Note: My answer for part c) isn't necessarily correctly done (correct answer though)
  For an isolated system, (it will still be approx. distributed as Boltzmann factor), entropy is maximized
  For a system in contact with a heat reservoir: Boltzmann distributed, but total entropy is maximized
  · for just the system of interest, $F = E - TS$ is minimized
                            (for chemical reaction equilibrium, these aren't the same)

Jan 2003 #2 (SM)

a. 2 Krypton atoms

$$Z_2 = \sum_r e^{-\beta E_r} \longrightarrow \int \frac{d^3\vec{r}_1 \, d^3\vec{p}_1}{h_o^3} \frac{d^3\vec{r}_2 \, d^3\vec{p}_2}{h_o^3} \cdot e^{-\beta E}$$

note: Partition function doesn't seem like a good approach to just 2 atoms, as there is no heat reservoir, and we can't use a mean energy E or temperature T to approximate it well

$$E = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(\vec{r}_1 - \vec{r}_2)$$

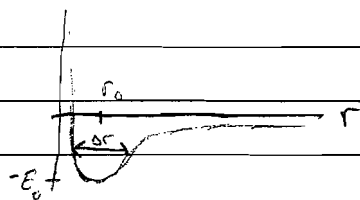$$U(\vec{r}_1 - \vec{r}_2) = U(r_1 - r_2)$$

ideal case: $U = 0$

$$Z_2^{id} = \frac{1}{h_o^6} \int d^3\vec{r}_1 \, d^3\vec{r}_2 \int d^3\vec{p}_1 \, d^3\vec{p}_2 \; e^{-\beta p_1^2/2m} e^{-\beta p_2^2/2m}$$

$$Z_2^{id} = \frac{V^2}{h_o^6} \int d^3\vec{p}_1 \, d^3\vec{p}_2 \; e^{-\frac{\beta}{2m}(p_1^2 + p_2^2)}$$

$$Z_2 = \frac{1}{V^2} \cdot \frac{V^2}{h_o^6} \int d^3\vec{p}_1 \, d^3\vec{p}_2 \; e^{-\frac{\beta}{2m}(p_1^2 + p_2^2)} \int d^3\vec{r}_1 \, d^3\vec{r}_2 \; e^{-\beta U}$$

$$Z_2 = Z_2^{id} \cdot \frac{1}{V^2} \int e^{-\beta U} d^3\vec{r}_1 \, d^3\vec{r}_2$$

$U(r) = U(r_1 - r_2)$:

U is 0 except in a small region around U_o

$\rightarrow e^{-\beta U}$ is 1 except in a small region around r_o, and as $r \to 0$, U gets very large, so $e^{-\beta U}$ gets very small, and this contributes negligibly to the integral. The small region Δr around r_o is small compared to the volume,

so $$\int e^{-\beta U} d^3\vec{r}_1 \, d^3\vec{r}_2 \approx V^2 + \int_{\substack{\text{around} \\ r = r_o}} e^{-\beta U} d^3\vec{r}_1 \, d^3\vec{r}_2$$

$$\int_{\text{around } r_o} e^{-\beta U(r_1 - r_2)} d^3\vec{r}_1 \, d^3\vec{r}_2 \qquad \text{Change variables from } (\vec{r}_1, \vec{r}_2) \to (\vec{r}_1 - \vec{r}_2, \vec{r}_2)$$

$$|J| = 1$$

$$= V \cdot \int_{\substack{\text{around} \\ r = r_0}} d^3(\vec{r}_1 - \vec{r}_2) \; e^{-\beta U(r_1 - r_2)} \qquad \text{let } r = r_1 - r_2$$

$$= 4\pi V \int_{\substack{\text{around} \\ r = r_0}} d^3 r \; r^2 \; e^{-\beta U(r)}$$

approximate $\int_{\substack{\text{around} \\ r = r_0}} d^3 r \; r^2 e^{-\beta U(r)}$ as constant over the width Δr

$$\to \sim \quad 4\pi V \, r_0^2 \, e^{-\beta(-E_0)} \cdot \Delta r$$

$$Z_2 = \frac{1}{V^2} Z_2^{id} \cdot \left[V^2 + 4\pi V r_0^2 \Delta r \; e^{\beta E_0} \right]$$

$$= \left(1 + \frac{4\pi r_0^2 \Delta r \, e^{\beta E_0}}{V} \right) Z_2^{id} \quad \Rightarrow \quad Z_2 = \left(1 + \frac{K}{V} \right) Z_2^{id}$$

$$K \cong \quad 4\pi r_0^2 \Delta r \, e^{\beta E_0}$$

proportional to the probability $\left(e^{\beta E_0} \right)$ that two atoms
form a molecule.

b. N Kr atoms· M molecules, $N \neq 2M$ free atoms
(The statement of this problem is different then n part a   There, we didn't
assume that the two atoms were or weren't in a molecule. Here, we
assume that $2M$ of the atoms do form molecules, so the sum
for the partition function is different.)

$$Z = \int \frac{d^3 \vec{r}_1 \cdots d^3 \vec{r}_N \cdot d^3 \vec{p}_1 \cdots d^3 \vec{p}_N}{h_0^{3N}} e^{-\beta U} e^{-\beta_{2m}(p_1^2 + \cdots + p_N^2)}$$

$= d(M,N)$ the # of ways to make M molecules from N atoms,
multiplied by a particular choice:

$$= d(M,N) \cdot \frac{1}{V^N} \cdot Z_N^{id} \cdot \int d^3 \vec{r}_1 \cdots d^3 \vec{r}_N \; e^{-\beta U}$$

choice: 1,2 interacting, $3 \leftrightarrow 4, \ldots \; 2M-1 \leftrightarrow 2M$
the rest of the atoms are free

$$Z = d(M,N) \cdot \frac{1}{V^N} Z_N^{id} \cdot V^{N-2M} \int d^3\vec{r}_1 \cdots d^3\vec{r}_{2m} \; e^{-\beta U}$$

assume each of the M molecules interacts pairwise only;

e.g. the integral splits up into M pieces, each equal

$$\int d^3\vec{r}_1 \, d^3\vec{r}_2 \; e^{-\beta U(\vec{r}_1 - \vec{r}_2)} = KV$$

(In part a, the integral came to $V^2 + KV$, but the V^2 part came from the possibility of the atoms not forming molecules, which we are disregarding here.

M such integrals $\rightarrow (KV)^M$

$$Z_{N,M} = d(M,N) \left(\frac{K}{V}\right)^M Z_N^{id} \qquad \left(Z_N^{id} = \frac{Z_1^N}{N!}\right)$$

$d(M,N)$: choose M groups of 2 atoms, but in each of the M molecules or groups, the order doesn't matter, and also the order of the molecules doesn't matter.

$$\underbrace{\binom{N}{2}}_{\text{first molecule}} \cdot \underbrace{\binom{N-2}{2}}_{2^{nd}} \cdot \binom{N-4}{2} \cdots \underbrace{\binom{N+2-2M}{2}}_{M\text{-th molecule}} \cdot \underbrace{\frac{1}{M!}}_{\substack{\text{order of molecules} \\ \text{doesn't matter}}}$$

$$= \frac{1}{M!} \cdot \frac{N!}{2(N-2)!} \cdot \frac{(N-2)!}{2(N-4)!} \cdot \frac{(N-4)!}{2(N-6)!} \cdots \frac{(N+2-2M)!}{2 \cdot (N-2M)!}$$

$$= \frac{1}{M!} \frac{N!}{2^M (N-2M)!}$$

c. $C_{Kr_2} = K \left[C_{Kr} \right]^2$ equilibrium condition

in equilibrium, the entropy is maximized

$$\frac{S}{K} = \ln Z + \beta \bar{E} \qquad \bar{E} = -\frac{\partial}{\partial \beta} \ln Z$$

$$\ln Z = \ln d + M \ln \frac{K}{V} + \ln Z_N^{id}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \ln Z_N^{id} = \bar{E}_N^{id} \qquad (\text{doesn't depend on } M)$$

maximize S wrt. M, the number of molecules:

$$\frac{\partial (S/k)}{\partial M} = \frac{\partial}{\partial M} \ln d + \ln \frac{K}{V} = 0$$

$$\ln d = \ln N! - \ln M! - M\ln 2 - \ln(N-2M)!$$
$$\approx \ln N! - M\ln M + M - M\ln 2 - (N-2M)\ln(N-2M) + (N-2M)$$

$$\frac{d\ln d}{dM} = -\ln M - \ln 2 + 2\ln(N-2M)$$

$$\ln \frac{K}{V} = \ln M + \ln 2 - \ln(N-2M)^2$$

$$\frac{K}{V} = \frac{2M}{(N-2M)^2}$$

$$2M = \frac{K(N-2M)^2}{V}$$

$$\frac{2M}{V} = \frac{K(N-2M)^2}{V^2}$$

$$\frac{2M}{V} \sim \text{concentration/density of } Kr_2 ?$$
$$(\text{shouldn't it be } \frac{M}{V}?)$$

$$\frac{(N-2M)^2}{V^2} \sim \text{concentration/density of } Kr$$

$$(12)\quad C_{Kr_2} = K[C_{kr}]^2$$

$$2C_{Kr_2} = K[C_{kr}]^2$$