Table I. **YOUR NAME:** Solution Turn in with your exam.

A. For $^{17}O_2$ Relative to $^{16}O_2$, Circle Below:

Internal Energy	Translation Part	- Higher Lower Differ Same
	Rotation Part	- Higher Lower Differ Same
	Vibrational Part	- Higher Lower Differ Same
	Total	- Higher Lower Differ Same
Heat Capacity	Translation Part	- Higher Lower Differ Same
	Rotation Part	- Higher Lower Differ Same
	Vibrational Part	- Higher Lower Differ Same
	Total	- Higher Lower Differ Same
Entropy	Translation Part	- Higher Lower Differ Same
	Rotation Part	- Higher Lower Differ Same
	Vibrational Part	- Higher Lower Differ Same
	Total	- Higher Lower Differ Same

B. For $^{16}O\text{-}^{18}O$ Relative to $^{17}O_2$, Circle Below:

Internal Energy	Translation Part	- Higher Lower Differ Same
	Rotation Part	- Higher Lower Differ Same
	Vibrational Part	- Higher Lower Differ Same
	Total	- Higher Lower Differ Same
Heat Capacity	Translation Part	- Higher Lower Differ Same
	Rotation Part	- Higher Lower Differ Same
	Vibrational Part	- Higher Lower Differ Same
	Total	- Higher Lower Differ Same
Entropy	Translation Part	- Higher Lower Differ Same
	Rotation Part	- Higher Lower Differ Same
	Vibrational Part	- Higher Lower Differ Same
	Total	- Higher Lower Differ Same

vib. part of $u \rightarrow \omega\downarrow$, $\frac{h\nu}{kT}\downarrow$ but $\frac{h\nu/kT}{e^{h\nu/kT}-1}\uparrow$, but $\frac{h\nu/kT}{e^{h\nu/kT}-1}$ is much smaller than $\frac{h\nu}{2kT}$

vib. part of $S \rightarrow \omega\downarrow$, $\frac{h\nu}{kT}\downarrow$ but $\frac{h\nu/kT}{e^{h\nu/kT}-1}\uparrow$; $\ln(1-e^{-h\nu/kT})$ is 1 order of magnitude smaller than other part

I. c

Take the vibrational difference to be very small since very few molecules are above the ground state and the frequencies should be very similar ~~an~~ any way.

then for $^{16}O\text{-}^{18}O$:

$$\frac{S}{Nk} = S_T + \ln \frac{8\pi^2 I k T e}{h^2}$$

$$+ S_{VIB} + S_{ELEC}$$

for $^{17}O_2$:

$$\frac{S}{Nk} = S_T + \ln \frac{8\pi^2 I k T e}{2h^2} + S_{VIB} + S_e$$

$$\frac{\left(S_{^{16}O\text{-}^{18}O} - S_{^{17}O_2}\right)}{Nk} = \ln \frac{8\pi^2 I k T e}{h^2} - \ln \frac{8\pi^2 I k T e}{2h^2}$$

$$= \cancel{\ln \frac{8\pi^2 I k T e}{h^2}} - \ln \frac{8\pi^2 I k T e}{h^2} = \ln\left(\frac{1}{2}\right)$$

$$\boxed{\frac{\Delta S}{Nk} = \ln 2}$$

$$\boxed{\Delta S = Nk \ln 2}$$

a small correction could be made for ΔI

II.

$\bar{h}_1 = a_1 + b_1 x_2^2$

$\bar{h}_2 = a_2 \; b_2 x_1^2$

A. Use Gibbs-Duhem:

$x_1 d\bar{h}_1 + x_2 d\bar{h}_2 = 0$

$d\bar{h}_1 = \cancel{da_1}^{0} + b_1 2x_2 dx_2$

$d\bar{h}_2 = \cancel{da_2}^{0} + b_2 2x_1 dx_1$

$x_1(\cancel{2}b_1 x_2 dx_2) + x_2(b_2 x_1 \cancel{2} \cancel{dx_1}) = 0$

$dx_1 = -dx_2$

$b_1 x_1 x_2 - b_2 x_1 x_2 = 0$

or $\boxed{b_1 = b_2}$

B.

for $x_1 \to 0$ & $x_2 \to 0$

$\bar{h}_1 \to h_1^0$ $\qquad \bar{h}_2 \to h_2^0$

$a_1 = h_1^0$

$a_2 = h_2^0$

C.

$\Delta h^{MIX} = \sum x_i \bar{h}_i - \sum x_i h_i^0$

$= \cancel{(x_1 h_1^0 + x_2 h_2^0)} + b x_1 x_2^2 + b x_2 x_1^2 \cancel{- x_1 h_1^0 - x_2 h_2^0}$

$= b x_1 x_2 (x_1 + x_2)$

$$\boxed{\Delta h^{MIX} = b x_1 x_2}$$

III.

$$f^L = \phi^{SAT} P^{SAT} (P.C.)$$

at 100°C, $P^{SAT} =$ ~~[illegible]~~ 2.90 atm

Use Pitzer for ϕ^{SAT}

$$\ln\phi = \frac{P_r}{T_r}\left(B^0 + \omega B^1\right)$$

$$\ln\phi = \frac{(2.9\text{ atm}/54\text{ atm})}{(373.16/536.6)}\left(-0.672 + 0.216(-.652)\right)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.672$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.652$$

$$\ln\phi = -0.0628$$

$$\phi = 0.939$$

$$f^L = (0.939)(2.9\text{ atm})\left(\exp\left(\frac{\bar{V}_L(100-2.9)}{RT}\right)\right)$$

$$\bar{V}_L = \frac{1\text{ cm}^3}{1.4\text{ gr}} \times \frac{119.4\text{ gr}}{\text{mole}} \times \frac{1\text{ lt}}{1000\text{ cm}^3} =$$

$$\bar{V}_L = 0.0853\ \text{lt/mole}$$

$$f^L = (0.939)(2.9\text{ atm})\exp\left(\frac{0.0853\ \text{lt/mole}\ (97.1\text{ atm})}{0.08205\ \frac{\text{lt-atm}}{\text{mole K}}\ 373.16\text{K}}\right)$$

$$f^L = (0.939)(2.9)(\underbrace{1.31}_{P.C.})$$

$$\boxed{f^L = \cancel{[illegible]}\ 3.567\text{ atm}}$$