PV^\gamma = P_0V_0^\gamma$



Now $dW = -pdV$ work done on gas

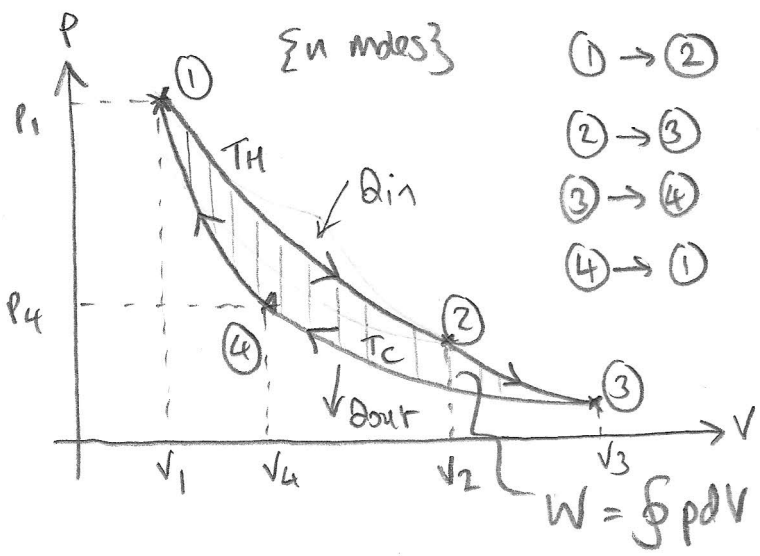
$\Delta W = -P_0V_0^\gamma \int_{V_0}^V \frac{dV}{V^\gamma}$

$\Delta W = -P_0V_0^\gamma \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_0}^V$

$\Delta W = \frac{P_0V_0^\gamma}{\gamma-1} [V^{1-\gamma} - V_0^{1-\gamma}] = \frac{P_0V_0}{\gamma-1} \left[\left(\frac{V_0}{V} \right)^{\gamma-1} - 1 \right]$

[$\gamma > 1$ from Mayer so it makes sense to write it this way \downarrow]

Idealized heat engines: CARNOT CYCLE



- ① → ②
- ② → ③
- ③ → ④
- ④ → ①

- isothermal expansion
- adiabatic expansion
- isothermal compression
- adiabatic compression

Define w as work done by gas (not on gas)

From isothermal processes:

$$Q_{in} = nRT_H \ln \frac{V_2}{V_1}$$

$$Q_{out} = nRT_C \ln \frac{V_3}{V_4}$$

and since the other stages are adiabatic (ie no more heat exchanged) and $\Delta U = 0$ for whole cycle (return to same values p_1, v_1)

$$\Rightarrow W = Q_{in} - Q_{out}$$

$$\Rightarrow W = nRT_H \ln \frac{V_2}{V_1} - nRT_C \ln \frac{V_3}{V_4}$$

Now for adiabatic stages:

$$P_2 V_2^\gamma = P_3 V_3^\gamma$$

$$P_1 V_1^\gamma = P_4 V_4^\gamma$$

$$\text{So } \frac{P_2}{P_1} \left(\frac{V_2}{V_1} \right)^\gamma = \frac{P_3}{P_4} \left(\frac{V_3}{V_4} \right)^\gamma \Rightarrow \frac{P_2 V_2}{P_1 V_1} \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \frac{P_3 V_3}{P_4 V_4} \left(\frac{V_3}{V_4} \right)^{\gamma-1}$$

Now $P_2 V_2 = nRT_H$ $P_3 V_3 = nRT_C$ from ideal gas equation
 $P_1 V_1 = nRT_H$ $P_4 V_4 = nRT_C$

$$\text{So } \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \left(\frac{V_3}{V_4} \right)^{\gamma-1} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\therefore W = nR(T_H - T_C) \ln \left(\frac{V_2}{V_1} \right)$$

So efficiency of Carnot cycle is: $\eta = \frac{W}{Q_{in}}$

$$\Rightarrow \eta = \frac{nR(T_H - T_C) \ln\left(\frac{V_2}{V_1}\right)}{nRT_H \ln\left(\frac{V_2}{V_1}\right)} = \boxed{1 - \frac{T_C}{T_H}}$$

So since for any heat engine $\eta \leq 1 - \frac{T_C}{T_H}$

\Rightarrow Carnot engine is \uparrow the most efficient possible.

one example \rightarrow

Work done by gas

NOTE ON ENTROPY

$$dU = dQ - dW$$

$$\frac{dQ}{T} = dS$$

Now for a heat engine $\oint dU = 0$

So if we plot a heat cycle in T, S space, the area enclosed is the work done per cycle.



$$\therefore dU = TdS - dW$$

$$\text{so } \boxed{\oint TdS = \oint dW}$$

For the **Carnot cycle**, no entropy changes in adiabatic phases, and since $T = \text{constant}$ in isothermal stages \Rightarrow Carnot cycle is a **rectangle** in T, S space!

Since: $Q_{in} = nRT_H \ln\left(\frac{V_2}{V_1}\right)$

$$Q_{out} = nRT_C \ln\left(\frac{V_3}{V_4}\right) = nRT_C \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = \frac{\Delta Q}{T} \quad \text{ie } \boxed{\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)}$$

Note

$$\boxed{\frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_C}}$$

since this cycle is rectangular

and since $Q_{in} = nRT_H \ln\left(\frac{V_2}{V_1}\right) \Rightarrow \frac{Q_{out}}{T_C} = nR \ln\left(\frac{V_2}{V_1}\right)$

so you can get $\eta = 1 - \frac{T_C}{T_H}$ without having to work out $\frac{V_3}{V_4} = \frac{V_2}{V_1}$ as above.

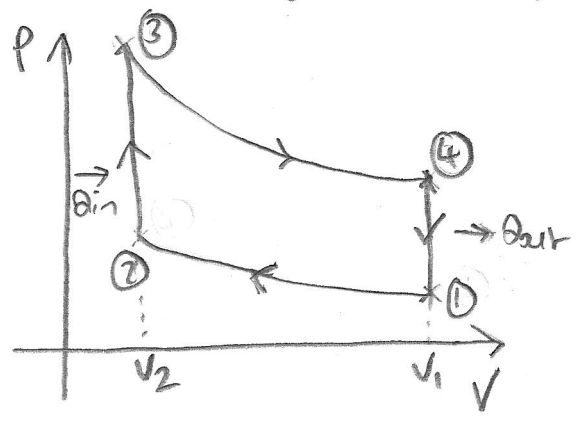
Other classic heat cycles

(See Ectechon notes on Heat Engines for details)

Otto cycle

(spark ignition petrol engines)

- ① → ② Adiabatic compression
- ② → ③ Isochoric heating (spark explosion of gas in piston!)
- ③ → ④ Adiabatic expansion
- ④ → ① Isochoric cooling (heat released when piston at max. expansion)



[Note at ① there is air exchange (exhaust) at constant pressure with atmosphere.]

One can show:

$$\eta = 1 - \frac{1}{r^{\gamma-1}}$$

where

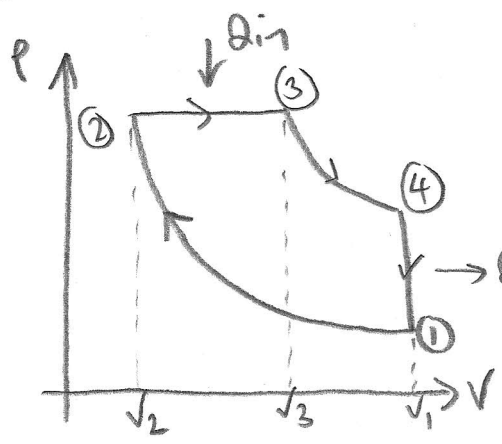
$$\gamma = \frac{c_p}{c_v}$$

$$r = \frac{V_1}{V_2}$$

Compression ratio

Diesel cycle

(Air compression sufficient to ignite fuel vapors)



- ① → ② Adiabatic compression
- ② → ③ Isobaric heating
- ③ → ④ Adiabatic expansion
- ④ → ① Isochoric cooling

one can show:

$$\eta = 1 - \frac{1}{r^{\gamma-1}} \left(\frac{s^{\gamma}-1}{\gamma(s-1)} \right)$$

$$r = \frac{V_1}{V_2} \quad s = \frac{V_3}{V_2}$$

so possibility for greater efficiency than a petrol engine - which is why most container ships use diesel, in huge engines.

→ [Example Excel sheets for Carnot, Otto & Diesel cycles]

Carnot Cycle model

Dr A. French, September 2017



Nicolas
Léonard Sadi
Carnot
(1796-1832)

Input parameters

Hot reservoir temperature /Celsius	150
Cold reservoir temperature /Celsius	20
Mass of gas /g	1.00
Volume of gas at lowest volume and highest pressure /litres	0.40
Volume of gas after isothermal expansion /litres	1.00
Degrees of freedom of molecular motion	3
Molar mass of gas /g/mol ⁻¹	28.966

Outputs

Heat input during isothermal expansion /kJ	0.111
Heat output during isothermal compression /kJ	0.077
Total work done by gas on surroundings /kJ	0.034
Entropy change during isothermal stages /JK ⁻¹	0.263
Efficiency (work done / heat input)	0.307

Theoretical efficiency

0.307

$$\eta = 1 - \frac{T_C}{T_H}$$

Note all temperatures incorporated into calculations will be converted to Kelvin first - i.e. add 273 to Celsius number.

Pressure, volume coordinates of heat cycle

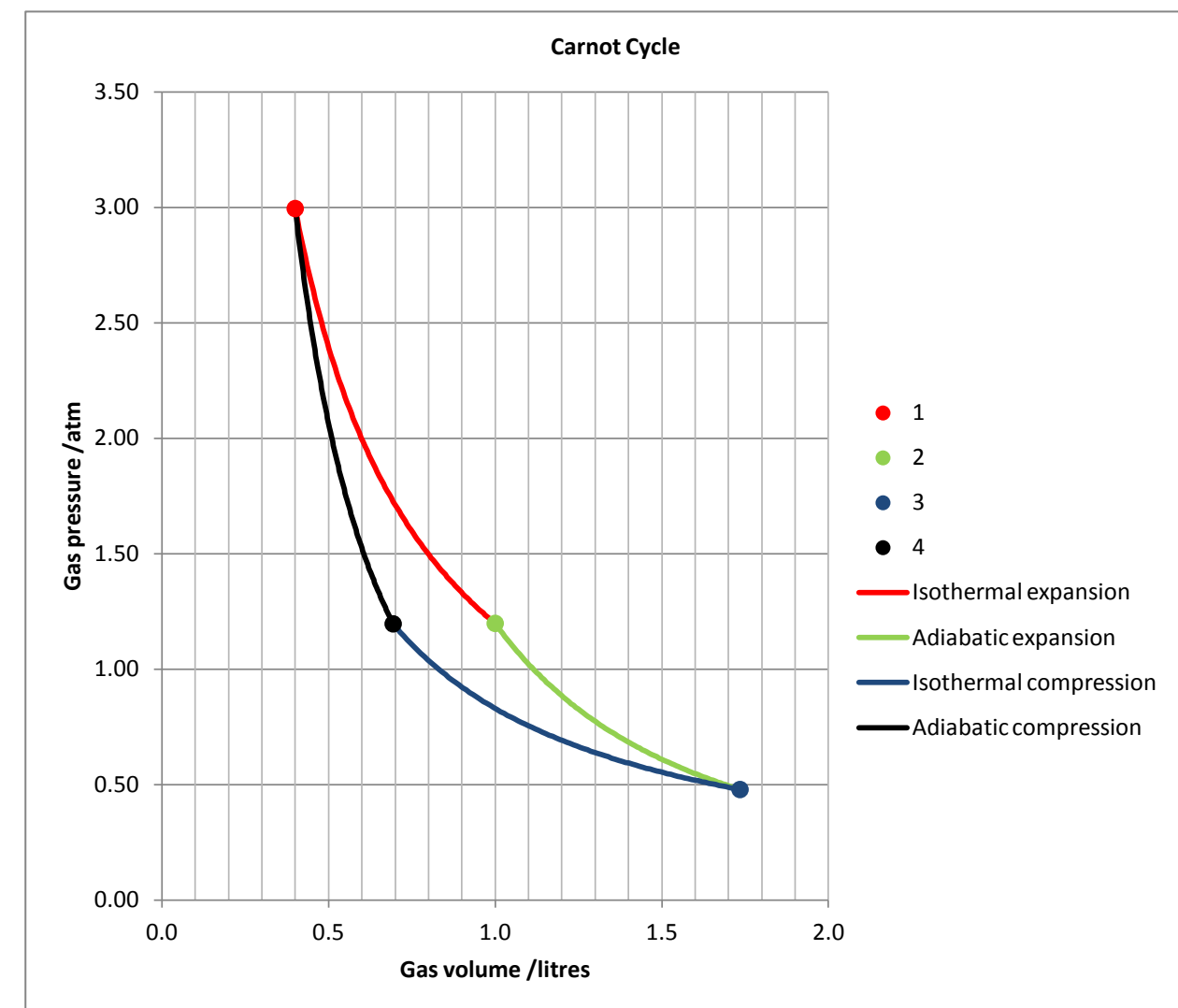
p1	3.00
V1	0.4
p2	1.20
V2	1.0
p3	0.48
V3	1.73
p4	1.20
V4	0.7

Note all pressures are quoted in atmospheres. 1atm = 101,325 Pa. Volumes in litres. T in K.

Reservoir temperatures in K

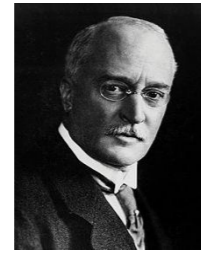
T_H	423
T_C	293

Number of moles of gas in engine	0.035
Ratio of specific heats gamma	1.667



V diff fraction	1 to 2		2 to 3		3 to 4		4 to 1	
	Isenthal expansion p	Isenthal expansion V	Adiabatic expansion p	Adiabatic expansion V	Isenthal compression p	Isenthal compression V	Adiabatic compression p	Adiabatic compression V
0	2.996	0.400	1.198	1.000	0.478	1.735	1.196	0.694
0.01	2.951	0.406	1.184	1.007	0.481	1.724	1.205	0.691
0.02	2.908	0.412	1.169	1.015	0.484	1.714	1.213	0.688
0.03	2.867	0.418	1.155	1.022	0.487	1.703	1.222	0.685
0.04	2.826	0.424	1.142	1.029	0.490	1.693	1.231	0.682
0.05	2.787	0.430	1.128	1.037	0.493	1.683	1.240	0.679
0.06	2.748	0.436	1.115	1.044	0.496	1.672	1.249	0.676
0.07	2.711	0.442	1.102	1.051	0.499	1.662	1.258	0.673
0.08	2.675	0.448	1.089	1.059	0.503	1.651	1.267	0.670
0.09	2.639	0.454	1.077	1.066	0.506	1.641	1.276	0.667
0.1	2.605	0.460	1.065	1.073	0.509	1.631	1.286	0.664
0.11	2.571	0.466	1.053	1.081	0.512	1.620	1.295	0.662
0.12	2.539	0.472	1.041	1.088	0.516	1.610	1.305	0.659
0.13	2.507	0.478	1.029	1.096	0.519	1.599	1.315	0.656
0.14	2.476	0.484	1.018	1.103	0.522	1.589	1.324	0.653
0.15	2.445	0.490	1.007	1.110	0.526	1.579	1.334	0.650
0.16	2.416	0.496	0.996	1.118	0.529	1.568	1.345	0.647
0.17	2.387	0.502	0.985	1.125	0.533	1.558	1.355	0.644
0.18	2.359	0.508	0.974	1.132	0.536	1.547	1.365	0.641
0.19	2.331	0.514	0.964	1.140	0.540	1.537	1.376	0.638
0.2	2.304	0.520	0.953	1.147	0.544	1.526	1.386	0.635
0.21	2.278	0.526	0.943	1.154	0.547	1.516	1.397	0.632
0.22	2.252	0.532	0.933	1.162	0.551	1.506	1.408	0.629
0.23	2.227	0.538	0.924	1.169	0.555	1.495	1.419	0.626
0.24	2.203	0.544	0.914	1.176	0.559	1.485	1.430	0.623
0.25	2.179	0.550	0.905	1.184	0.563	1.474	1.441	0.620
0.26	2.155	0.556	0.895	1.191	0.567	1.464	1.453	0.617
0.27	2.132	0.562	0.886	1.198	0.571	1.454	1.465	0.615
0.28	2.110	0.568	0.877	1.206	0.575	1.443	1.476	0.612
0.29	2.088	0.574	0.868	1.213	0.579	1.433	1.488	0.609
0.3	2.066	0.580	0.860	1.220	0.584	1.422	1.500	0.606
0.31	2.045	0.586	0.851	1.228	0.588	1.412	1.512	0.603
0.32	2.024	0.592	0.843	1.235	0.592	1.402	1.525	0.600
0.33	2.004	0.598	0.834	1.242	0.597	1.391	1.537	0.597
0.34	1.984	0.604	0.826	1.250	0.601	1.381	1.550	0.594
0.35	1.964	0.610	0.818	1.257	0.606	1.370	1.563	0.591
0.36	1.945	0.616	0.810	1.264	0.610	1.360	1.576	0.588
0.37	1.926	0.622	0.803	1.272	0.615	1.350	1.589	0.585
0.38	1.908	0.628	0.795	1.279	0.620	1.339	1.603	0.582
0.39	1.890	0.634	0.787	1.287	0.625	1.329	1.616	0.579
0.4	1.872	0.640	0.780	1.294	0.630	1.318	1.630	0.576
0.41	1.855	0.646	0.773	1.301	0.635	1.308	1.644	0.573
0.42	1.838	0.652	0.765	1.309	0.640	1.298	1.658	0.570
0.43	1.821	0.658	0.758	1.316	0.645	1.287	1.672	0.567
0.44	1.805	0.664	0.751	1.323	0.650	1.277	1.687	0.565
0.45	1.788	0.670	0.744	1.331	0.655	1.266	1.702	0.562
0.46	1.773	0.676	0.738	1.338	0.661	1.256	1.717	0.559
0.47	1.757	0.682	0.731	1.345	0.666	1.245	1.732	0.556
0.48	1.742	0.688	0.724	1.353	0.672	1.235	1.747	0.553
0.49	1.727	0.694	0.718	1.360	0.678	1.225	1.763	0.550
0.5	1.712	0.700	0.711	1.367	0.684	1.214	1.778	0.547
0.51	1.697	0.706	0.705	1.375	0.689	1.204	1.794	0.544
0.52	1.683	0.712	0.699	1.382	0.695	1.193	1.811	0.541

Diesel Cycle model
Dr A. French. September 2017



Rudolf Diesel
(1858-1913)

Input parameters

Temperature T1 of air draw into piston /Celsius	25
Low pressure state p1 /atm	1.00
Volume V1 of uncompressed gas /litres	1820
Volume V2 of compressed gas /litres	79
Volume V3 of compressed gas after isobaric heating /litres	170
Degrees of freedom of molecular motion	3
Molar mass of gas /gmol^-1	28.966

Outputs

Heat input during isobaric heating /kJ	4267
Heat output during isochoric cooling /kJ	710
Total work done by gas on surroundings /kJ	3557
Efficiency (work done / heat input)	0.834

Theoretical efficiency

	0.834
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$$\eta = 1 - \frac{1}{r^{\gamma-1}} \left(\frac{s^{\gamma} - 1}{\gamma(s-1)} \right)$$

$$r = \frac{V_1}{V_2} \quad s = \frac{V_3}{V_2} \quad \gamma = \frac{c_p}{c_v}$$

Note all temperatures incorporated into calculations will be converted to Kelvin first - i.e. add 273 to Celsius number.

Pressure, volume, temperature coordinates of heat cycle

p1	1.0
V1	1820
T1	298
p2	186.0
V2	79.1
T2	2410
p3	186.0
V3	169.7
T3	5168
p4	3.6
V4	1820.0
T4	1063

Single cylinder power output

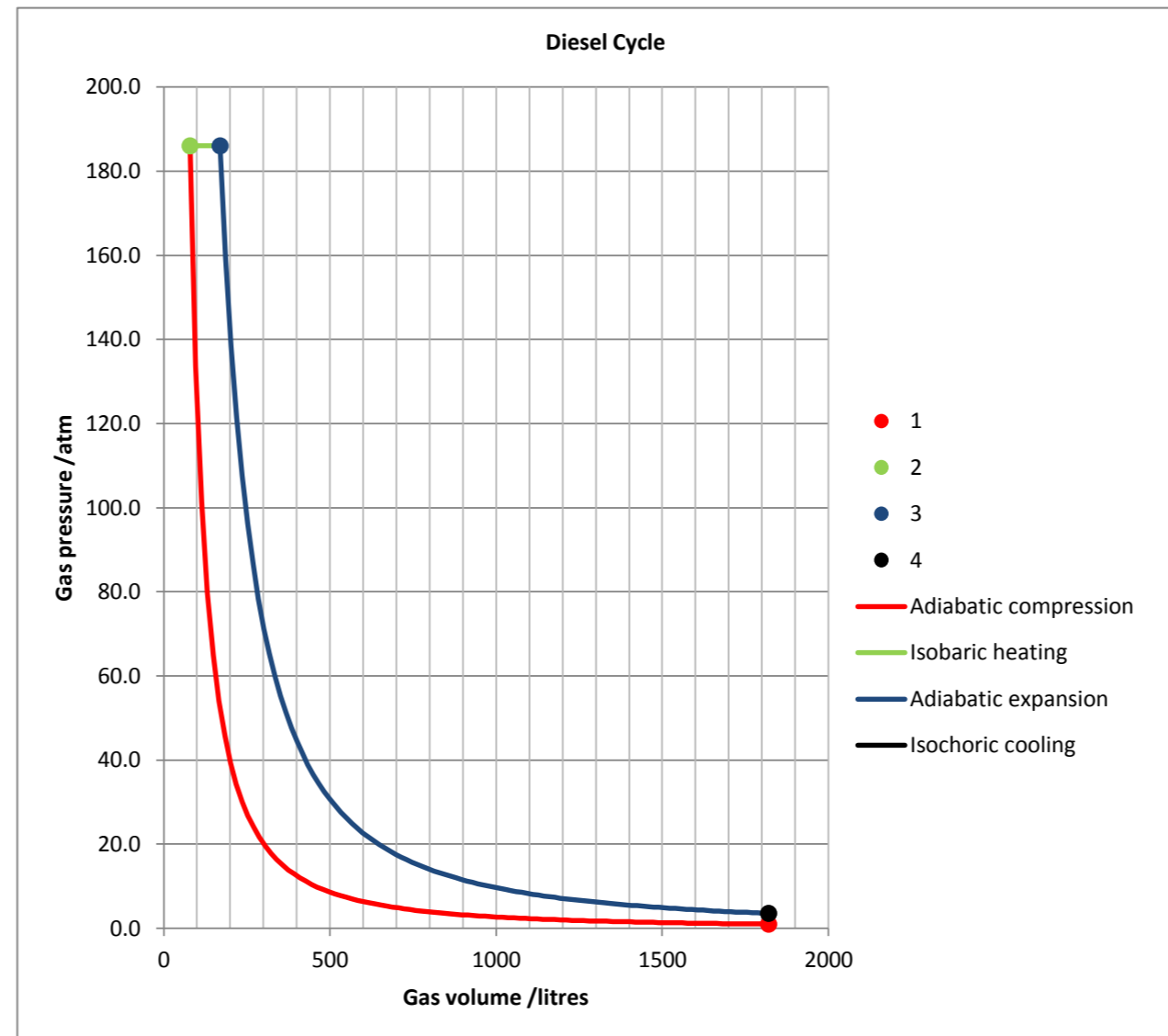
Engine RPM	84
Power output /kW	4,980

Number of cylinders	14
Total power output /kW	69,717

Note all pressures are quoted in atmospheres. 1atm = 101,325 Pa. Volumes in litres, T in K

Number of moles of gas in engine	74
Ratio of specific heats gamma	1.667
Constant volume specific heat capacity /Jkg^-1K^-1	431
Constant pressure specific heat capacity /Jkg^-1K^-1	718

Note real petrol engines have an efficiency of more like 20%, whereas diesels can be up to 40%. In other words, significant losses!



World's largest container ship in 2014
MV CSCL Globe



MAN B&W 12S90ME-C Mark 9.2 diesel engine. 69,720kW at 84RPM

Assume about 1820 litre cylinder volume V1

Max compression ratio:
V1/V2 = 23

V3 guessed at:
V1/10.726

V or p diff fraction	1 to 2		2 to 3		3 to 4		4 to 1	
	Adiabatic compression		Isobaric heating		Adiabatic expansion		Isochoric cooling	
	p	V	p	V	p	V	p	V
0	1.000	1820.000	186.014	79.130	186.014	169.681	3.566	1820.000
0.01	1.016	1802.591	186.014	80.036	159.354	186.184	3.540	1820.000
0.02	1.033	1785.183	186.014	80.941	138.322	202.688	3.514	1820.000
0.03	1.050	1767.774	186.014	81.847	121.404	219.191	3.489	1820.000
0.04	1.067	1750.365	186.014	82.752	107.569	235.694	3.463	1820.000
0.05	1.085	1732.957	186.014	83.658	96.095	252.197	3.437	1820.000
0.06	1.104	1715.548	186.014	84.563	86.461	268.700	3.412	1820.000
0.07	1.122	1698.139	186.014	85.469	78.285	285.203	3.386	1820.000
0.08	1.142	1680.730	186.014	86.374	71.279	301.707	3.360	1820.000
0.09	1.162	1663.322	186.014	87.280	65.225	318.210	3.335	1820.000
0.1	1.182	1645.913	186.014	88.186	59.954	334.713	3.309	1820.000
0.11	1.204	1628.504	186.014	89.091	55.332	351.216	3.284	1820.000
0.12	1.225	1611.096	186.014	89.997	51.256	367.719	3.258	1820.000
0.13	1.248	1593.687	186.014	90.902	47.639	384.223	3.232	1820.000
0.14	1.271	1576.278	186.014	91.808	44.414	400.726	3.207	1820.000
0.15	1.295	1558.870	186.014	92.713	41.525	417.229	3.181	1820.000
0.16	1.319	1541.461	186.014	93.619	38.925	433.732	3.155	1820.000
0.17	1.344	1524.052	186.014	94.524	36.577	450.235	3.130	1820.000
0.18	1.370	1506.643	186.014	95.430	34.447	466.739	3.104	1820.000
0.19	1.397	1489.235	186.014	96.335	32.508	483.242	3.078	1820.000
0.2	1.425	1471.826	186.014	97.241	30.739	499.745	3.053	1820.000
0.21	1.453	1454.417	186.014	98.146	29.119	516.248	3.027	1820.000
0.22	1.483	1437.009	186.014	99.052	27.631	532.751	3.001	1820.000
0.23	1.513	1419.600	186.014	99.957	26.264	549.254	2.976	1820.000
0.24	1.544	1402.191	186.014	100.862	25.011	565.757	2.951	1820.000
0.25	1.576	1384.782	186.014	101.767	23.864	582.260	2.926	1820.000
0.26	1.609	1367.373	186.014	102.672	22.824	598.763	2.901	1820.000
0.27	1.643	1349.964	186.014	103.577	21.881	615.266	2.876	1820.000
0.28	1.678	1332.555	186.014	104.482	21.036	631.769	2.851	1820.000
0.29	1.714	1315.146	186.014	105.387	20.289	648.272	2.826	1820.000
0.3	1.751	1297.737	186.014	106.292	19.641	664.775	2.801	1820.000
0.31	1.789	1280.328	186.014	107.197	19.091	681.278	2.776	1820.000
0.32	1.828	1262.919	186.014	108.102	18.639	697.781	2.751	1820.000
0.33	1.868	1245.510	186.014	109.007	18.285	714.284	2.726	1820.000
0.34	1.909	1228.101	186.014	109.912	18.029	730.787	2.701	1820.000
0.35	1.951	1210.692	186.014	110.817	17.871	747.290	2.676	1820.000
0.36	1.994	1193.283	186.014	111.722	17.811	763.793	2.651	1820.000
0.37	2.038	1175.874	186.014	112.627	17.849	780.296	2.626	1820.000
0.38	2.083	1158.465	186.014	113.532	17.886	796.799	2.601	1820.000
0.39	2.129	1141.056	186.014	114.437	17.921	813.302	2.576	1820.000
0.4	2.176	1123.647	186.014	115.342	17.954	829.805	2.551	1820.000
0.41	2.224	1106.238	186.014	116.247	17.985	846.308	2.526	1820.000
0.42	2.273	1088.829	186.014	117.152	18.014	862.811	2.501	1820.000
0.43	2.323	1071.420	186.014	118.057	18.041	879.314	2.476	1820.000
0.44	2.374	1054.011	186.014	118.962	18.066	895.817	2.451	1820.000
0.45	2.426	1036.602	186.014	119.867	18.089	912.320	2.426	1820.000
0.46	2.479	1019.193	186.014	120.772	18.110	928.823	2.401	1820.000
0.47	2.533	1001.784	186.014	121.677	18.129	945.326	2.376	1820.000
0.48	2.588	984.375	186.014	122.582	18.146	961.829	2.351	1820.000
0.49	2.644	966.966	186.014	123.487	18.161	978.332	2.326	1820.000
0.5	2.701	949.557	186.014	124.392	18.174	994.835	2.301	1820.000
0.51	2.759	932.148	186.014	125.297	18.185	1011.338	2.276	1820.000
0.52	2.818	914.739	186.014	126.202	18.194	1027.841	2.251	1820.000
0.53	2.878	897.330	186.014	127.107	18.201	1044.344	2.226	1820.000
0.54	2.939	879.921	186.014	128.012	18.206	1060.847	2.201	1820.000

Otto Cycle model

Dr A. French. September 2017



Nikolaus Otto (1832-1891)

Input parameters

Temperature T1 of air draw into piston /Celsius	20
Low pressure state p1 /atm	1.00
High pressure state p3 /atm	100
Volume V1 of uncompressed gas /litres	1
Volume V2 of compressed /litres	0.1
Degrees of freedom of molecular motion	3
Molar mass of gas /gmol^-1	28.966

Outputs

Heat input during isochoric heating /kJ	0.814
Heat output during isochoric cooling /kJ	0.175
Total work done by gas on surroundings /kJ	0.639
Efficiency (work done / heat input)	0.785

Theoretical efficiency

0.785

$$\eta = 1 - \frac{1}{r^{\gamma-1}}$$

$$r = \frac{V_1}{V_2} \quad \gamma = \frac{c_p}{c_v}$$

Note all temperatures incorporated into calculations will be converted to Kelvin first - i.e. add 273 to Celsius number.

Pressure, volume, temperature coordinates of heat cycle

p1	1.00
V1	1.000
T1	293
p2	46.42
V2	0.100
T2	1360
p3	100.00
V3	0.100
T3	2930
p4	2.15
V4	1.000
T4	631

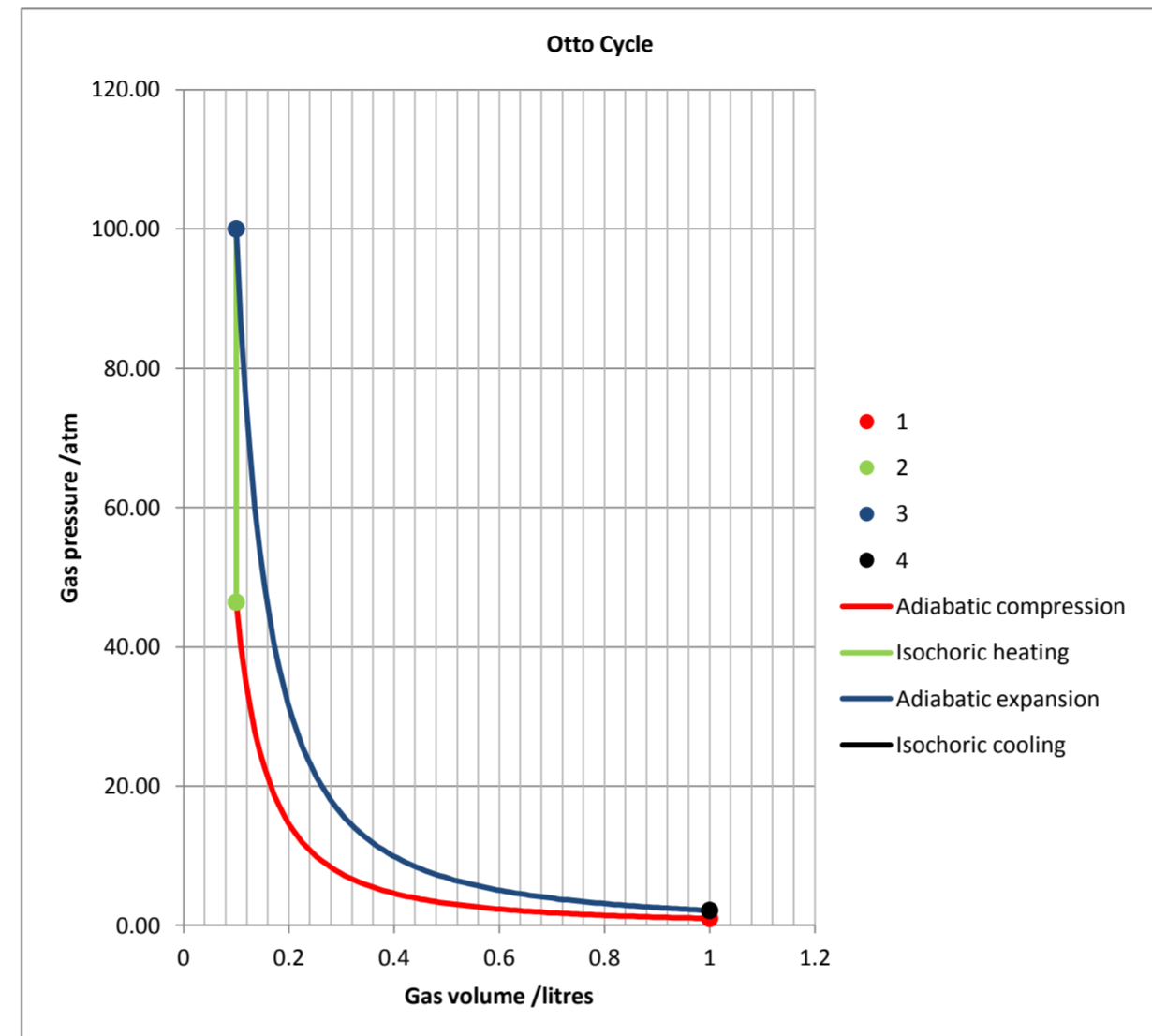
Power per cylinder

Engine RPM	6500
Power output /kW	69.21979

Number of cylinders	1
Total power output /kW	69.22

Note all pressures are quoted in atmospheres. 1atm = 101,325 Pa. Volumes in litres. T in K.

Number of moles of gas in engine	0.042
Ratio of specific heats gamma	1.667
Constant volume specific heat capacity /Jkg^-1K^-1	431
Constant pressure specific heat capacity /Jkg^-1K^-1	718

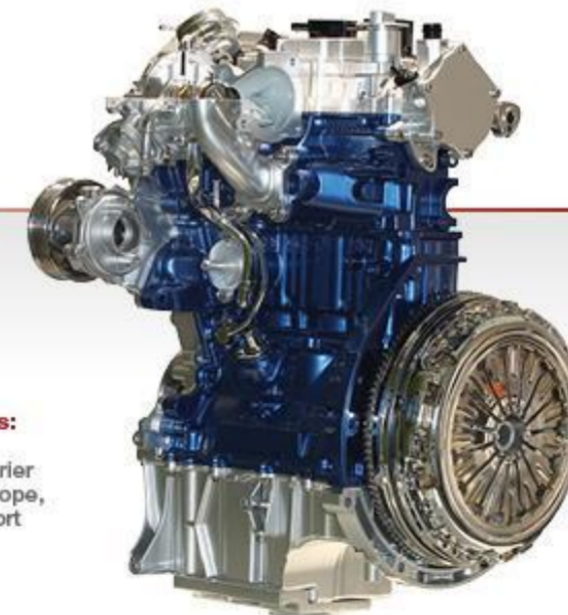


Note real petrol engines have an efficiency of more like 20%, whereas diesels can be up to 40%. In other words, significant losses!

FORD MOTOR CO. 1.0L ECOBOOST DOHC DI I-3

Displacement: 999 cc
Block / head material: cast iron / aluminum
Horsepower (SAE net): 123 @ 6,000 rpm
Torque: 125 lb.-ft. (169 Nm) @ 2,500 rpm
Specific output: 123 hp/L
Bore x stroke: 71.9 x 82 mm
Compression ratio: 10.0:1

EPA city / highway: 31 / 43 mpg
Assembly site: Cologne, Germany; Craiova, Romania
Application tested: '14 Ford Fiesta SE
Additional applications: Ford Focus, C-Max, Mondeo, Transit Courier (Europe); B-Max (Europe, Asia/Pacific); EcoSport (Asia/Pacific)



V or p diff fraction	1 to 2		2 to 3		3 to 4		4 to 1	
	Adiabatic compression		Isochoric heating		Adiabatic expansion		Isochoric cooling	
	p	V	p	V	p	V	p	V
0	1.000	1.000	46.416	0.100	100.000	0.100	2.154	1.000
0.01	1.015	0.991	46.952	0.100	86.621	0.109	2.143	1.000
0.02	1.031	0.982	47.488	0.100	75.892	0.118	2.131	1.000
0.03	1.047	0.973	48.023	0.100	67.142	0.127	2.120	1.000
0.04	1.063	0.964	48.559	0.100	59.901	0.136	2.108	1.000
0.05	1.080	0.955	49.095	0.100	53.834	0.145	2.097	1.000
0.06	1.097	0.946	49.631	0.100	48.693	0.154	2.085	1.000
0.07	1.115	0.937	50.167	0.100	44.295	0.163	2.074	1.000
0.08	1.133	0.928	50.703	0.100	40.500	0.172	2.062	1.000
0.09	1.151	0.919	51.238	0.100	37.199	0.181	2.051	1.000
0.1	1.170	0.910	51.774	0.100	34.309	0.190	2.039	1.000
0.11	1.190	0.901	52.310	0.100	31.762	0.199	2.027	1.000
0.12	1.210	0.892	52.846	0.100	29.505	0.208	2.016	1.000
0.13	1.230	0.883	53.382	0.100	27.494	0.217	2.004	1.000
0.14	1.252	0.874	53.918	0.100	25.693	0.226	1.993	1.000
0.15	1.273	0.865	54.454	0.100	24.074	0.235	1.981	1.000
0.16	1.296	0.856	54.989	0.100	22.613	0.244	1.970	1.000
0.17	1.319	0.847	55.525	0.100	21.288	0.253	1.958	1.000
0.18	1.343	0.838	56.061	0.100	20.083	0.262	1.947	1.000
0.19	1.367	0.829	56.597	0.100	18.984	0.271	1.935	1.000
0.2	1.392	0.820	57.133	0.100	17.978	0.280	1.924	1.000
0.21	1.418	0.811	57.669	0.100	17.054	0.289	1.912	1.000
0.22	1.444	0.802	58.204	0.100	16.205	0.298	1.900	1.000
0.23	1.472	0.793	58.740	0.100	15.421	0.307	1.889	1.000
0.24	1.500	0.784	59.276	0.100	14.696	0.316	1.877	1.000
0.25	1.529	0.775	59.812	0.100	14.024	0.325	1.866	1.000
0.26	1.559	0.766	60.348	0.100	13.400	0.334	1.854	1.000
0.27	1.590	0.757	60.884	0.100	12.819	0.343	1.843	1.000
0.28	1.622	0.748	61.419	0.100	12.277	0.352	1.831	1.000
0.29	1.655	0.739	61.954	0.100	11.772	0.361	1.820	1.000
0.3	1.689	0.730	62.489	0.100	11.302	0.370	1.808	1.000
0.31	1.724	0.721	63.023	0.100	10.866	0.379	1.797	1.000
0.32	1.760	0.712	63.557	0.100	10.463	0.388	1.785	1.000
0.33	1.797	0.703	64.091	0.100	10.092	0.397	1.774	1.000
0.34	1.835	0.694	64.625	0.100	9.752	0.406	1.762	1.000
0.35	1.874	0.685	65.159	0.100	9.442	0.415	1.751	1.000
0.36	1.914	0.676	65.693	0.100	9.161	0.424	1.740	1.000
0.37	1.955	0.667	66.227	0.100	8.908	0.433	1.728	1.000
0.38	2.000	0.658	66.761	0.100	8.682	0.442	1.717	1.000
0.39	2.046	0.649	67.295	0.100	8.482	0.451	1.705	1.000
0.4	2.094	0.640	67.829	0.100	8.307	0.460	1.694	1.000
0.41	2.144	0.631	68.363	0.100	8.156	0.469	1.681	1.000
0.42	2.200	0.622	68.921	0.100	8.028	0.478	1.670	1.000
0.43	2.261	0.613	69.457	0.100	7.922	0.487	1.658	1.000
0.44	2.317	0.604	69.993	0.100	7.836	0.496	1.646	1.000
0.45	2.376	0.595	70.529	0.100	7.768	0.505	1.635	1.000
0.46	2.437	0.586	71.065	0.100	7.717	0.514	1.623	1.000
0.47	2.501	0.577	71.600	0.100	7.682	0.523	1.612	1.000
0.48	2.567	0.568	72.136	0.100	7.661	0.532	1.600	1.000
0.49	2.636	0.559	72.672	0.100	7.653	0.541	1.589	1.000
0.5	2.709	0.550	73.208	0.100	7.657	0.550	1.577	1.000
0.51	2.784	0.541	73.744	0.100	7.673	0.559	1.566	1.000
0.52	2.863	0.532	74.280	0.100	7.699	0.568	1.554	1.000
0.53	2.946	0.523	74.815	0.100	7.735	0.577	1.543	1.000



Kinetic theory

A Statistical theory of the motion of molecules. A

macroscopic (i.e. human sized) quantity of gas has physical properties that can be explained by considering averages of molecular properties. LARGE numbers of molecules here!

* 1 m³ has $\times \left(\frac{1}{10^{-10}}\right)^3 = 10^{30}$ abms
 (Solid) $[1 \text{ \AA} = 10^{-10} \text{ m}]$

* 1 mole = 6.02×10^{23} molecules \approx atomic size
 \uparrow
 Avogadro's number N_A

Molecular motion is essentially a random process eg **Brownian Motion** of pollen grains and unseen air molecules



MEAN FREE PATH l

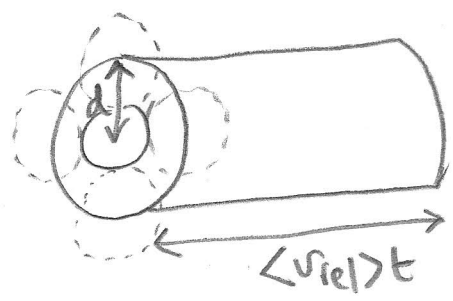
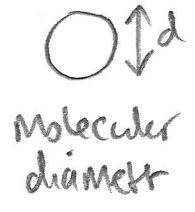
"average distance between molecular collisions"

$$l = \frac{\text{distance travelled in time } t}{\# \text{ molecules it will collide with}} = \frac{\sqrt{\langle v^2 \rangle} t}{n \times \text{"interaction volume"}}$$

\uparrow
molecules/unit volume

$\sqrt{\langle v^2 \rangle}$ is the root-mean-squared (RMS) speed

Interaction volume



A kind of 'collision tube' between molecules

$$\langle v_{rel} \rangle = \sqrt{\langle |\underline{v}_i - \underline{v}_j|^2 \rangle}$$

$$= \sqrt{\langle v_i^2 + v_j^2 - 2\underline{v}_i \cdot \underline{v}_j \rangle}$$

$\langle \underline{v}_i \cdot \underline{v}_j \rangle = 0$ $\therefore \langle v_{rel} \rangle = \sqrt{2} \sqrt{\langle v^2 \rangle}$

So interaction volume = $\pi d^2 \sqrt{2} \sqrt{\langle v^2 \rangle}$

$$l = \frac{1}{\pi \sqrt{2} d^2 n}$$

Define Knudsen's number $Kn = \frac{l}{d}$

$$Kn = \frac{l}{d}$$

$Kn \gg 1$ Statistical mechanics
 $Kn \ll 1$ Continuum mechanics

So $Kn = \frac{1}{\pi \sqrt{2} n d^3}$

For ideal gas and $\frac{R}{N_A} = k_B$

$pV = \left(\frac{nV}{N_A}\right) RT$
 \leftarrow # moles

Boltzmann's constant.

$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$

So $p = n k_B T$

$n = \frac{p}{k_B T}$

$k n = \frac{k_B T}{\pi \sqrt{2} d^3 p}$

$d = 0.3 \times 10^{-9} \text{ m}$ $T = 293 \text{ K}$

$p = 10^5 \text{ Pa}$ (atmospheric pressure)

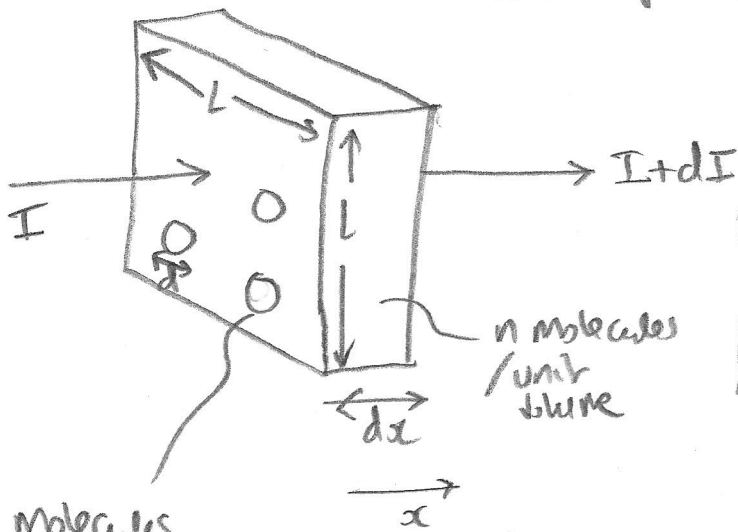
$\Rightarrow k n \approx 333$ and $l \approx 1.0 \times 10^{-7} \text{ m}$

So Statistical mechanics is justified for air at S.T.P (Standard temp & pressure).

Beer Lambert law & mean free path (Similar idea to attenuation of γ rays)

Another exponential decay!

consider a particle beam of I molecules / unit area passing through a slab of matter of dimensions $L \times L \times dx$.



$dI = -I \times \text{probability of absorption over range } dx$

molecules with colliding cross section $\sigma = \sqrt{2} d^2 \pi$

$P_{\text{absorb}} = \text{molecules in } L^2 dx \times \frac{\text{molecular area}}{L^2}$

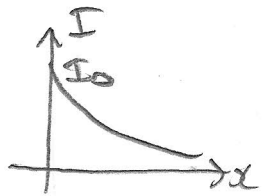
So $\sqrt{2} d^2 \pi$ is a little convoluted...!

$= n L^2 dx \times \frac{\sigma}{L^2}$

$dI = -I n \sigma dx$
 $\Rightarrow \int_{I_0}^I \frac{dI}{I} = -n \sigma \int_0^x dx$

$\ln\left(\frac{I}{I_0}\right) = -n \sigma x$

$I = I_0 e^{-n \sigma x}$



"Survival probability" (or probability of a molecular collision)

is $p(x) dx = k e^{-n \sigma x} dx$

Now $\int_0^{\infty} p(x) dx = 1$

$\Rightarrow k = n \sigma$

So $p(x) = n \sigma e^{-n \sigma x}$

between x and $x + dx$

So mean free path $l = \int_0^{\infty} x p(x) dx$

$l = \int_0^{\infty} n \sigma x e^{-n \sigma x} dx$

$$\Rightarrow l = \left[-x n_0 \frac{1}{n_0} e^{-n_0 x} \right]_0^\infty - \int_0^\infty \left(-\frac{1}{n_0} \right) e^{-n_0 x} n_0 dx$$

$$l = \frac{1}{n_0}$$

so

$$l = \frac{1}{n \sqrt{2} \pi d^2}$$

as before

In summary:

$$I = I_0 e^{-x/l}$$

$$p(x) = \frac{e^{-x/l}}{l}$$

$$l = \frac{1}{n \sqrt{2} \pi d^2}$$

mean free path.

A random walk



consider a 1D motion

$$x = l \sum_{i=1}^N a_i$$

Displacement

where step size is mean free path l

and $a_i = \begin{cases} +1 \\ -1 \end{cases}$, randomly selected.

N steps.

$$\text{Now } \sqrt{\langle x^2 \rangle} = l \sqrt{\left\langle \left(\sum_{i=1}^N a_i \right)^2 \right\rangle} = l \sqrt{\left\langle \sum_{i=1}^N a_i^2 + \sum_{i=1}^N \sum_{j=1, j \neq i}^N a_i a_j \right\rangle}$$

$N \times 1$

zero since random choice of $+1, -1$

$$\sqrt{\langle x^2 \rangle} = l \sqrt{N}$$

Now if average speed is $\sqrt{\langle v^2 \rangle}$

$$\# \text{ steps } N = \frac{\sqrt{\langle v^2 \rangle} t}{l}$$

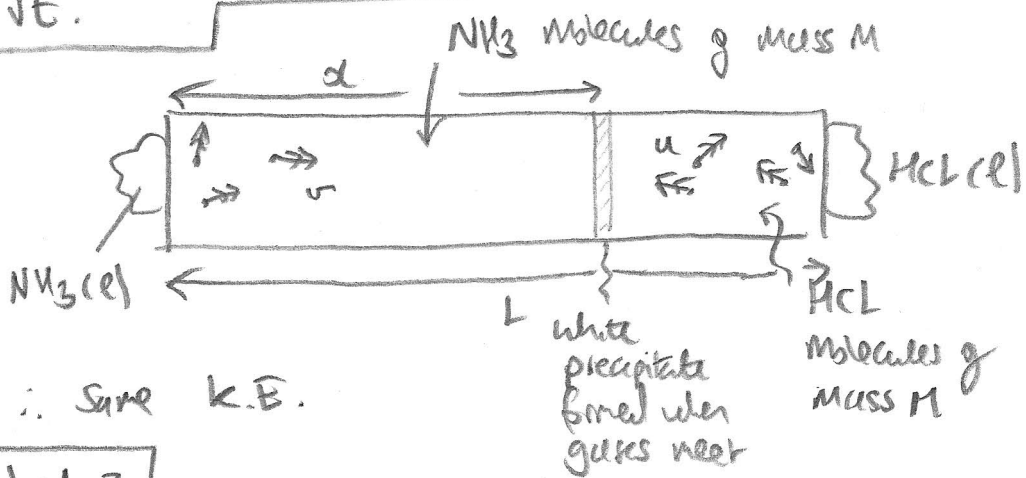
$$\sqrt{\langle x^2 \rangle} = \left(l \sqrt{\langle v^2 \rangle} t \right)^{1/2}$$

we expect diffusion of molecules to have RMS diffusion distance $\propto \sqrt{t}$.

Graham's law

If two gases are in thermal equilibrium \rightarrow same temperature \therefore same k.E.

$$\text{So } \frac{1}{2} m v^2 = \frac{1}{2} M u^2$$



(11)

v, u average (RMS) speeds

Now if precipitate forms after t seconds:

$$\alpha = vt$$

$$L - \alpha = ut$$

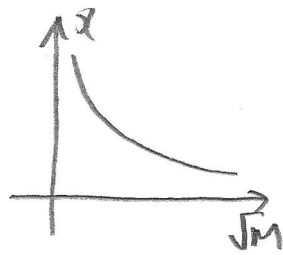
$$\therefore \frac{\alpha}{L - \alpha} = \frac{v}{u}$$

Now $\left(\frac{v}{u}\right)^2 = \frac{M}{m}$

$$\therefore \frac{\alpha}{L - \alpha} = \sqrt{\frac{M}{m}}$$

So expect diffusion distance

$$\alpha \propto \frac{1}{\sqrt{M}}$$



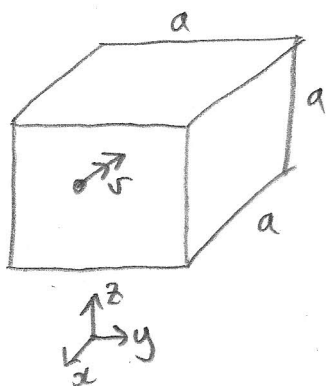
In this example:

$$m = 17 \text{ g/mol}$$

$$M = 36.5 \text{ g/mol}$$

$$\Rightarrow \frac{\alpha}{L - \alpha} = \sqrt{\frac{36.5}{17}} \approx 1.47 \quad \text{or about } 3:2$$

Pressure from kinetic theory



* Assume molecules with velocity $\underline{v} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}$ glide elastically with walls of container of side a .

* \therefore momentum transferred per collision is $\Delta p_{x,y,z} = 2m v_{x,y,z}$



BEFORE

AFTER

* Time between collisions with the same wall is

$$\Delta t_{x,y,z} = \frac{2a}{v_{x,y,z}}$$

* \therefore force on wall = rate of change of momentum \times # particles

$$= \Delta p_{x,y,z} / \Delta t_{x,y,z} = \frac{m v_{x,y,z}^2 N}{a}$$

* pressure is force/area

$$P = \frac{m v_{x,y,z}^2 N}{a^3}$$

$$P = \frac{1}{3} \rho \langle v^2 \rangle$$

Now $v^2 = v_x^2 + v_y^2 + v_z^2$
 So $\langle v^2 \rangle = 3 \langle v_{x,y,z}^2 \rangle$
 Also density $\rho = mN/a^3$

THE BOLTZMANN FACTOR

$$e^{-\epsilon/k_B T}$$

MOLECULAR SPEEDS

Probability of a particle having energy ϵ_i (in a large system of particles with which it can exchange energy) is given by:

$$P(\epsilon_i) \propto e^{-\epsilon_i/k_B T}$$

T absolute temp/K
 $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$

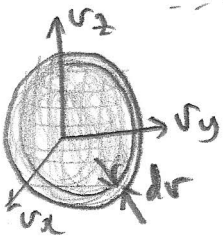
{ for proof see Edexcel notes }

For a gas of molecules of mass m , the probability of molecular speed being between v and $v+dv$ is

$$P(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{1}{2}mv^2/k_B T} dv$$

i.e. $P(v) dv = \text{constant} \times (4\pi v^2 dv) \times \text{Boltzmann factor } e^{-\frac{1}{2}mv^2/k_B T}$

$(4\pi v^2 dv)$ is the volume of a spherical shell in velocity space. The number of ways of achieving v^2 are proportional to this volume, hence so is $P(v) dv$.



$$v^2 = v_x^2 + v_y^2 + v_z^2$$

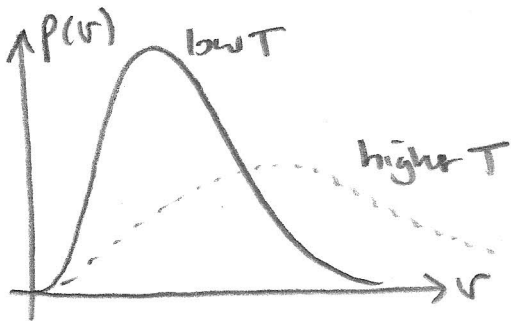
You can find the constant from using some standard integrals of the form

$$\int_0^\infty x^n e^{-ax^2} dx = I_n$$

$$\int_0^\infty P(v) dv = 1$$

$$I_0 = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad I_1 = \frac{1}{2a}$$

$$I_2 = \frac{\sqrt{\pi}}{4a^{3/2}} \quad I_n = \frac{n-1}{2a} I_{n-2}$$



Now $E[\frac{1}{2}mv^2]$ i.e. average KE

$$= \frac{1}{2}m \int_0^\infty v^2 P(v) dv$$

$$= \frac{3}{2}k_B T$$

(So average KE $\propto T$)

which indicates the result on page (1) of

$$U = \# \text{ degrees of freedom} \times \frac{1}{2}k_B T$$

BOLTZMANN & GIBBS ENTROPY S

* Clausius proposes 2nd law: $dS_{tot} \geq 0$ where $dS = \frac{dQ}{T}$

* Boltzmann & Gibbs propose a statistical basis for entropy

$$S = -k_B \sum_i p_i \ln p_i$$

Gibbs entropy

For a system with N possible states each with probability p_i

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Simplest case is $p_i = \frac{1}{W}$

where W is the number of ways of arranging the system (eg in spatial, or indeed energy terms - or both!)

For N particles with n_1 of energy level 1, n_2 " " " 2 etc

$$W = \frac{N!}{\prod_i n_i!}$$

← Think # permutations of 100000 since 4 x "0" (equivalent to same energy level)

$$\frac{6!}{4!} = 30$$

$$S = -k_B \sum_i p_i (-\ln W) = k_B \ln W \sum_i p_i$$

$$\sum_i p_i = 1$$

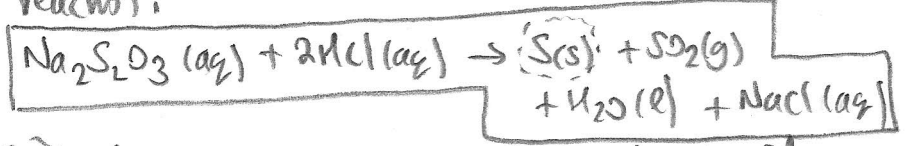
$$S = k_B \ln W \quad \text{Boltzmann entropy}$$

BOLTZMANN FACTOR & CHEMICAL KINETICS

Rate of reaction $r = A e^{-\frac{E}{RT}}$

- E 'Activation energy' J/mol
- R Molar gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
- A Rate constant

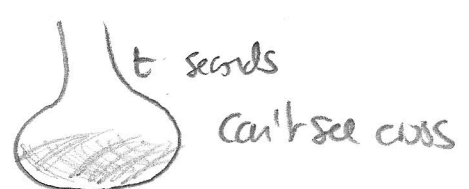
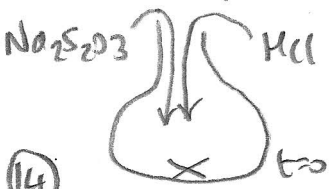
For example 'Sodium Thiosulphate cross' reaction.



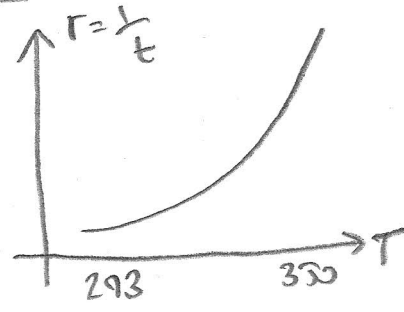
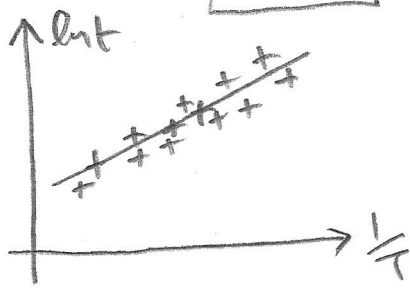
Amorphous sulphur makes the liquid opaque

$$r \approx \frac{1}{t}$$

Time for cross to vanish.



So if $\frac{1}{t} = A e^{-\frac{\epsilon}{RT}}$ $\ln t = -\ln A + \frac{\epsilon}{RT}$

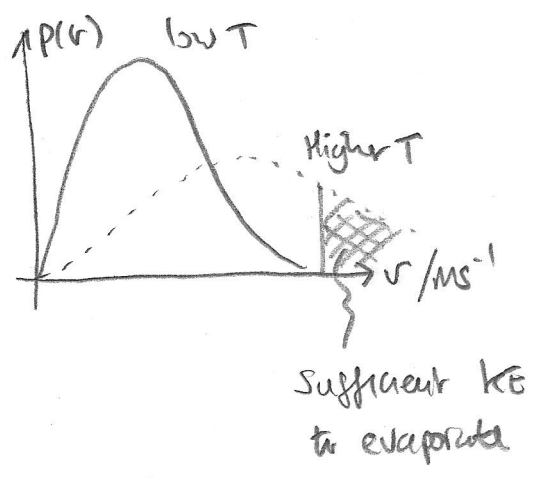


{ 31/1/2019 in Winal lab }

$\epsilon \approx 37.1 \text{ kJ/mol}$
 $A \approx 6.4 \times 10^4 \text{ s}^{-1}$

For 10 cm^3 sodium diarsulphate, 5 cm^3 of HCl

EVAPORATIVE COOLING AND THE MAXWELL BOLTZMANN SPEED DISTRIBUTION

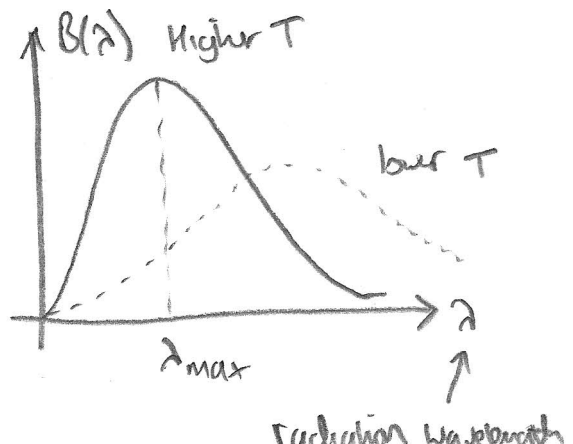


when drying wet clothes, or using air conditioning, idea is to remove the higher energy molecules that have KE sufficient to overcome the latent heat of vaporisation to change state from liquid to gas.

'Removal' is usually via a breeze, open window, and a lack of humidity. (water vapor in the air)

once the most energetic molecules are removed, the average KE \downarrow
 Since $E(\frac{1}{2}mv^2) = \frac{3}{2}k_B T$ this will lower the average temperature.

PLANCK RADIATION DISTRIBUTION



spectral power density of light emitted by a body is:

$$B(\lambda) = \frac{2\pi^5 h c^2}{15} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

By setting $\frac{dB}{d\lambda} = 0$

$$\lambda_{max} \approx \frac{hc}{4.965 k_B T}$$

RED 620-750nm

BLUE 450-495nm