

7.6

Since the total energy is additive,

$$E_i = \epsilon_i(p_i) + U(q_1, \dots, q_n) = \frac{p_i^2}{2m} + U(q_1, \dots, q_n)$$

Where  $U$  is the energy of interaction, the equipartition theorem still applies and

$$\bar{\epsilon} = \frac{3}{2}kT$$

7.7

If the gas is ideal, its mean energy per particle is  $\bar{\epsilon} = \frac{\overline{p_x^2}}{2m} + \frac{\overline{p_y^2}}{2m} = kT$   
and the mean energy per mole becomes  $\bar{E} = NAKT$

$$\text{Thus } C = \frac{\partial \bar{E}}{\partial T} = NAK = R$$

7.10

(a) Let the restoring force be  $-\alpha x$ . Then the mean energy of  $N$  particles is

$$\bar{E} = N \left( \frac{1}{2}m\bar{x^2} + \frac{1}{2}\alpha\bar{x^2} \right)$$

By equipartition  $\bar{E} = N \left( \frac{1}{2}kT + \frac{1}{2}kT \right) = NkT$

$$\text{Thus } C = \frac{\partial \bar{E}}{\partial T} = NK$$

(b) If the restoring force is  $-\alpha x^3$ , the mean energy per particle is

$$\bar{\epsilon} = \frac{1}{2}m\bar{x^2} + \frac{1}{4}\alpha\bar{x^4}$$

The kinetic energy term contributes  $\frac{1}{2}kT$  by equipartition. The mean of the potential energy is found from

$$\begin{aligned} \frac{\overline{\alpha x^4}}{4} &= \frac{\int_{-\infty}^{\infty} \exp\left[-\frac{\beta\alpha x^4}{4}\right] \frac{\alpha x^4}{4} dx}{\int_{-\infty}^{\infty} \exp\left[-\frac{\beta\alpha x^4}{4}\right] dx} \\ &= -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} e^{-\beta(\alpha x^4/4)} dx = -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} e^{-\alpha y^{4/4}/\beta} dy^{-1/4} \end{aligned}$$

where we have made the substitution,  $y = \beta^{1/4}x$ .

$$\text{Thus } \frac{\overline{\alpha x^4}}{4} = -\frac{\partial}{\partial \beta} \left( -\frac{1}{4} \ln \beta + \ln \int_{-\infty}^{\infty} e^{-\alpha y^{4/4}/\beta} dy \right) = \frac{1}{4\beta} = \frac{1}{4}kT$$

$$\text{Hence } \bar{\epsilon} = \frac{1}{2}m\bar{x^2} + \frac{1}{4}\alpha\bar{x^4} = \frac{1}{2}kT + \frac{1}{4}kT = \frac{3}{4}kT$$

$$\text{Then the total energy is } \bar{E} = N\bar{\epsilon} \text{ and } C = \frac{\partial \bar{E}}{\partial T} = \frac{3}{4}NK$$

8.2

(a) For the solid,  $\ln P = 23.03 - \frac{3754}{T}$  and for the liquid  $\ln P = 19.49 - \frac{3063}{T}$ . At the triple point, the pressures of the solid and liquid are equal.

$$23.03 - \frac{3754}{T} = 19.49 - \frac{3063}{T}$$

hence  $T = \frac{691}{3.54} = 195\text{ K}$

(b) Since  $\ln P = -\frac{\ell}{RT} + \text{constant}$  where  $\ell$  is the latent heat, we have

$$\ell_{\text{sublimation}} = 3754 R = 31220 \text{ joules/mole}$$

$$\ell_{\text{vaporization}} = 3063 R = 25480 \text{ joules/mole}$$

(c)  $\ell_{\text{melting}} = \ell_{\text{sublimation}} - \ell_{\text{vaporization}}$

$$= 31220 - 25480 = 5740 \text{ joules/mole}$$