1.
The plot shows experimental data for CO_2 gas. The gas, initially in state A, is compressed at constant temperature of 20°C, by pushing a piston. (a) Explain what happens as the system moves from the point A to the point F. (b) How different will the plot look if a van der waals' equation model was used for CO_2?

Ans. Compress gas initially in state A at constant T by pushing a piston: Near A, pressure rises $\approx$ as in Boyle's law

At C ($\approx$ 60 atm for CO_2), all similarity to perfect behaviour is lost, for suddenly the piston slides in without any rise in pressure: horizontal line CDE

just to the left of C, liquid appears, and there are two phases separated by a sharply defined surface. As volume is decreased from C through D to E, the amount of liquid increases

pressure on line CDE, when both liquid and vapour are present in equilibrium, is the vapour pressure of liquid at the temperature of the experiment
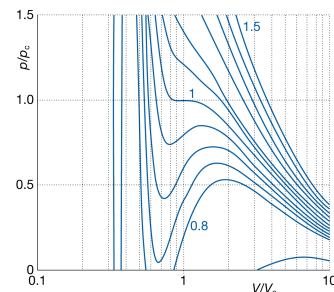
At E, sample is entirely liquid and the piston rests on its surface

further reduction of volume requires exertion of considerable pressure
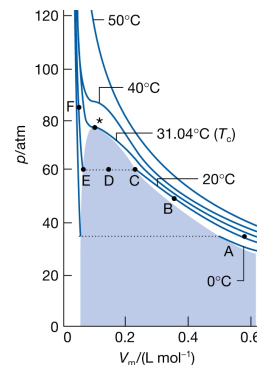
If a van der waals' equation model was used for CO_2, then the plots will look as shown (label : $\frac{T}{T_C}$) :

2.

(a) Why can't you open the door of a refrigerator to cool a room? Explain.

Ans. For a refrigerator in its usual state, the system being cooled is inside its closed chamber.

With energy provided by the external power supply, the refrigerator uses it as work, say w, and adds it to the heat, say, q_c, taken from inside and dumps $q_h = q_c + w$ amount of heat to the space in the room outside the closed chamber, which acts as the surroundings or sink.

With door open, the entire room becomes the system, as well as the sink and instead of cooling, as the heat is dumped, the room keeps getting hotter. This makes the refrigerator use more and more power continuously dumping more and more heat to the room and making it hotter. Eventually the refrigerator will break down as the mechanism is overtaxed (the coolant or whatever else used cannot perform continuously in cycles).

(b) A system containing a perfect gas with volume V and pressure p undergoes an IRREVERSIBLE isothermal free expansion to volume $2V$, at temperature T. What are the changes in entropy of : (i) the system and (ii) its surroundings?

Ans. We construct a reversible isothermal expansion from volume V to volume $2V$

$\Delta S_{\text{sys}} = R \ln \frac{2V}{V} = R \ln 2$; for the perfect gas, $(\Delta U)_T = 0$ and $\therefore q = -w = p_{ex}(2V - V) = p_{ex}.V < RT \ln 2$ (rev. work).

For the surroundings, $q = -p_{ex}.V$ and $\Delta S_{\text{surr}} = -\frac{p_{ex}.V}{T}$. If we take $p_{ex} = 0$ (ideal free expansion), then $\Delta S_{\text{surr}} = 0$.

3. Starting from definition of enthalpy, H, (i) derive expressions for $\left(\frac{\partial H}{\partial p}\right)_S$ and $\left(\frac{\partial H}{\partial S}\right)_p$ (the symbols have the usual meaning);
and (ii) obtain Gibbs' free energy by a Legendre Transform of H.

Ans. (i) $H \equiv H(S, p)$;　 $dH = d(U + pV) = dU + pdV + V dp = dU - dq + V dp = TdS + V dp$, for infinitesimal processes and

with no mechanical work; $\therefore \left(\frac{\partial H}{\partial p}\right)_S = V$

(ii) Using $dH = TdS + V dp$ from part (i), $\left(\frac{\partial H}{\partial S}\right)_p = T$ $\therefore$ Legendre Transform of H using the variable S : $G = -S \left(\frac{\partial H}{\partial S}\right)_p + H = H - TS$

4.
(a) Compare the change in disorder in a system with increase in internal energy by the same amount at two different
temperatures $T_1 < T_2$ keeping the volume constant.

Ans. $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$

$T_1 < T_2 \implies \frac{1}{T_1} > \frac{1}{T_2}$; $\therefore$ for increase in internal energy by the same amount , $\Delta S_1 > \Delta S_2$.

(b) Use a Maxwell relation to derive the Clausius-Clapeyron equation for vaporisation of a liquid at temperature T, $\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$. Explain the terms.

Ans. $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$. For finite changes, RHS$= \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$

For a gas, $\Delta V \approx V_{\text{gas}} \approx \frac{RT}{p}$; $\therefore \frac{dp}{dT} = p \frac{\Delta H}{RT^2} \implies \frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$.

5.
(a) What is the number of intensive variables of state sufficient to specify the state of one mole of common form of ice?
Briefly explain.

Ans. $F = C - P + 2 = 1 - 1 + 2 = 2$

(b) (i) Explain the slopes (sign) for the different phase equilibria curves shown in the plot; (ii)
How will the figure be different for water? (iii) Discuss how cooling curves are used to
obtain the solid-liquid equilibrium curve.

Ans. (i) $\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}$ shows that the slope of p versus T plot depends on the sign of ΔV.

Going from liquid to gas and solid to gas, the volume increases, and $\Delta H > 0$. $\therefore$ slope for
these cases is always positive.

Going from solid to liquid : in most cases, $\Delta V > 0$ and the slope is therefore positive.
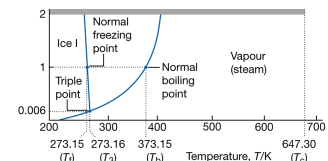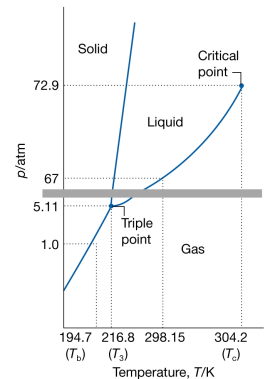
(ii) In case of water, $\Delta V < 0$. $\therefore$ in case of water, slope for the p versus T plot for
solid-liquid equilibrium is negative.

(iii) At a constant pressure, the melt of a solid is cooled from a high temperature. It cools at a fixed rate with time and at one point, as it freezes to solid, the temperature remains constant for the period until all of the liquid is solidified and then it cools again at a slight slower rate than that of the liquid. The temperature of freezing is recorded. This is done at many different pressures, and the equilibrium curve for the solid-liquid equilibrium is thus obtained.
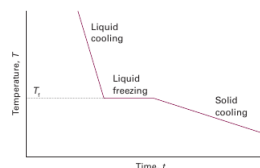
6. For the reaction $\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\longrightarrow H^+(aq)+Cl^-(aq)$, is $\Delta_r G^\ominus = -131.23$kJ mol^{-1}.

(a) Find $\Delta_f G^\ominus$ (Cl$^-$,aq). 1

Ans. By definition, standard free energy of formation of elements is zero, and by convention, for aqueous protons, free energy of formation is zero.

The standard reaction free energy is the difference of sum of standard free energies of formation for the products and that of the reactants. The free energy of formation of all other entities being zero, $\Delta_f G^\ominus(Cl^-,aq) = -131.23$kJ mol^{-1}

Draw a schematic plot of the reaction free energy for a process as a function of the degree of advancement.

(b)
Ans. The black curve is the required plot.
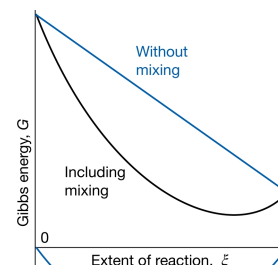
7. Define pH of an acidic/basic solution. Can pH be negative? Explain your answer briefly.

Ans. pH$= -\log a_{H^+}$. Yes, it can be negative, if the concentration of the acid is very high. For example, say the molality, $b = 5$mol/kg and the activity coefficient is $\gamma = 0.4$, then pH$= -\log(5\times 0.4) = -\log 2 = -0.301$

(a)
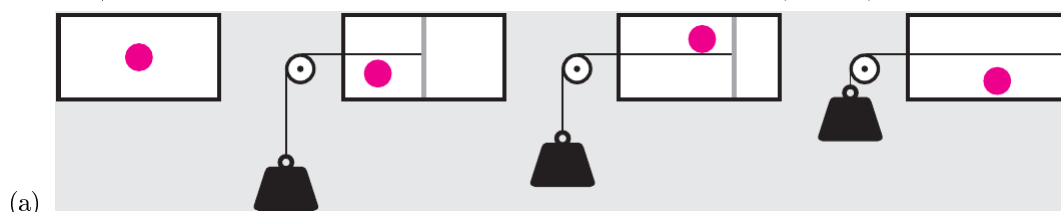
Consider a single particle in a box with diathermal boundaries. If the particle is found on the box's left-hand side (half), an observer inserts a movable wall and attaches a weight to its left side. The free expansion of the one-particle gas pushes the wall to the right, lifts the weight, and thereby performs work against gravity; (i) What is the maximum work, w_{max}, that can be extracted using this engine? (ii) Discuss this in terms of relation between the thermodynamic and information entropy.

Ans. Free expansion of a single particle $\Longrightarrow \Delta U = 0$

(i) max. work$= \Delta A = 0 - T\Delta S = k_B T \ln 2$

(ii)The increase in entropy is associated with loss of information. The information entropy, $H = \ln 2$; $\Delta S = k_B H$

3

(b) At absolute zero of temperature, a pair of carbon monoxide molecules may assume one of two possible configurations - identical atoms or hetero atoms next to (stacked above) each other. Estimate the residual entropy for CO.

Ans. $S = \frac{1}{2} R \ln 2 = \frac{1}{2} \times 8.314 \times 0.693 = 2.88 \mathrm{J/(mol.K)}$

8. The figure shows temperature dependence of the equilibrium constant for the binding of DNA to two different proteins. Why are the plots linear? Find the standard enthalpy for binding for the two proteins (Hint : use the slopes). At 22°C, what are their standard entropies for binding?

Ans. The linearity shows that the enthalpy of binding for each case is nearly constant over the range of temperature shown.
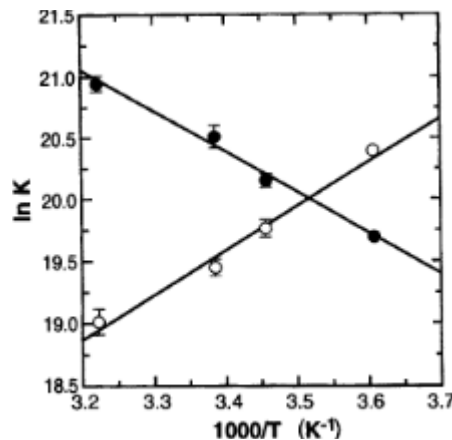
Let us denote the two cases by the superscripts '+' (positive slope) and '-' (negative slope).

Using $\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_r H^{\ominus}}{R}$, get $\Delta_r^+ H^{\ominus} \approx -\frac{20.7-18.9}{3.7-3.2} \times 8.314 = -29.93$ kJ/mol and $\Delta_r^- H^{\ominus} \approx \frac{21.05-19.4}{3.7-3.2} \times 8.314 = 27.43$ kJ/mol

at 22°C, $T = 295$K and $\frac{1000}{T} = 3.39 \implies \Delta_r^- G^{\ominus} = -8.314 \times 10^{-3} \times 295. \ln K^+ \approx -50.28 \mathrm{kJ/mol}$

and $\Delta_r^+ G^{\ominus} = -8.314 \times 10^{-3} \times 295. \ln K^- = -47.83 \mathrm{kJ/mol}$

$\therefore \Delta_r^- S^{\ominus} = \frac{27.43+50.28}{295} = 0.263$ kJ/(mol.K) and $\Delta_r^+ S^{\ominus} = \frac{-29.93+47.83}{295} = 0.063$ kJ/(mol.K) respectively.

Bonus: In the novel 'Cat's Cradle' by Kurt Vonnegut, the villain gets hold of a crystal of thermodynamically stable 'ice nine'. When ice-nine comes into contact with liquid water below 45.8 °C, it acts as a seed crystal and causes the solidification of the entire body of water, which quickly crystallizes as more ice-nine. As people are mostly water, ice-nine kills nearly instantly when ingested or brought into contact with soft tissues exposed to the bloodstream. A critic states that ice-nine represents a collaboration between science and the military that, like with the atomic bomb, proves their indifference to the fate of the human race, and the inhuman and immoral results of pure research (en.wikipedia.org/wiki/Ice-nine).

As a student of thermodynamics, what is your take on ice-nine ?

Ans. If ice-nine is thermodynamically more stable than ordinary water, then the process : ordinary water → ice-nine, must be exoergic, i.e. $\Delta G < 0$.

Naturally, this is not a desirable situation, because all water will freeze and convert to ice-nine.

We can reverse the process by pumping in energy, as example using sunlight or other sources like lasers, and hope that the energy barrier in the conversion back to ice-nine must be high, so that we can retain ordinary water for a reasonably long time.

-No marks for social commentary : Scientists ought to be responsible and sensitive about the research they carry out, The least that they must do is to make people aware of the hazards of the research output. If Ice-nine is a hazard, all information on it must be made public and appropriate policies and laws must be enacted so that no one can use it as a weapon.

Note : There is a phase of ice, called ice-IX, that does not have any known hazardous property. Ice-nine of Vonnegut is an fictitious

idea.