

E3-1

NAME: _____, UFID: _____

(Start each problem on a clean sheet with your name and problem # at top of page)

	True	False
1. The change in entropy of a reaction near absolute zero temperature is taken to be zero by convention but does not have experimental confirmation made at finite temperatures.		✓
2. In a Joule expansion an ideal gas in a volume V irreversibly expands into an equivalent volume within a thermally isolated container. Since entropy increases and no work is done, the general statement can be made that pure forces derived solely from entropic considerations are not possible		✓
3. Adiabatic demagnetization is a two-step process in which an isothermal increase of magnetic field is followed by an adiabatic decrease of magnetic field.	✓	
4. The cohesive force between charge neutral atoms of a gas is due to attractive forces between magnetic dipoles.		✓
5. A mug containing 0.2 kg of water is allowed to cool from 90°C to 18°C. The specific heat capacity is 4200 J K ⁻¹ kg ⁻¹ . Determine the change of entropy of the water to three place accuracy. Include sign and units. Write answer in either box.		-185.7 J/K

} See next page

2. Heat is supplied to an engine at the rate of 10⁶ J/min and the engine has an output of 10 horsepower (hp) where 1 hp = 745.7 J/s.

- (a) What is the efficiency (%) of this engine?
 (b) How much heat per minute is rejected to the low temperature surroundings?
 (c) If the engine is running at room temperature (20°C) what temperature would be needed in the high temperature reservoir supplying the heat to compete with a reversible Carnot engine running under the same conditions?

3. (25 pts) The Gibb's free energy of a system of N particles is given by,

$$G(T, p) = -Nk_B T \ln \left(\frac{aT^{5/2}}{p} \right)$$

- (a) $dG = ?$ (write in differential form similar to $dU = TdS - pdV$) (5 pts)
 (b) Find expressions for S and V written as partial derivatives with respect to G . (4 pts.)
 (c) Compute the constant pressure heat capacity C_p of the system: $C_p = T(dS/dT)_p$

Exam 3 solutions

#1) Question 5 0.2 kg H_2O cooling from $90^\circ C$ (363 K) to $18^\circ C$ (291 K)

$$dS = \frac{dQ}{T} = \frac{C dT}{T} \Rightarrow \Delta S = C \int_{T_h}^{T_c} \frac{dT}{T} = C \ln \frac{T_{cold}}{T_{hot}} = -C \ln \frac{T_{hot}}{T_{cold}}$$

For specific heat capacity of $4200 \text{ J K}^{-1} \text{ kg}^{-1}$, C (for 0.2 kg) = 840 J K^{-1}

$$\therefore \Delta S = -840 \ln \frac{363}{291} \text{ J K}^{-1} = -1857 \text{ J K}^{-1}$$

& heat leaving system gives decrease in entropy

#2) (a) $10 \text{ hp} = 10 \times 745.7 \frac{\text{J}}{\text{s}} = 7457 \frac{\text{J}}{\text{s}} \Rightarrow 7457 \left[\frac{\text{J}}{\text{s}} \right] 60 \frac{\text{s}}{\text{min}} = 7457 (60) \text{ J min}^{-1}$

$$\eta = \frac{W_{out}}{Q_h} = \frac{7457(60) \text{ J/min}}{10^6 \text{ J/min}} = 0.45 \Rightarrow 45\% \text{ efficient}$$

(b) $Q_h - Q_c = W_{out} \Rightarrow Q_c = Q_h - W_{out} = 10^6 - 7457(60) = 0.547 \times 10^6 \frac{\text{J}}{\text{min}}$

(c) If this was a Carnot reversible engine, we would have

$$\frac{T_c}{T_h} = \frac{Q_c}{Q_h} = \frac{0.547 \times 10^6}{1.0 \times 10^6} = 0.547 \text{ for Carnot efficiency}$$

and $\eta_c = 1 - \frac{T_c}{T_h} \geq \eta$

Less efficient for $\eta < \eta_c = 1 - \frac{T_c}{T_h}$ or $\frac{T_c}{T_h} > 0.547$ or $T_h < \frac{T_c}{0.547} = 536 \text{ K}$

\therefore for $T_c = 20^\circ C$ (293 K) $\Rightarrow T_h = \frac{T_c}{0.547} = \frac{293}{0.547} = 536 \text{ K}$ ($263^\circ C$)

Exam 3 solutions - cont

$$\#3(a) \quad G(T, p) = -Nk_B T \ln\left(\frac{aT^{5/2}}{p}\right) = U + pV - TS = -Nk_B T \ln\left[aT^{5/2}/p\right]$$

$$\Rightarrow dG = \cancel{TdS} - \cancel{p dV} + \cancel{p dV} + V dp - \cancel{T dS} - S dT = \boxed{-S dT + V dp = dG(T, p)}$$

$$(b) \quad dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \Rightarrow \boxed{S = -\left(\frac{\partial G}{\partial T}\right)_p \quad \& \quad V = \left(\frac{\partial G}{\partial p}\right)_T}$$

$$(c) \quad C_p = T \left(\frac{\partial S}{\partial T}\right)_p = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

$$\begin{aligned} &= -T \frac{\partial^2}{\partial T^2} \left[-Nk_B T \ln[aT^{5/2} p^{-1}] \right] \Big|_p = Nk_B T \frac{\partial^2}{\partial T^2} \left[T \ln a + \frac{5}{2} T \ln T - T \ln p \right] \Big|_p \\ &= Nk_B T \frac{\partial}{\partial T} \left[\ln a + \frac{5}{2} + \frac{5}{2} \ln T - \ln p \right] \Big|_p = \frac{5}{2} Nk_B = \frac{5}{2} R \quad (\text{ideal gas}) \end{aligned}$$

$$\begin{aligned} (d) \quad V &= \left(\frac{\partial G}{\partial p}\right)_T = \frac{\partial}{\partial p} \left[-Nk_B T \ln(aT^{5/2} p^{-1}) \right] \Big|_T = -Nk_B T \frac{\partial}{\partial p} \left[\ln a + \frac{5}{2} \ln T - \ln p \right] \Big|_T \\ &= Nk_B T / p \Rightarrow \boxed{pV = Nk_B T = RT} \quad \text{ideal gas} \end{aligned}$$

#4 Show $K_T - K_S = TV\beta_p^2 / C_p$ where $K_{T,S} = \frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{T,S}$, $\beta_p = (\partial V / \partial T)_p / V$
and $C_{V,p} = T(\partial S / \partial T)_{V,p}$

$$(a) \quad V(p, T) \Rightarrow dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \Rightarrow (b) \quad \boxed{\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S}$$

$$(c) \quad dG(T, p) = -S dT + V dp \Rightarrow -S = \left(\frac{\partial G}{\partial T}\right)_p \quad \& \quad V = \left(\frac{\partial G}{\partial p}\right)_T \Rightarrow \boxed{-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T}}$$

which is the needed Maxwell relation.

$$(d) \quad (b) \Rightarrow -K_S = -K_T + \beta_p \left(\frac{\partial T}{\partial p}\right)_S \Rightarrow K_T - K_S = \beta_p \left(\frac{\partial T}{\partial p}\right)_S$$

$$\text{but } \left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T = -(\partial S / \partial p)_T / (\partial S / \partial T)_p = -T(\partial S / \partial p)_T / C_p = T(\partial V / \partial T)_p / C_p \quad \text{by (c)}$$

$$\therefore K_T - K_S = \beta_p \left(\frac{\partial T}{\partial p}\right)_S = \frac{T \beta_p}{C_p} \left(\frac{\partial V}{\partial T}\right)_p = \frac{TV \beta_p^2}{C_p} \quad \dots \text{QED.}$$

$$(e) \quad \boxed{K_T - K_S \xrightarrow{\text{ideal}} TV \left(\frac{1}{T^2}\right) \frac{1}{\frac{5}{2} R} = \frac{2}{5} \frac{V}{RT} = \frac{2}{5p}} \quad \text{Agrees with } K_T = \frac{1}{p} \quad \& \quad K_S = \frac{1}{\gamma p} = \frac{3}{5p}$$