

ON AIR LIQUEFIERS

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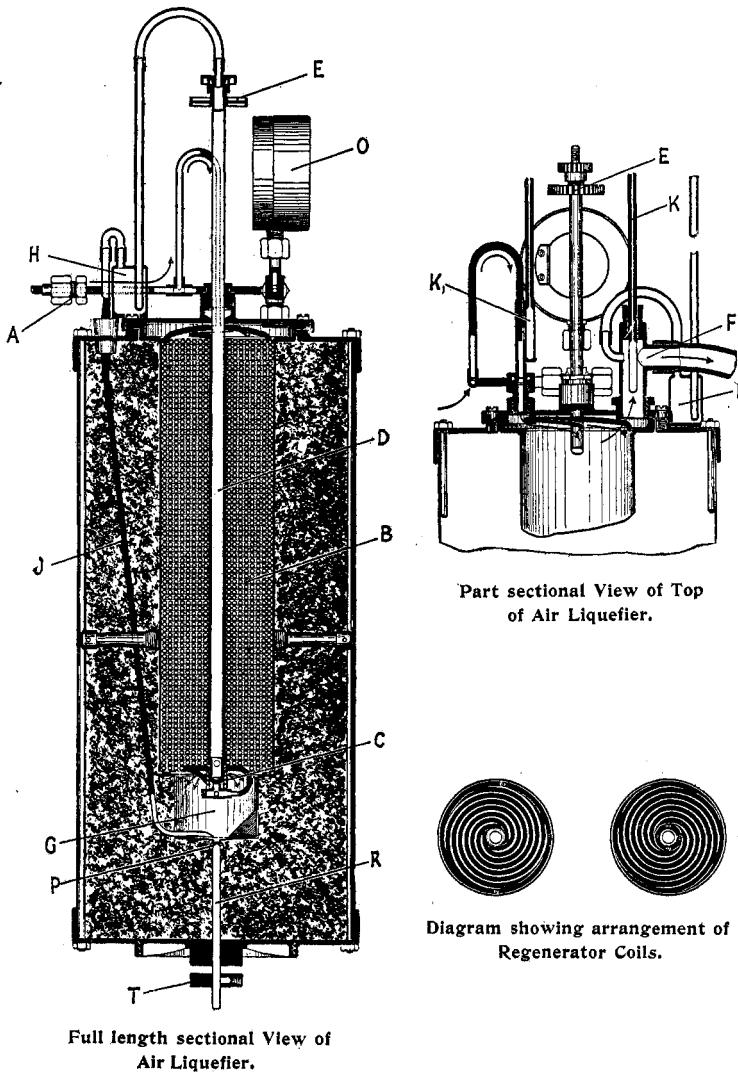
Introduction Note

At the time the following work was undertaken the article by Bradley and Hale cited in the first paragraph below had escaped the author's notice, and in fact it only came to his attention after the experiments here described were completed and a first draft of this article written out. As the present installment represented only the beginning of our original laboratory program and the article above cited suggested much the same general field for investigation, the author, after forwarding this manuscript to the editors, wrote Prof. Bradley outlining what had been already accomplished here and what further work was contemplated and suggested the desirability of some sort of co-operation in the future. Prof. Bradley heartily indorsed this suggestion and further stated that experiments very similar to those here described had been completed some time ago in his own laboratory and with essentially the same results. As the two sets are entirely independent and mutually support each other at least as far as the facts are concerned it has been arranged through the courtesy of the editors of this Journal to publish the two articles simultaneously.¹

Through the courtesy of Prof. Bradley I have had the opportunity of reading his manuscript while correcting the proof of the present article and feel that the two articles contain no essential contradictions. The inferences which we are disposed to draw may differ somewhat, but as it is hoped that further experiments will remove many of these points it seems hardly expedient to discuss them at present.

I am glad to have this opportunity to express my appreciation of the friendly and courteous spirit with which the authors of the other paper have entered into the present matter.

¹ See article entitled "Precooling in the Liquefaction of Air," by W. P. Bradley and G. O. P. Fenwick, pages 275 to 289 this Journal.



Sectional Views of Air Liquefier.

Fig. 1

The question as to just where and under what conditions liquefaction takes place in air liquefiers of the Hampson and Linde types has of late been raised by several authors. A sum-

mary of the present state of our knowledge together with some very interesting measurements of temperature in the return air current may be found in a paper by Bradley and Hale.¹ The consensus of opinion, which is also supported by the direct temperature measurements in the paper cited, seems to be that in the liquefiers of this type little or no liquefaction takes place before the air reaches the expansion valve.

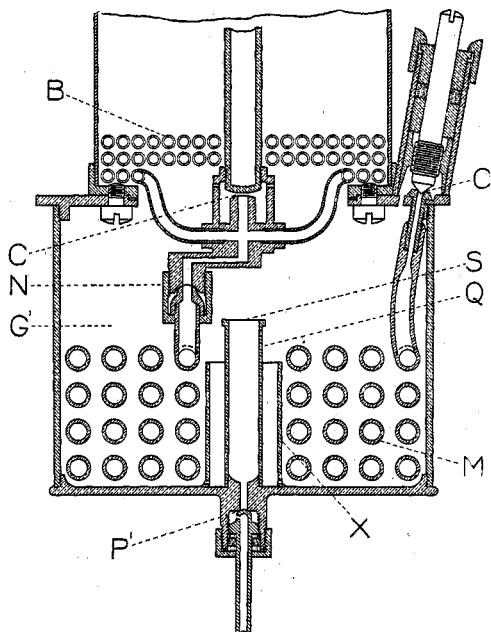


Fig. 2

The efficiency of the apparatus, both while starting up and under steady running conditions, would thus seem to depend wholly upon upon the Joule-Thomson effect. In order to determine what would happen were more complete cooling effected before the air reached the expansion valve the following experiment was undertaken with the liquefier of the Chemistry Department of the University of California. The apparatus is a regular Hampson laboratory type liquefier receiving its air from a four-stage belt-driven air compressor designed and built for

¹ W. P. Bradley and C. F. Hale: *Phys. Rev.*, 19, 387-395, (1904).

the purpose by the Rix Compressed Air and Drill Co., of San Francisco. Fig. 1 represents the liquefier as supplied by the Brin's Oxygen Co.¹ Fig. 2 shows how the liquid reservoir was modified for the experiment in hand. C is the regulating valve on the ordinary liquefier, G the reservoir for the liquid air and B the regenerator coils. For the experiment in hand a large container G' 8 cm deep by 10 cm diameter was substituted and a coil M of nearly 3 meters of copper tubing 4.5 mm internal diameter and wall 1 mm thick was arranged as shown in the figure in four layers of four turns each, being connected to the main coil of the liquefier by a small brass union N in such manner that the air might be allowed to take its old course through the valve C as usual or be sent through this new coil and escape at the valve C', both of these valves discharging freely into the reservoir G'. The liquid in this chamber had to rise to the top of the tube Q before it could overflow into this through the wire gauze S and be drawn off through the valve P', thus ensuring the complete covering of the coil M. The sleeve X perforated with a ring of holes at the bottom was simply to ensure good circulation of the liquid in the chamber G'. Evidently though there may be a question as to the liquefaction of the gas before it reaches the valve C, this can hardly be the case if it is allowed to pass on to C' before escaping. In fact it should be not only liquefied but reduced in temperature very nearly to its boiling-point at atmospheric pressure which is practically the condition of the liquid in G'.

To test the relative efficiencies of the liquefier in the two forms the compressor was run at a steady rate for about half an hour after the liquid began to flow, *i. e.*, after the lower coil was entirely immersed. The compressor was making about 120 revolutions per minute. The cylinder receiving the free air is 8 inches in diameter with a 6-inch stroke, single-acting. The pressure of the air delivered to the liquefier was held as constant as possible at 200 atmospheres. It was found that it made no appreciable difference through which of the valves, C or C', the

¹ The cut is reproduced from the company's circular,

air was allowed to escape. Liquefaction took place in either case and the quantity per minute was the same within the limits of observational error. The mean rate of production was in the neighborhood of 2 liters per hour which is a little lower than the regular output with the simple reservoir system, the difference being evidently due to greater losses by conduction of heat from without. The comparisons were for the most part made by drawing liquid every three minutes into a graduated vacuum cylinder, using valves C and C' during alternate periods. By the arrangement of the valves, described above, the discharge could be shifted instantly from one valve to the other. Continuous runs on one valve extending over several periods were also made. The quantities of liquid for a series of successive three-minute periods all with one valve showed irregular variations among themselves sometimes as high as 3 percent or 4 percent, due to variations in speed of compressor, adjustment of outlet valve, and most important of all, rapidity and other conditions of drawing off the liquid. The difference between runs on the two valves showed no larger variations than those on a single valve and were in favor sometimes of the one, sometimes of the other. Since from the valve C' it can scarcely be maintained that much gas emerges as such it is evident that in this case at least the Joule-Thomson effect in its ordinary sense nearly disappears. Of course we may have an analogous effect for the slight expansion of the liquid but experimental data as to its magnitude fail us, and it is probably very small. The fact that the performance of the apparatus is sensibly the same with either valve suggests at least a lurking possibility that the same conditions may really occur in the ordinary type of liquefier.

Waiving the question of identity in the two processes it is at least of interest to analyze the new cycle. For this purpose we may best separate it into six parts: (1) Cooling within the pressure tube. (2) Condensation to liquid. (3) The conduction of heat from the inner to the outer wall of the tube; this may be lengthwise of the tube as well as straight through the wall. (4) The passage of the liquid as such through the valve C'. (5)

The evaporation of the liquid without. (6) The warming of the vapor from the external surface of the pressure tube.

Of these it is obvious that (2) is thermodynamically a reversible process; (5) is also reversible in so far as it is not too violent and we may neglect the dynamic factors such as kinetic energy of the gas current. (3) and (4) and to a lesser extent perhaps (1) and (6) are necessarily the irreversible steps of the cycle, and improvements in its practical operation must depend upon reducing their effect to a minimum.

We may turn now to what this suggests as regards the possibility of future improvements in liquefiers of this type. Up to the present the inefficiency of the liquefiers in converting mechanical work, represented in compression, into refrigeration has been laid upon the free expansion at the escape valve and because the return air from the regenerator coils was nearly the same temperature as the ingoing pressure air, it has been assumed that the thermal interchange in these coils is highly efficient. If the liquid is formed before reaching the valve the only loss at this point is due to the friction of the liquid flowing through the valve. This can be readily calculated as it is simply the volume of this liquid multiplied by the difference of pressure on the two sides of the valve, *i. e.*, 200 atmospheres in the above experiment. Assuming the validity of Boyle's law up to this pressure and the density of the liquid as about 1/800 that of air at atmospheric temperature and pressure we find the loss to be about 5 percent of the total energy represented in isothermal compression of the gas.

The fact seems not to have been thoroughly appreciated that the difference in temperature of the ingoing and outcoming air at the top of the regenerator coils is not a complete measure of their thermodynamic efficiency. To define this completely the form of temperature gradient in both currents must be known. Reference to Fig. 3 will serve to make this clear.

A steady state is assumed to have been reached; we further assume that there is no temperature difference between the enter-

ing (pressure) air and returning (free) air¹ and also that the liquefier system is completely insulated as regards direct heat conduction from without. Let the temperature at the outer end of the coil be T_1 and the temperature at the escape valve T_2 . Let Q be the heat taken up between T_2 and T from the copper coils by the quantity of free air returned in unit time, Q_1 the special value of Q for $T = T_1$. Further let Q' be the heat given out between T_1 and T by the quantity of pressure air supplied to the coils in unit time, Q_2' the value of Q' for $T = T_2$.

The copper wall of the pressure tubing we may consider as an intermediate reservoir of heat. In Curve A of Fig. 3 the ordinates are the temperatures of the returning free air current at different points in its course while the abscissae are $(Q_1 - Q)$.

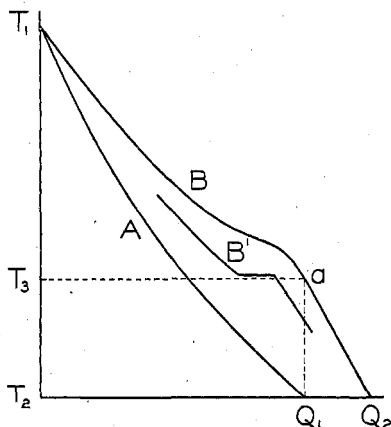


Fig. 3

If the specific heat at constant pressure (C_p) is constant over this range of temperature, A will be a straight line. If it increases with decreasing temperature² A will have more the form indicated in the figure, but for our present purpose this matters little. In curve B the ordinates refer to the temperature of the air within the pressure tube and the abscissae are the correspond-

¹ In practice with our regular equipment as described above this difference usually amounts to about 2° C. In tests with an improved liquefier described by Bradley and Rowe (Phys. Rev. 19, 230-343) this is reduced more than tenfold.

² See C. v. Linde, Engineer (London), 82, 509, Nov. 20, 1896.

ing values of Q' . Were C_p constant B would start from T_1 as a straight line. The greater the percentage of air liquefied the less Q_1 will be and the greater will be the angle between A and B at T_1 . If C_p increases with increase of pressure¹ this will also increase the angle and if C_p varies with temperature, B will cease to start as a straight line. Should we be working with a single gas (*e. g.*, nitrogen) and at a pressure below the critical, the temperature of liquefaction for the given pressure would be marked by a discontinuity of the type shown in B'. With rising pressure the horizontal part would become shorter and disappear at the critical pressure (probably leaving a point of inflection in its place) and with a gaseous mixture like the air no actual discontinuity would occur at any pressure but simply an inflexion such as shown in B which would flatten out with increase of pressure but need not, and probably does not, entirely disappear even above the critical pressure of all the components of the mixture. The increase of pressure would, of course, also displace this region of the curve steadily toward T_1 . The cooling of the ingoing air from T_1 to T_3 is what is accomplished by the return air (specific heat), the remainder of the cooling from T_3 to T_2 is accomplished by the evaporation of that part of the liquid (latent heat) necessary to produce this return air. The distance between the points marked Q_1 and Q_2' represents the amount of heat abstracted from the air which is drawn off as liquid; *i. e.*, it measures the useful output of the process.

The path $T_1Q_2'Q_1T_1$ represents the interchange of heat for the mass of copper tubing considered as a heat reservoir with a given mass of gas passing down the coils under pressure and the corresponding (but not equal) mass of free air returning. The total amount of heat given to and taken from this reservoir is the same, *i. e.*, the integral taken about the whole cycle.

$$\int_{T_1}^{T_1} dQ = 0$$

but the entropy

$$\int_{T_1}^{T_1} \frac{dQ}{T} > 0.$$

¹ See C. v. Linde, *Engineer* (London), 82, 509, Nov. 20, 1896.

In other words the greater the area enclosed by the above path the greater is the increase in entropy in describing the cycle.

The entropy-temperature diagram will appear essentially the same in form as the heat-temperature diagram, the chief difference being that both curves are more convex toward the origin. In the heat-temperature diagram it is not easy to give an exact and simple physical interpretation to area, but in the entropy-temperature diagram the area corresponding to $T_1, a Q_1 T_1$ has the dimensions of heat and is the equivalent of the work wasted in the interchange of heat in the copper tubes above the reservoir of liquid. The area corresponding to $a Q_2' Q_1 a$ gives the waste in the interchange between evaporating liquid and pressure air. Of course the point a may lie above the point of inflection on the curve. If the argument of the present paper is correct it is chiefly in the reduction of these areas that essential improvements in this type of liquefier are to be looked for.

It is interesting to note in this connection that Linde explains the higher efficiency of his system on the grounds that the Joule-Thomson effect is proportional to the difference of pressure ($p_1 - p_2$) on the two sides of the expansion valve while the work of compression is proportional to $\log \frac{p_1}{p_2}$. He therefore works between two relatively high pressures (200 and 16 atmospheres), instead of one high and one equal to atmospheric as in the Hampson system. This argument is undoubtedly valid as far as starting up the machine is concerned, but once in steady state it would seem from the above that the higher efficiency may quite possibly be due to the curve A approaching curve B. Curve B is, of course, the same in the two systems if working at the same initial pressure.

Linde¹ points out his belief that the Joule-Thomson effect ceases to obey the above law for very high pressures and for this reason appears to look upon 200 atmospheres as approaching

¹ l. c.

the limit of practicability. It would seem, however, that if the Joule-Thomson effect is not the governing factor this question must come up anew.

If we are dealing with reversible processes throughout, the more heat we abstract from the gas before it goes to the liquefier the less will have to be removed from it in that instrument to bring it to a given standard state. An increased initial pressure means more heat removed in the cooling water of the compressor. The possible disadvantage that the increased pressure brings with it is increase in friction at the escape valve. As long as the escaping substance obeys the $p v = RT$ law this friction loss is independent of the pressure, the increase of the latter being exactly compensated for by the decrease of the volume passed. But we have here to deal with a liquid whose compressibility we do not know. At 200 atmospheres as pointed out above, this loss does not exceed 5 percent of the total useful work of compression even if we assume the liquid as incompressible and, even making this latter assumption, doubling the pressure would only double this loss. The other factor of importance in the problem is the change in shape of Curve B which this increase in pressure would produce. It seems certain than any residual flexure left from the critical phenomena would tend to be smoothed out. Beyond this, little can be said at present as the only values for specific heats at these pressures and temperatures appear to be those deduced by Linde¹ from the performance of the apparatus itself.

The experimental work of Bradley and Rowe already referred to points strongly to the conclusion that we have by no means reached the optimum of initial pressure at 200 atmospheres and for small plants, at least, there seems no valid mechanical objection to using higher pressures. Experiments in this line are at present under way in this laboratory. It was the original intention to delay the present paper until definite results in the latter line could be secured, but as the program of the work has grown somewhat and now bids fair to consume more time than

¹ l. c.

originally expected, the liberty is taken of presenting this isolated step in the hope it may prove suggestive to other workers in the same field and encourage cooperation.

Summary

In the present paper it is pointed out that although in the Hampson and Linde liquefiers it may be questioned whether any liquefaction takes place before the gas reaches the expansion valve the output of the Hampson at least is not altered when the coil system is so altered as to ensure complete condensation before release of pressure, thus eliminating the Joule-Thomson effect.

The theory and possibilities of this modified cycle are then discussed.

The question is left an open one as to how closely the older cycle approaches this new one.

The losses in the interchangers (of either system) are discussed.

In conclusion, I wish to express my indebtedness to Mr. Val. Arntzen, mechanician of this department, for the care with which he constructed the apparatus described; likewise to Mr. A. C. Wright, of the Department of Mechanics, for the draft of Fig. 2, and to Dr. T. C. McKay, of the Department of Physics, for friendly criticism of the thermodynamics involved.

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Dept. of Chemistry,
Berkeley, Nov. 6, 1905.*