Introductory Chemical Engineering Thermodynamics

CHAPTER 6

(6.01) CO2 has two significant…

CO_2 has two significant vibrations at ε/k=952K that represent the axial stretches of both bonds. Other vibrations exist but at higherT.

(a) Plot Cv/R vs T for CO_2 in the range 200-400K. Include the polynomial as a dashed line and the NIST data as points. (b) What fraction of the IR spectrum does 903cm^{-1} comprise?(c) If absorption efficiency is proportional to concentration, what fraction of IR energy could be absorbed in this case.

Solution : a. For a linear ideal gas molecule, we must include the degrees of freedom for translation.(cf. HW4.1) Including only the given vibration (ignoring higher temperature vibrations), and adapting Eqn. 6.50,

Cv/R = 3/2(translation) + 2/2 (rotation about linear axis doesn't count) +
+2(2symmetric bonds)*(βε)2*exp(-βε)/[exp(-βε)-1]2 +...(higher vibs)
= 2.5 +2*(βε)2*exp(-βε)/[exp(-βε)-1]2 ~off by ignoring higher vibs.

T(K)	220	230	240	250	260	270	280	290	300	310
Cv/R(nist)	3.07	3.11	3.17	3.22	3.27	3.33	3.38	3.44	3.49	3.54
beps	4.33	4.14	3.97	3.81	3.66	3.53	3.40	3.28	3.17	3.07
Cv/R(calc)	3.01	3.06	3.12	3.17	3.23	3.28	3.33	3.37	3.42	3.46
Cv/Rpoly	3.02	3.08	3.14	3.20	3.26	3.32	3.37	3.43	3.48	3.53

T(K)	320	330	340	350	360	370	380	390	400
Cv/R(nist)	3.59	3.65	3.70	3.74	3.79	3.84	3.89	3.93	3.98
beps	2.98	2.88	2.80	2.72	2.64	2.57	2.51	2.44	2.38
Cv/R(calc)	3.50	3.54	3.58	3.62	3.65	3.68	3.72	3.75	3.77
Cv/Rpoly	3.59	3.64	3.69	3.74	3.78	3.83	3.88	3.92	3.97

b. IR runs from 12800-10cm^{-1}, so 903 represents 1/12799=0.008% of IR range.

c. 380ppm = 380/1E6 => 8E-9% of IR could be absorbed by CO_2.

d. It is not unreasonable to ask questions about global warming by CO_2.

(6.02) Express in terms of P, V, T, C_P, C_V, and their derivatives. Your answer may include absolute values of S if it is not associated with a derivative.

a. $(\partial G/\partial P)_T = (\partial H/\partial P)_T - T(\partial S/\partial P)_T = [V - T(\partial V/\partial T)_P] + T(\partial V/\partial T)_P = V$ or using expansion rule:
$(\partial G/\partial P)_T = -S(\partial T/\partial P)_T + V(\partial P/\partial P)_T = V$ (6.7)

b. $(\partial A/\partial P)_V = -S(\partial T/\partial P)_V - P(\partial V/\partial P)_V = -S(\partial T/\partial P)_V \Rightarrow (\partial P/\partial A)_V = -(\partial P/\partial T)_V/S$

c. $(\partial T/\partial P)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$ (6.37)

or, by triple product rule: $\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$

d. $H = U + PV \Rightarrow \left(\frac{\partial H}{\partial T}\right)_U = \left(\frac{\partial U}{\partial T}\right)_U + V\left(\frac{\partial P}{\partial T}\right)_U + P\left(\frac{\partial V}{\partial T}\right)_U = V\left(\frac{\partial P}{\partial T}\right)_U + \frac{-PCv}{\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]}$

$(\partial P/\partial T)_U = -(\partial U/\partial T)_P/(\partial U/\partial P)_T$ TPR

$(\partial U/\partial T)_P = C_V(\partial T/\partial T)_P + [T(\partial P/\partial T)_V - P](\partial V/\partial T)_P$ (6.41)

$(\partial U/\partial P)_T = C_V(\partial T/\partial P)_T + [T(\partial P/\partial T)_V - P](\partial V/\partial P)_T$ (6.41)

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_U = -\frac{C_V + [T(\partial P/\partial T)_V - P](\partial V/\partial T)_P}{[T(\partial P/\partial T)_V - P](\partial V/\partial P)_T}$$

$$\left(\frac{\partial H}{\partial T}\right)_U = -V\left(\frac{C_V + [T(\partial P/\partial T)_V - P](\partial V/\partial T)_P}{[T(\partial P/\partial T)_V - P](\partial V/\partial P)_T}\right) + \frac{-PCv}{\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]}$$

alt: starting with H(T,P), then applying the expansion

rule: $\left(\frac{\partial H}{\partial T}\right)_U = C_P\left(\frac{\partial T}{\partial T}\right)_U + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]\left(\frac{\partial P}{\partial T}\right)_U$ (6.40)

Insert for $(\partial P/\partial T)_U$ as determined above:

$$\Rightarrow \left(\frac{\partial H}{\partial T}\right)_U = C_P - \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]\left\{\frac{C_V + [T(\partial P/\partial T)_V - P](\partial V/\partial T)_P}{[T(\partial P/\partial T)_V - P](\partial V/\partial P)_T}\right\}$$

Note the relation between Cp and Cv can be inserted for answers that look different.

Note another expression for the last term on the first line:

$$\frac{PC_V}{T(\partial P/\partial T)_V - P} = \frac{P\left(C_P - T(\partial P/\partial T)_V(\partial V/\partial T)_P\right)}{T(\partial P/\partial T)_V - P}$$

e. $(\partial H/\partial T)_S = T(\partial S/\partial T)_S + V(\partial P/\partial T)_S = -V(\partial S/\partial T)_P(\partial P/\partial S)_T = V\frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$;

$(\partial H/\partial T)_S = \frac{T}{VC_P}\left(\frac{\partial V}{\partial T}\right)_P$ using (6.5 + 6.37), $(\partial T/\partial H)_S = \frac{T}{VC_P}\left(\frac{\partial V}{\partial T}\right)_P$

f. expansion rule $(\partial A/\partial V)_P = -S(\partial T/\partial V)_P - P(\partial V/\partial V)_P = -S(\partial T/\partial V)_P - P$ (6.6)

g. $(\partial T/\partial P)_H = -\frac{1}{Cp}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$ (cf. eqn. 6.40)

or by triple product rule, $\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$

h. $(\partial A/\partial S)_P = -S(\partial T/\partial S)_P - P(\partial V/\partial S)_P = -ST/C_P - P(\partial V/\partial S)_P$ (6.6 + 6.37)

$(\partial V/\partial S)_P = T/C_P\ (\partial V/\partial T)_P$ (6.39)

$(\partial A/\partial S)_P = -T[S + P(\partial V/\partial T)_P]/C_P$

c. $(\partial S/\partial P)_G = -(\partial G/\partial P)_S/(\partial G/\partial S)_P$ TPR

expansion rule $(\partial G/\partial P)_S = -S(\partial T/\partial P)_S + V(\partial P/\partial P)_S =$ (6.7)

$$(\partial T/\partial P)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P \quad (6.37)$$

expansion rule $(\partial G/\partial S)_P = -S(\partial T/\partial S)_P + V(\partial P/\partial S)_P = -ST/C_P$ (6.7 + 6.37)

$(\partial S/\partial P)_G = -[-S(\partial T/\partial P)_S + V]/[-ST/C_P] = C_P[-S(\partial T/\partial P)_S + V]/[ST]$

$$= \frac{C_P\left[\frac{-ST}{C_P}\left(\frac{\partial V}{\partial T}\right)_P + V\right]}{ST} = \frac{VC_P}{ST} - \left(\frac{\partial V}{\partial T}\right)_P$$

(6.03) Derive in terms of *U,H,S,G,S,P,V,T* and their derivatives.

$$\left(\frac{\partial\left(G/RT\right)}{\partial T}\right)_P = \frac{1}{RT}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{RT^2} = \frac{-S}{RT} - \left(\frac{H}{RT^2} - \frac{S}{RT}\right) = \frac{-S}{RT} + \frac{S}{RT} - \frac{H}{RT^2} = -\frac{H}{RT^2}$$

FYI: We can rearrange these as:

$\beta \equiv 1/RT \Rightarrow d\beta/dT = -1/RT^2 = -\beta/T \Rightarrow d\beta/\beta = -dT/T.$

$$T\left(\frac{\partial\left(A/RT\right)}{\partial T}\right)_V = -\frac{U}{RT} = -\beta\left(\frac{\partial(\beta A)}{\partial \beta}\right)_V \Rightarrow A/RT = \int \frac{U}{RT}\frac{d\beta}{\beta}$$

$$T\left(\frac{\partial\left(G/RT\right)}{\partial T}\right)_P = -\frac{H}{RT} = -\beta\left(\frac{\partial(\beta G)}{\partial \beta}\right)_P$$

Thus transformations between U and A are quick (and common).

(6.04) Derive $(dH/dP)_T$ and $(dU/dP)_T$ in terms of measurable properties…

a. Starting with U, H and applying expansion rule.

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

b. Taking difference of result of part a.

$$\left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial U}{\partial P}\right)_T = V + P\left(\frac{\partial V}{\partial P}\right)_T$$

Applying Expansion Rule

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V$$

The desired difference is the same.

(6.05) In Chapter 2, internal energy of condensed phases….

a. Starting with U, H and applying expansion rule.

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T = -TV\alpha_P + PV\kappa_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -TV\alpha_P + V$$

P =	0.1	MPa			
T =	293	K			
Liquid	MW	rho	1E3 alpha	1E6*kappa	V
		(g/cm3)	(K^{-1})	(bar-1)	(cm3/mol)
Acetone	58.08	0.7899	1.487	111	73.528295
Ethanol	46.07	0.7893	1.12	100	58.368174
Benzene	78.12	0.87865	1.237	89	88.909122
Carbon disulfide	76.14	1.258	1.218	86	60.524642
Chloroform	119.38	1.4832	1.273	83	80.488134
Ethyl ether	74.12	0.7138	1.656	188	103.83861
Mercury	200.6	13.5939	0.18186	3.95	14.756619
Water	18.02	0.998	0.207	49	18.056112
Note: Since J is given by (cm3MPa/mol), then (cm3/mol) is J/MPa					

Liquid	-T(dV/dT)P	-P(dV/dP)T	(dU/dP)T	(dH/dP)T
	(cm3/mol)	(cm3/mol)	J/MPa	J/MPa
Acetone	-32.0356	0.081616	-31.954	41.49268
Ethanol	-19.1541	0.058368	-19.0957	39.21407
Benzene	-32.2243	0.079129	-32.1452	56.68481
Carbon disulfide	-21.5997	0.052051	-21.5476	38.92497
Chloroform	-30.0212	0.066805	-29.9544	50.46695
Ethyl ether	-50.3833	0.195217	-50.1881	53.45529
Mercury	-0.78631	0.000583	-0.78572	13.97031
Water	-1.09512	0.008847	-1.08627	16.96099

The derivatives are larger for organics than for mercury and water. Molar volume is the largest contribution to $(dH/dP)_T$, especially for water and mercury. The coefficient of thermal expansion is most important in determining $(dU/dP)_T$.

(6.06) Express $(dH/dV)_T$ in terms of …

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T \qquad \text{where } \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha_P}{\kappa_T}$$

$$= \frac{\alpha_P T - 1}{\kappa_T}$$

(6.07) Express the adiabatic compressibility…

First use triple product rule

$$k_S = \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_V$$

now interpose temperature using chain rule, because temperature derivatives of S are heat capacities.

$$k_S = \frac{1}{V}\left[\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P\right]\left[\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V\right]$$

$$= \frac{1}{V}\frac{C_V}{C_P}\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V$$

Now, using triple product rule on last two derivatives

$$k_S = -\frac{1}{V}\frac{C_V}{C_P}\left(\frac{\partial V}{\partial P}\right)_T = \frac{C_V}{C_P}k_T$$

(6.08) Express the Joule-Thomson coefficient in terms of measurable ...

(a) Van der Waals equation given in Example 6.6

(b) An ideal gas.

$(\partial T/\partial P)_H = \dfrac{-1}{C_P}\left[V - T\left(\dfrac{\partial V}{\partial T}\right)_P\right]$ (6.40)

a. $P = RT/(V-b) - a/V^2$. => $P(V-b) = RT - a(V-b)/V^2$. Differentiating implicitly,

$P(\partial V/\partial T)_P = -a(\partial V/\partial T)_P[1/V^2 - 2(V-b)/V^3]$

$=>(\partial V/\partial T)_P = 1/(P+a[1/V^2 - 2(V-b)/V^3]) = V^3/[PV^3+aV-2a(V-b)]$

Alt. $PV^2 = RTV^2/(V-b) - a => 2PV(\partial V/\partial T)_P = (\partial V/\partial T)_P[RT2V/(V-b) + RTV^2/(V-b)^2]$.

$(\partial V/\partial T)_P = 1/[2PV-2RTV/(V-b) - RTV^2/(V-b)^2]=(V-b)^2/[2P(V-b)^2-2RTV(V-b)-RTV^2)]$

b. $PV = RT => (\partial V/\partial T)_P = RT/P = V =>(\partial T/\partial P)_H = 0$.

(6.09) Prove $(\partial P/\partial T)_S$ = …

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{TV\left(\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right)}$$

a)

$$= \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$$

Rearranging:

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

By Maxwell

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

plugging back in,

$$-\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial S}{\partial P}\right)_T=\left(\frac{\partial S}{\partial T}\right)_P$$

This is just triple product rule, proof complete.

b) $\frac{P}{P^i}=\left(\frac{T}{T^i}\right)^{\frac{C_P}{R}}$

$$\left(\frac{\partial P}{\partial T}\right)_S=P^i\left(\frac{1}{T^i}\right)^{\frac{C_P}{R}}\frac{C_P}{R}T^{\left(\frac{C_P}{R}-1\right)}=\frac{C_PP^iT^{\frac{C_V}{R}}}{R\left(T^i\right)^{\frac{C_P}{R}}}$$

note: $\frac{P}{P^i}=\left(\frac{T}{T^i}\right)^{\frac{C_P}{R}}\Rightarrow\frac{P^i}{(T^i)^{C_P/R}}=\frac{P}{T^{C_P/R}}$

$$\left(\frac{\partial P}{\partial T}\right)_S=\frac{C_PP}{RT^{(C_P-C_V)/R}}=\frac{C_PP}{RT}$$

Now, compare with result from part (a).

$$\left(\frac{\partial P}{\partial T}\right)_S=\frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P;\qquad V=\frac{RT}{P}$$

$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{P}$; plugging in results into part (a)

$$\left(\frac{\partial P}{\partial T}\right)_S=\frac{C_P}{TV\left(\frac{1}{V}\frac{R}{P}\right)}=\frac{C_PP}{RT}$$

Results agree.

Note: there are many ways to do a proof that also might be correct.

(6.10) Determine the difference….

Liquid	MW	rho	1E3 alpha	1E6* kappa	V	Cp-Cv
		(g/cm3)	(K^{-1})	(bar^{-1})	(cm^3/mol)	J/mol-K
Acetone	58.08	0.7899	1.487	111	73.53	42.9
Ethanol	46.07	0.7893	1.12	100	58.37	21.45
Benzene	78.12	0.8787	1.237	89	88.91	44.79
Carbon disulfide	76.14	1.258	1.218	86	60.52	30.59
Chloroform	119.38	1.4832	1.273	83	80.49	46.04
Ethyl ether	74.12	0.7138	1.656	188	103.84	44.38
Mercury	200.6	13.594	0.1819	3.95	14.76	3.62
Water	18.02	0.998	0.207	49	18.06	0.46

Liquid	A	B	C	T	Cp
					J/mol-K
Acetone					
Ethanol	33.866	-1.73E-01	3.49E-04	293	110.3276

Benzene	-0.747	6.80E-02	-3.78E-05	293	132.3747
Carbon disulfide					
Chloroform	19.215	-4.29E-02	8.30E-05	293	114.5217
Ethyl ether					
Mercury					
Water	8.712	1.25E-03	1.08E-07	293	75.55366

(6.11) A rigid container is filled with liquid acetone…

a) $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{1.478\times10^{-3}}{111\times10^{-6}} =$ 13.4 bar/°C

100 bar / (13.4 bar/°C) = 7.5 °C

b) $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$

$C_V = C_P + T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 = C_P - TV\frac{\alpha_P^2}{k_T}$

$= 125 - (293)(73.5)\frac{(1.487\times10^{-3})^2}{111\times10^{-6}}$ (J/(10 bar cm³)) = 82 J/mol K

$\Delta U = \int C_V dT =$ (82)(7.5) = 615 J/mol

Liquid is incompressible,

$\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P = 615 + \frac{73.5(100)}{10} =$ 1350 J/mol

Alternatively

$\Delta H = \int\left(\frac{\partial H}{\partial T}\right)_V dT$

Expansion Rule:

$\left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_T$

$= C_V - V\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = C_V + V\frac{\alpha_P}{k_T}$

= 82 + (73.5 cm³)(1.487×10⁻³ bar)/(111×10⁻⁶)/(10 cm³ bar/J) = 180 J/mol K

$\Delta H = \int 180 dT =$ 180(7.5) = 1350 J/mol

$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V dT = C_V \ln\frac{T_2}{T_1} = 82\ln\frac{300.5}{293} =$ 2.07 J/mol K

Note: These answers are different from those obtained by constant pressure heating where $\Delta U \approx \Delta H$.

c) $\Delta U = Q =$ 615 J/mol

(6.12) The fundamental internal energy relation for a rubber band is...

(a) we seek $\left(\frac{\partial T}{\partial L}\right)_S$, which we should be able to find in terms of other derivatives.

Using the triple product rule, $\left(\frac{\partial T}{\partial L}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_L \left(\frac{\partial S}{\partial L}\right)_T = -\frac{T}{C_L}\left(\frac{\partial S}{\partial L}\right)_T$.

Now, C_L must be positive, let use explore $\left(\frac{\partial S}{\partial L}\right)_T$. The fluid analog of this derivative is $\left(\frac{\partial S}{\partial V}\right)_T$ which we find as a Maxwell from the Helmholtz energy. Defining an analog of the Helmholtz energy, $A' = U - TS$, $dA' = dU - TdS - SdT = -SdT - FdL$. The cross derivatives result in the relation that we are seeking:

$\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial F}{\partial T}\right)_L$, and the temperature dependence of F is given, but must be analyzed carefully since $F_{applied}$ is given. $F = -F_{applied} = -k(T)(L-L_o)$, and since k(T) increases with T, then F *decreases* with T at fixed L, meaning, $\left(\frac{\partial S}{\partial L}\right)_T < 0$. therefore, $\left(\frac{\partial T}{\partial L}\right)_S > 0$, so the temperature of the rubber band rises when you do work on it by stretching it quickly. (Note that you do work on the rubber band by stretching, whereas you do work on a fluid by compressing).

(b) If we can find $\left(\frac{\partial L}{\partial T}\right)_F$ then we will have the sign.

Again starting with the triple product rule, $\left(\frac{\partial L}{\partial T}\right)_F = -\left(\frac{\partial L}{\partial F}\right)_T \left(\frac{\partial F}{\partial T}\right)_L$. Both derivatives on the right hand side are easy to determine since the force law is given, $\left(\frac{\partial F}{\partial L}\right)_T < 0$, and we already determined, $\left(\frac{\partial F}{\partial T}\right)_L < 0$, therefore $\left(\frac{\partial L}{\partial T}\right)_F < 0$. Therefore length goes down when T goes up, and length goes up when T goes down, in other words, the rubber band is easier to stretch a given length at lower T. (Put one in the freezer and try it!) Note: it is possible to answer this question by just looking at the force law without using the derivatives).

(c) Perform an analog of example 5.10.

$dS = \left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL$, using the expansion rule for T with respect to F,

$$\left(\frac{\partial S}{\partial T}\right)_F = \left(\frac{\partial S}{\partial T}\right)_L \left(\frac{\partial T}{\partial T}\right)_F + \left(\frac{\partial S}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_F$$

$C_F = C_L + T\left(\frac{\partial S}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_F \Rightarrow C_F - C_L = T\left(\frac{\partial S}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_F$, and $\left(\frac{\partial S}{\partial L}\right)_T < 0$ from part (a), and $\left(\frac{\partial L}{\partial T}\right)_F < 0$ from part (b), therefore, $C_F - C_L > 0$.

(d) $dQ = C_L\, dT_L = C_F dT_F$, Since $C_F > C_L$, $dT_L > dT_F$.

(e) In part (a) we analyzed $\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial F}{\partial T}\right)_L$ and found it less than zero. This is because a rubber band is made from molecular strands which are like molecular spaghetti when processed and all tangled. When you pull on it, it aligns some of the molecules, and the entropy goes down. That is why the force law seems non-intuitive at first.