

## Summary for Exam 1

### Ideal Gas:

$pV = NkT = \nu RT$  and microscopic picture

### Equipartition Theorem:

$U_{\text{therm}} = N \frac{f}{2} kT$  (apply and determine  $f$ )

### 1st Law of Thermodynamics:

$\Delta U = Q + W$        $W = - \int p dV$

( $pV$  diagrams, adiabat, isotherm, straight lines)

### Heat Capacities and Enthalpy:

$C = \frac{Q}{\Delta T}$        $C_V = \left( \frac{\partial U}{\partial T} \right)_V$        $C_p = \left( \frac{\partial H}{\partial T} \right)_p$

$C = m c$

$H = U + pV$  (apply to reactions; if on exam, then table will be provided)

**Heat Conduction, Diffusion:** microscopic picture

### Multiplicities:

systems: 2-state, Einstein solid, ideal gas (& similar)

derive  $\Omega$ ,  $\Omega_{\text{tot}}$ , apply Stirling formula and  $\ln(1+x) \approx x$ , know EXCEL commands

**Entropy:**  $S = k \ln \Omega$

determine  $S$ ,  $\Delta S$

**2nd Law of Thermodynamics:** major concept

## Formulae for Exam #1

$$k = 1.381 \cdot 10^{-23} \text{ J/K} = 8.617 \cdot 10^{-5} \text{ eV/K}$$

$$h = 6.626 \cdot 10^{-34} \text{ Js} = 4.136 \cdot 10^{-15} \text{ eVs}$$

$$N_A = 6.022 \cdot 10^{23}$$

$$\Delta U = Q + W_{\text{on}} \quad \text{where} \quad W_{\text{on}} = - \int p dV$$

$$C = \frac{Q}{\Delta T}$$

$$pV = NkT \quad pV^\gamma = \text{const.}, \text{ where } \gamma = (f + 2)/f$$

$$U = \frac{f}{2} NkT \quad \frac{1}{2} kT \text{ for each quadratic degree of freedom}$$

$$H = U + pV$$

$$\Omega = \binom{q + N - 1}{q} \quad \Omega = \binom{N}{n} = \frac{N!}{n!(N-n)!}$$

$$\ln N! \approx N \ln N - N \quad \ln(1 + x) \approx x$$

$$S = k \ln \Omega$$

$$S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

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For an ideal gas you change

$$p \rightarrow 3p \quad N \rightarrow 4N \quad V \rightarrow 8V$$

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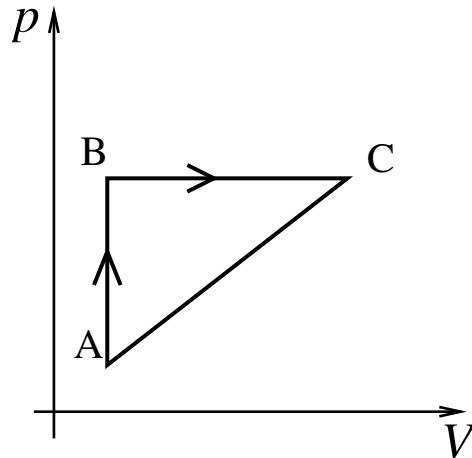
**Answer:**

$$pV = NkT \longrightarrow T = \frac{pV}{Nk}$$

$$T \rightarrow \frac{(3p)(8V)}{(4N)k} = 6\frac{pV}{Nk} = 6T$$

## Ideal Gas: (2 J)

An ideal diatomic gas is made to undergo the following process:

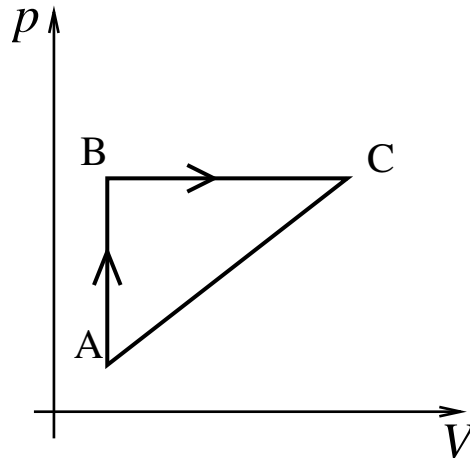


**Question:** For this process fill all empty entries in the following table with +, -, or 0 depending on the sign of each quantity.

	$W$	$Q$	$\Delta U$
$A \rightarrow B$			
$B \rightarrow C$			
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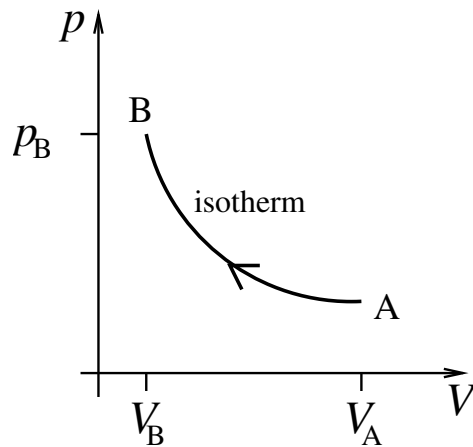
**Question:** For this process fill all empty entries in the following table with +, -, or 0 depending on the sign of each quantity.

**Answer:**

	$W$	$Q$	$\Delta U$
$A \rightarrow B$	0	+	+
$B \rightarrow C$	-	+	+
$A \rightarrow B \rightarrow C \rightarrow A$	-	+	0

## Ideal Gas: (3 J)

An ideal diatomic gas at very high temperature is compressed along an isotherm as sketched in the figure below.

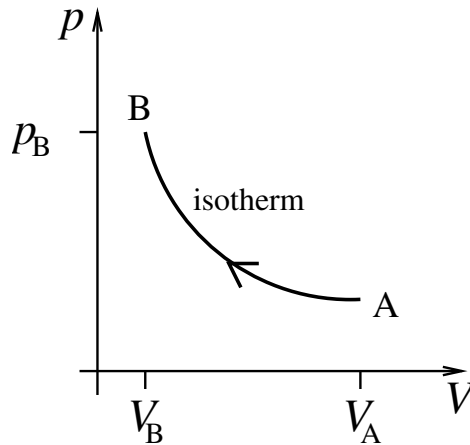


**Question:** For this process determine  $\Delta U$ ,  $Q$ , and  $W$ .

Express your results in terms of  $p_B$ ,  $V_A$ , and  $V_B$ .

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**Answer:**

$$W = - \int p dV = - \int \frac{NkT}{V} dV = -NkT \int \frac{1}{V} dV = -NkT \ln V \Big|_{V_A}^{V_B}$$

$$W = -p_B V_B \ln \left( \frac{V_B}{V_A} \right)$$

$$\Delta U = \frac{f}{2} Nk \Delta T = 0$$

$$\Delta U = Q + W \quad \longrightarrow \quad Q = -W = p_B V_B \ln \left( \frac{V_B}{V_A} \right)$$



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### Answer:

$$\Omega(q, N) = \binom{q + N - 1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \approx \frac{(q+N)!}{q!N!}$$

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### Question:

Approximate  $\Omega(q, N) = \frac{(q+N)!}{q!N!}$  assuming that both  $q$  and  $N$  are very large, and that  $q \gg N$  (that corresponds to large temperature. Do the derivation (even if you remember the result).

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### Answer:

$$\begin{aligned}\ln \Omega(q, N) &\approx (q + N) \ln(q + N) - \cancel{(q + N)} - q \ln q + \cancel{q} - N \ln N + \cancel{N} \\ &= (q + N) \ln(q + N) - q \ln q - N \ln N \\ &= (q + N) \ln \left( q \left( 1 + \frac{N}{q} \right) \right) - q \ln q - N \ln N \\ &= (q + N) \ln q + (q + N) \ln \left( 1 + \frac{N}{q} \right) - q \ln q - N \ln N \\ &\approx (q + N) \ln q + (q + N) \left( \frac{N}{q} \right) - q \ln q - N \ln N \\ &= q \ln q + N \ln q + N + \frac{N^2}{q} - q \ln q - N \ln N \\ &\approx \cancel{q \ln q} + N \ln q + N - \cancel{q \ln q} - N \ln N \\ &= N \ln \left( \frac{q}{N} \right) + N \\ \ln \Omega(q, N) &= \ln \left( \frac{q}{N} \right)^N + \ln (e^N)\end{aligned}$$

$$\Omega = e^{\ln \Omega} \approx \left( \frac{qe}{N} \right)^N$$

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For the Einstein solid with  $q, N \gg 1$  and the case  $q \ll N$  (low temperature) the multiplicity is approximately

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### Question:

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### Question:

Determine  $\Delta S$  if you keep  $q$  fixed but increase  $N$  to  $3N$ .

### Answer:

$$\begin{aligned} \Delta S &= S(q, 3N) - S(q, N) = k \ln \Omega(q, 3N) - k \ln \Omega(q, N) \\ &= kq \ln \left( \frac{3Ne}{q} \right) - kq \ln \left( \frac{Ne}{q} \right) \\ &= kq \ln \left( \frac{3Ne/q}{Ne/q} \right) = \boxed{kq \ln 3} \end{aligned}$$

## Equipartition Thm & Heat Capacity: (1 J)

### Question:

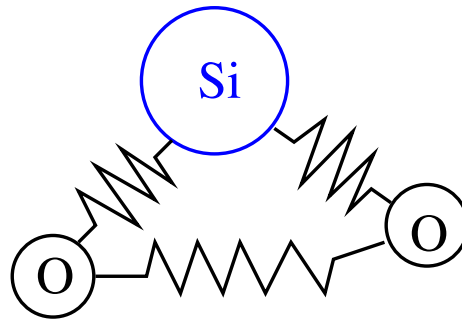
Determine the number of degrees of freedom for  $\text{SiO}_2$  at very high temperature.

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### Answer:



$f = 3$  translational + 3 rotational +  $3 \times 2$  vibrational

$$f = 12$$



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### Answer:

$$\begin{aligned} C_p &= \left( \frac{Q}{\Delta T} \right)_p \stackrel{\text{1st Law}}{=} \left( \frac{\Delta U - W}{\Delta T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p \\ &\stackrel{\text{diatom., high T}}{=} \frac{\partial}{\partial T} \left( N \frac{(3 + 2 + 2)}{2} kT \right)_p + p \frac{\partial}{\partial T} \left( \frac{NkT}{p} \right)_p \\ &= \frac{7}{2} Nk + Nk = \boxed{\frac{9}{2} Nk} \end{aligned}$$