

Behaviour of Gases Answer Sheet

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1 Outlines of the measurement

----- 1Watt = 683lumens for light at 555nm -----

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{\lambda k_b T}} - 1} \quad (1)$$

Called the Planck equation, it is a function of temperature and the wavelength of the radiated light.

1.i Regarding the common assumption that the exponential term does not convey any units,

$$\frac{[\emptyset][J \cdot s][\frac{m^2}{s^2}]}{[m^5]} \cdot \frac{[\emptyset]}{[\emptyset]} \equiv \frac{W}{A \cdot \lambda} \left[\frac{J}{s \cdot m^3} \right]$$

1.ii

$$E_0 = \frac{(2)(6.626 \cdot 10^{-34})(3 \cdot 10^8)^2}{(555 \cdot 10^{-9})^5} \cdot \frac{1}{e^{\frac{(6.626 \cdot 10^{-34})(3 \cdot 10^8)}{(555 \cdot 10^{-9})(1.38 \cdot 10^{-23})(500)}} - 1} = 6.485 \cdot 10^{-8} E$$
$$E_{555nm}^{1500^\circ K} = \frac{(2)(6.626 \cdot 10^{-34})(3 \cdot 10^8)^2}{(555 \cdot 10^{-9})^5} \cdot \frac{1}{e^{\frac{(6.626 \cdot 10^{-34})(3 \cdot 10^8)}{(555 \cdot 10^{-9})(1.38 \cdot 10^{-23})(1500)}} - 1} = 6.929 \cdot 10^7 E$$
$$\frac{E_{555nm}^{1500^\circ K}}{E_0} = 1.068 \cdot 10^{15}$$

1.iii

$$E_0 = E_{660nm}^{X1^\circ}; \text{ then}$$
$$X1^\circ = \frac{hc}{\lambda_{660nm} k_b} \cdot \frac{1}{\ln \left(\frac{2hc^2}{E_0 \lambda_{660nm}^5} + 1 \right)}$$
$$X1^\circ = 447.793^\circ K$$

1.iv There are 120 diodes in series in each row, where 5% of the diodes don't contribute to the voltage drop. Bear in mind the efficiency of the system is a property of the diodes, and hence does not contribute to the voltage drop.

$$V_{row} = 120 \cdot 5mV \cdot (100\% - 5\%) = 0.57V$$

1.v

$$A_{board} = (200 \cdot 15.5mm)(120 \cdot 15.5mm) = 5.766m^2$$

$$E_{board} = \frac{V_{row} \cdot N_{parallel} \cdot i_{fwd} \cdot e\%}{A_{board}}$$

$$e\% = \frac{586.6}{683} = 85.89\%$$

$$E_{board} = \frac{0.57 \cdot 200 \cdot 0.02 \cdot 85.89\%}{5.766} = 0.3396W/m^2$$

$$E_0/E_{board} = 1.910 \cdot 10^{-7}$$

1.vi

$$C_v = d_{rot} \frac{R}{2} + d_{trs} \frac{R}{2} + d_{vib} R \quad (2)$$

From figure, we can deduce there are 3 rotational (axial rotations that would change the orientation of the molecule in space) and 3 translational degrees of freedom for the molecule of C_{2v} symmetry. However, for the molecule of D_{2h} symmetry, there are 2 rotational and 3 translational degrees of freedom. On top of that, of course, there are the vibrational dimensions of freedom.

$$C_v^{D_{2h}} = 2 \frac{R}{2} + 3 \frac{R}{2} + 4R = \frac{13}{2} R$$

$$C_v^{C_{2v}} = 3 \frac{R}{2} + 3 \frac{R}{2} + 3R = 6R$$

1.vii -

2 Onto thermodynamics

$$T \propto V^2 \text{ at constant } P, n$$

$$n \propto V^2 \text{ at constant } P, T$$

$$P \propto \frac{1}{V^2} \text{ at constant } n, T$$

2.i

$$PV^2 = nYT \quad (3)$$

2.ii

$$\begin{aligned}
[atm][L^2] &\equiv [mol][Y][K] \\
[Y] &\equiv \left[\frac{atm \cdot L^2}{K \cdot mol} \right] \\
[Y] &\equiv [R][\epsilon]
\end{aligned} \tag{4}$$

$$\begin{aligned}
\left[\frac{atm \cdot L^2}{K \cdot mol} \right] &\equiv \left[\frac{atm \cdot L}{K \cdot mol} \right][\epsilon] \\
[\epsilon] &\equiv [L]
\end{aligned} \tag{5}$$

2.iii

$$\begin{aligned}
\delta w_{rev} &= -PdV \\
\text{from } P &= \frac{nYT}{V^2}; \\
\int \delta w &= nYT \int \frac{1}{V^2} dV \\
\Delta w_{rev} &= nYT \left(\frac{1}{V_f} - \frac{1}{V_i} \right) = nYT \left(\frac{V_i - V_f}{V_i V_f} \right)
\end{aligned} \tag{6}$$

2.iv Applying the new gas law,

$$\begin{aligned}
1.2 \cdot V^2 &= 1 \cdot 0.082 \cdot (500 + 273.15) \cdot 0.0316 \\
V &= 1.292L
\end{aligned}$$

2.v The classic definition of dH is as follows:

$$\begin{aligned}
dH &= dU + d(nRT) \\
&= dU + d(PV) \\
&= TdS - PdV + PdV + VdP \\
&= TdS + VdP
\end{aligned} \tag{7}$$

Using the ideal gas law for the gas giant;

$$\begin{aligned}
dH &= dU + d(nRT) \\
&= dU + \frac{d(PV^2)}{\epsilon} \\
&= TdS - PdV + \frac{V^2}{\epsilon} dP + \frac{2PV}{\epsilon} dV \\
&= TdS + \frac{V^2}{\epsilon} dP + \left(\frac{2PV}{\epsilon} - P \right) dV
\end{aligned} \tag{8}$$

2.vii

$$\begin{aligned} dU &= \delta \overset{0}{q} + \delta w \\ C_v dT &= -P dV \end{aligned} \quad (9)$$

$$\begin{aligned} dH &= dU + \frac{V^2 dP}{\epsilon} + \frac{2PV dV}{\epsilon} \\ \underbrace{(C_p - C_v)}_R dT &= \frac{V^2 dP}{\epsilon} + \frac{2PV dV}{\epsilon} \\ dT &= \frac{V^2 dP}{Y} + \frac{2PV dV}{Y} \end{aligned} \quad (10)$$

Plugging equation (10) into (9);

$$\begin{aligned} C_v \left(\frac{V^2 dP}{Y} + \frac{2PV dV}{Y} \right) &= -P dV \\ -\frac{C_v}{Y} V^2 dP &= \left(\frac{2C_v PV}{Y} + P \right) dV \\ -\frac{C_v}{Y} \cdot \frac{\cancel{nYT}}{P} &= \left(\frac{2C_v}{Y} \cdot \frac{\cancel{nYT}}{V} + \frac{\cancel{nYT}}{V^2} \right) dV \\ -C_v \int \frac{dP}{P} &= 2C_v \int \frac{dV}{V} + Y \int \frac{dV}{V^2} \\ -C_v \cdot \ln \left(\frac{P_f}{P_i} \right) &= 2C_v \cdot \ln \left(\frac{V_f}{V_i} \right) - Y \cdot \left(\frac{1}{V_f} - \frac{1}{V_i} \right) \\ \ln \left(\frac{P_i}{P_f} \right) &= \ln \left[\left(\frac{V_f}{V_i} \right)^2 \cdot e^{\frac{Y}{C_v} \cdot \left(\frac{1}{V_i} - \frac{1}{V_f} \right)} \right] \\ \frac{P_i}{P_f} &= \left(\frac{V_f}{V_i} \right)^2 \cdot e^{\frac{Y}{C_v} \cdot \left(\frac{1}{V_i} - \frac{1}{V_f} \right)} \\ P_i V_i^2 \cdot e^{\frac{-Y}{C_v} \frac{1}{V_i}} &= P_f V_f^2 \cdot e^{\frac{-Y}{C_v} \frac{1}{V_f}} \\ P V^2 \cdot e^{\frac{-Y}{C_v} \frac{1}{V}} &= K \end{aligned} \quad (11)$$

2.vii

$$\begin{aligned} (dH)_P &= T dS + \underbrace{\frac{V^2 dP}{\epsilon}}_{\text{because } dP=0} + \left(\frac{2PV}{\epsilon} - P \right) dV \\ \int (dH)_P &= \int T dS + \frac{2P}{\epsilon} \int V dV - P \int dV \\ (\Delta H)_P &= Q + \frac{P \Delta(V^2)}{\epsilon} - P \Delta V \end{aligned} \quad (12)$$

$$\begin{aligned}
(dH)_T &= dU + d(nRT) \\
(dH)_T &= \underbrace{nC_v dT + nR dT}_{\text{because } dT=0} \xrightarrow{0} \\
(\Delta H)_T &= 0
\end{aligned} \tag{13}$$

$$\begin{aligned}
(dH)_V &= TdS + \frac{V^2}{\epsilon} dP + \underbrace{\left(\frac{2PV}{\epsilon} - P \right) dV}_{\text{because } dV=0} \xrightarrow{0} \\
\int (dH)_V &= \int TdS + \frac{V^2}{\epsilon} \int dP \\
(\Delta H)_V &= Q + \frac{V^2 \Delta P}{\epsilon}
\end{aligned} \tag{14}$$

$$(dH)_H = 0 \tag{15}$$

Equation (11) comes to our help at applying our adiabatic constraint at the 2 \rightarrow 3 step:

$$\begin{aligned}
(dH)_Q &= (dU)_Q + \left(\frac{dPV^2}{\epsilon} \right)_Q \\
&= -PdV + \underbrace{TdS}_{\text{because } dq=0} \xrightarrow{0} + d \left(\frac{PV^2}{\epsilon} \right)_Q \\
&= -\frac{K}{V^2} \cdot e^{\frac{Y}{C_v} \frac{1}{V}} dV + \frac{K}{\epsilon} d \left(e^{\frac{Y}{C_v} \frac{1}{V}} \right)
\end{aligned} \tag{16}$$

2.viii We have to check which dH definition holds under isochoric conditions; alternatives being the one we had just solved above, and the classic definition where;

$$dH_{classic} = TdS + VdP$$

Integrating both sides and regarding the constraints, we get;

$$(\Delta H)_{V_{classic}} = Q + V\Delta P$$

Since we come across with Q in both equations, let's find Q by first solving for E_i and E_f .

$$\begin{aligned}
 E_i &= \frac{1.065 \cdot 10^{-12} \text{lm}}{683 \frac{\text{lm}}{\text{W}}} = 1.56 \cdot 10^{-15} & E_f &= \frac{1.134 \cdot 10^{-12} \text{lm}}{683 \frac{\text{lm}}{\text{W}}} = 1.66 \cdot 10^{-15} \\
 T_{\text{matter}}^{\circ} &= \frac{hc}{\lambda_{555\text{nm}} k_b} \cdot \frac{1}{\ln\left(\frac{2hc^2}{E\lambda_{555\text{nm}}^5} + 1\right)} \\
 \Delta T_{\text{matter}}^{\circ} &= \frac{hc}{\lambda_{555\text{nm}} k_b} \cdot \left(\frac{1}{\ln\left(\frac{2hc^2}{E_f \lambda_{555\text{nm}}^5} + 1\right)} - \frac{1}{\ln\left(\frac{2hc^2}{E_i \lambda_{555\text{nm}}^5} + 1\right)} \right) \\
 Q &= \rho_{\text{matter}} \cdot C_{\text{matter}} \cdot d_{\text{thickness}} \cdot \frac{hc}{\lambda_{555\text{nm}} k_b} \cdot \left(\frac{1}{\ln\left(\frac{2hc^2}{E_f \lambda_{555\text{nm}}^5} + 1\right)} - \frac{1}{\ln\left(\frac{2hc^2}{E_i \lambda_{555\text{nm}}^5} + 1\right)} \right) \\
 Q &= 9000 \frac{\text{g}}{\text{L}} \cdot 2100 \frac{\text{J} \cdot \text{dm}^2}{\text{g} \cdot \text{K}} \cdot 0.004 \text{dm} \cdot \frac{6.626 \cdot 10^{-34} \cdot 8 \cdot 10^8}{555 \cdot 10^{-9} \cdot 1.38 \cdot 10^{-23}} \\
 &\quad \cdot \left(\frac{1}{\ln\left(\frac{2 \cdot 6.626 \cdot 10^{-34} \cdot (8 \cdot 10^8)^2}{1.66 \cdot 10^{-15} \cdot (555 \cdot 10^{-9})^5} + 1\right)} - \frac{1}{\ln\left(\frac{2 \cdot 6.626 \cdot 10^{-34} \cdot (8 \cdot 10^8)^2}{1.56 \cdot 10^{-15} \cdot (555 \cdot 10^{-9})^5} + 1\right)} \right) \\
 &\hspace{15em} Q = 25.30 \text{kJ}
 \end{aligned}$$

Then, let's compare both functions;

$$(\Delta H)_{V_{\text{classic}}} = Q + V \Delta P \qquad (\Delta H)_{V_{\text{new}}} = Q + \frac{V^2 \Delta P}{\epsilon}$$

$$\begin{aligned}
 V \Delta P &= 3L \cdot (25 - 200) \text{atm} \cdot 0.101325 \frac{\text{kJ}}{\text{L} \cdot \text{atm}} = -53.20 \text{kJ} \\
 \frac{V^2 \cdot \Delta P}{\epsilon} &= \frac{3^2 \cdot (25 - 200)}{\epsilon} \cdot 0.101325 \frac{\text{kJ}}{\text{L} \cdot \text{atm}} = 29.01 \text{kJ}
 \end{aligned}$$

$$(\Delta H)_{V_{\text{classic}}} = 25.3 \text{kJ} - 53.20 \text{kJ} = -28.2 \text{kJ}, \quad (\Delta H)_{V_{\text{new}}} = 25.3 \text{kJ} - 29.01 \text{kJ} = -3.71 \text{kJ}$$

Since we know only very little amount of gas condenses into its liquid form, and released energy is proportional to the amount of phase transition that takes place, we expect $(\Delta H)_{V_{\text{new}}}$ to be our definition of dH for this gas giant.

2.ix From equation (5) in the question paper,

$$\begin{aligned} \left(\frac{P_i}{P_f}\right) &= \left(\frac{V_f}{V_i}\right)^{\frac{1}{3}} \cdot e^{\left(\frac{C_v}{R} \cdot \left(\frac{V_f}{V_i}\right)\right)} \\ \left(\frac{P_i}{P_f}\right)^3 &= \left(\frac{V_f}{V_i}\right) \cdot e^{\left(\frac{3C_v}{R} \cdot \left(\frac{V_f}{V_i}\right)\right)} \\ W\left[\frac{3C_v}{R} \cdot \left(\frac{P_i}{P_f}\right)^3\right] &= \frac{3C_v}{R} \cdot \left(\frac{V_f}{V_i}\right) \cdot e^{\left(\frac{3C_v}{R} \cdot \left(\frac{V_f}{V_i}\right)\right)} \\ W\left(\frac{3C_v}{R} \cdot \left(\frac{P_i}{P_f}\right)^3\right) &= \frac{3C_v}{R} \cdot \left(\frac{V_f}{V_i}\right) \\ V_f &= V_i \cdot \frac{R}{3C_v} \cdot W\left(\frac{3C_v}{R} \cdot \left(\frac{P_i}{P_f}\right)^3\right) \\ V_f &= 25 \cdot \frac{\cancel{R}}{3 \cdot 6\cancel{R}} \cdot W\left(\frac{3 \cdot 6\cancel{R}}{\cancel{R}} \cdot \left(\frac{75}{137}\right)^3\right) \\ V_f &= \frac{25}{18} \cdot \left[1 + \frac{(2.71 - e)}{2e} - \frac{3 \cdot (2.71 - e)^2}{16e^2} + \frac{19 \cdot (2.71 - e)^3}{192 \cdot e^3}\right] \\ V_f &= 1.4L \end{aligned}$$

2.x For this approximation to work, we need to input a reasonably close value to e inside the Lambert W function. We indeed observe that the term inside the function is about 2.71, which is indeed in the vicinity of value e .

2.xi Using equation (5) from the question paper,

$$\begin{aligned} \frac{75}{P_f} &= \left(\frac{1.4}{25}\right)^{\frac{1}{3}} \cdot e^{\frac{6R \cdot 1.4}{R \cdot 25}} \\ P_f &= 140 \text{ atm} \\ r &= \frac{137 - 140}{137} = 2.19\% > 2\% \end{aligned}$$

Correct answer is no.